

Titre: Solid State Laser Cooling in Ytterbium Doped Oxide Glass
Title:

Auteur: Jyothis Thomas
Author:

Date: 2023

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Thomas, J. (2023). Solid State Laser Cooling in Ytterbium Doped Oxide Glass
Citation: [Thèse de doctorat, Polytechnique Montréal]. PolyPublie.
<https://publications.polymtl.ca/56784/>

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URL de PolyPublie: <https://publications.polymtl.ca/56784/>
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**Directeurs de
recherche:** Raman Kashyap
Advisors:

Programme: Génie physique
Program:

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Solid state laser cooling in ytterbium doped oxide glasses

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Département de génie physique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

Génie physique

Novembre 2023

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Cette thèse intitulée :

Solid state laser cooling in ytterbium doped oxide glasses

présentée par **Jyothis THOMAS**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*

a été dûment acceptée par le jury d'examen constitué de :

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DEDICATION

To my parents Mr. Thomas P. K and Mrs. Jolly Emmanuel

ACKNOWLEDGEMENTS

I would like to extend my sincere gratitude to Prof. Raman Kashyap, my supervisor and research director, for his invaluable guidance, assistance, and support during my PhD journey. His unwavering commitment and mentorship have enabled me to pursue my scientific aspirations with success, while also fostering my personal growth and curiosity.

I have been surrounded by wonderful colleagues Frédéric Monet, Anthony Roberge, Yalina García Puente, Antsar Hlil, Jean Sebastian Boisvert, Yannick Cuerno, Foroogh Jafari, Ehsan Rezagholizadeh, Qingtao Chen, Reyhane Mirzaee, Amirhossein Tehranchi, Sébastien Loranger and others. I would like to express my gratitude to them for the fruitful discussions, collaborative work, and unwavering support throughout my five years of studies. I am deeply grateful to the collaborators who have offered me their unwavering support and assistance throughout my journey. Specifically, I would like to express my heartfelt thanks to Prof. Younes Messadeq and Thomas Meyneng for their invaluable contributions to my research. Additionally, I extend my sincere appreciation to Prof. Lauro Maia, Prof. Krishnaiah, and Prof. Denis Seletskiy for their remarkable support and collaborative efforts, which have significantly enriched my research experience. I am sincerely grateful to MPB Communications Inc., and especially to Dr. Vladimir Karpov, for their generous support in providing the essential tunable fiber laser for my experiments.

I wish to extend my heartfelt gratitude to the dedicated technicians and support personnel who have played an indispensable role in the realization of this research. From Poly-Grames, I am immensely thankful to Jules Gauthier, Steve Dubé, Jean-Sébastien Décarie, Louis-Philippe Carignan, Traian Antonescu, and Rachel Lortie. Additionally, from the Engineering Physics department, my sincere appreciation goes to Jean-Paul Lévesque and Mikael Leduc.

I would like to acknowledge my parents Thomas P K and Jolly Emmanuel, sister Thejus Thomas, and husband Amol Kanjirathinkal Thankachan for their constant love and encouragement. Without their support, I would not have been able to achieve this milestone.

Finally, I would like to express my appreciation to all the individuals who have contributed to my research in one way or another. Your contributions have greatly influenced my academic and professional journey.

RÉSUMÉ

Le refroidissement par lasers de l'état solide, basé sur le phénomène de fluorescence anti-Stokes, a des implications importantes pour un large éventail d'applications telles que les cryoréfrigérateurs, les capteurs, les instruments satellitaires, les lasers auto-réguler, etc. Ses caractéristiques uniques, notamment de faibles vibrations mécaniques, l'absence de composants mécaniques et une fiabilité accrue, en font une option attrayante pour ces applications. Comme prédit par l'industrie des cryoréfrigérants, près de 70 % des premiers utilisateurs ont manifesté leur intérêt pour les monocristaux à faible énergie de phonons. Cependant, leur coût élevé et leur géométrie fixe génère une demande pour des matériaux plus malléables pouvant s'adapter à l'application désirée. Les verres de silice et les vitrocéramiques dopés aux terres rares sont très intéressants en raison de leurs excellentes propriétés, telles qu'une grande stabilité, une durabilité mécanique et chimique élevée, une résistance thermique, une facilité de mise en forme et une grande pureté. Cependant, le problème de l'énergie élevée des phonons et de l'agrégation des ions Yb pour un dopage élevé dans les verres d'oxyde, rend difficile la maximisation de l'efficacité du refroidissement, nécessitant une meilleure purification du matériau et une augmentation de la concentration des terres rares, principalement d'ions Yb. C'est pourquoi le sujet de la thèse est axé sur le « refroidissement laser de l'état solide dans un verre d'oxyde dopé à l'ytterbium ».

Pour contrer les limitations susmentionnées, les deux premières publications se sont concentrées sur la création artificielle d'un environnement à faibles phonons pour la terre rare dans des verres d'oxyde à haute énergie de phonon avec différentes compositions hôtes, en utilisant différents nanocristaux de fluorure. L'environnement nanocristallin de fluorure offre aux ions de terre rare un environnement à faible énergie de phonon, supérieur à celui de l'hôte étant vitreux. En outre, les vitrocéramiques peuvent être produites directement à partir de matériaux vitreux, ce qui les rend robustes, faciles à mouler et peu coûteuses, présentant ainsi une option viable pour la réalisation pratique du refroidissement par laser de l'état solide.

La première publication de la thèse montre comment les propriétés optiques des germanates dopés à l'ytterbium et des vitrocéramiques d'oxyfluorure d'aluminosilicate avec différentes concentrations d'ions de terres rares (0,5 à 3,0 % molaire) synthétisées par la technique conventionnelle de trempe par fusion peuvent être utilisées pour évaluer leur potentiel pour des applications de réfrigération optique. On constate que la teneur en Yb^{3+} affecte considérablement

l'émission de photoluminescence et le rendement quantique, et donc les caractéristiques de refroidissement/chauffage. En utilisant des réseaux de Bragg inscrit dans la fibre pour effectuer des mesures calorimétriques, il a été déterminé que les vitrocéramiques avec 1,50 - 2,00 % molaires de Yb^{3+} ont un échauffement net proche de zéro à une excitation de ~ 1030 nm, ce qui indique leur potentiel pour des applications de réfrigération optique.

Dans le deuxième article, nous avons étudié systématiquement les propriétés optiques des vitrocéramiques (GC) contenant des nanocristaux d' YF_3 et des cristaux d' YLiF_4 . Nous avons mené une étude plus détaillée des GC en modulant la composition initiale en fonction du temps et de la température de fusion. Nous avons également comparé les propriétés optiques des GC purifiés et non purifiés et avons constaté que la purification augmente l'intensité de l'émission PL et le rendement quantique interne (iQY) tout en diminuant l'absorption de fond. Les résultats de l'article 1 et de l'article 2 permettent de mieux comprendre les propriétés optiques des vitrocéramiques d'oxyfluorure dopées à l'ytterbium en fonction de leur composition, en tant que matériau approprié pour le refroidissement par laser. Malgré l'amélioration de l'efficacité quantique de l'émission et l'augmentation des durées de vie démontrées par cette technique, la technique de fabrication a été limitée par la pureté des matériaux de départ et le processus de fabrication des verres, ce qui a nécessité une modification radicale du processus de fabrication du verre.

Dans la troisième publication, nous avons étendu la technique de dépôt chimique en phase vapeur modifié (MCVD), en introduisant de l'alumine dans la silice hôte afin d'augmenter la solubilité des terres rares. Cela a permis de produire une préforme en verre de silice avec une concentration élevée en Yb (4×10^{26} ions/ m^3) et de favoriser la séparation de phase de la terre rare dans le verre d'oxyde. Grâce à cette méthode, les ions de terres rares actives sont immergés dans une autre terre rare non active, formant un environnement d'oxyde à faible énergie de phonon et protégeant la terre rare de l'énergie de phonon élevée de la silice hôte. La contrainte fondamentale du refroidissement du verre de silice induit par le laser, causée par le regroupement des ions de terres rares, a été considérablement atténuée. Dans l'ensemble, l'approche MCVD constitue une voie prometteuse pour l'obtention de matériaux intrinsèquement purs. Nous avons pu démontrer un refroidissement de $-0,9$ K avec une puissance de pompe de $6,5$ W à 1029 nm dans le verre GAYY (verre d'oxyde d'aluminium, d'yttrium et d'ytterbium) à la pression atmosphérique, même si nos résultats préliminaires ont été obtenus avec une longueur d'onde de pompe non optimisée et une

puissance de pompe limitée. Cette réalisation remarquable est le résultat de la réduction des sources de relaxation non radiative, telles que l'extinction de la concentration et la perte d'absorption de fond, grâce à une conception minutieuse du matériau. Il n'est pas surprenant que les propriétés optiques de ces verres, telles que l'efficacité quantique, la durée de vie, etc. aient été améliorées par rapport au verre de silice dopé à l'Yb normal.

Une vaste étude sur le changement de température dépendant de la longueur d'onde dans les verres GAYY ainsi que l'estimation de la température minimale réalisable (MAT) globale pour les applications de réfrigération optique ont été menées, ce qui fait l'objet du quatrième article décrit dans la thèse. Nous avons atteint une baisse de température record de -4 K à partir de la température ambiante (TA) en utilisant 20 W à une longueur d'onde d'excitation de 1037 nm dans le verre GAYY. En outre, nous avons démontré une MAT globale de 165 K dans le même verre. En outre, nous avons mené une étude complète pour évaluer comment les changements de composition peuvent influencer les propriétés du refroidissement. Parallèlement à nos recherches sur les verres GAYY, nous avons également développé et étudié un nouveau type de verre de silice dopé à l'Yb composé de lanthano-alumino-silicate (verre GALY). Étant donné la sensibilité de la photoluminescence des ions Yb à l'énergie des phonons de la matrice hôte, un matériau à faible énergie de phonon comme La_2O_3 (à environ 400 cm^{-1}) devrait être idéal pour fabriquer des verres destinés à des applications de refroidissement par laser. En résumé, le quatrième article donne un aperçu des changements de température en fonction de la longueur d'onde dans les verres GAYY et GALY, ainsi qu'une estimation de la MAT pour les applications de réfrigération optique.

En résumé, cette thèse étudie les propriétés spectroscopiques des verres céramiques d'oxyfluorure dopés aux terres rares fabriqués par la technique conventionnelle de trempe par fusion et des verres d'oxyde de silice fabriqués par MCVD pour les applications de refroidissement par laser de l'état solide. Nous pensons que cette recherche exploratrice pourrait ouvrir la voie à l'utilisation de verres de silice fortement dopés aux terres rares dans les applications de refroidissement par laser, ce qui permettrait de découvrir de nouvelles compositions de verre innovantes avec différents modificateurs de réseau. Cela offrira des possibilités futures de combiner diverses terres rares avec de la silice pour des lasers et des amplificateurs autoréguler en température.

ABSTRACT

Solid-state optical cooling, which utilizes the anti-Stokes fluorescence phenomenon, has significant implications for diverse applications such as cryocooler systems, sensors, satellite devices, radiation balanced lasers, and more. Its unique features, including minimal mechanical vibrations, absence of mechanical components, and enhanced reliability, make it an attractive option for these applications. As foreseen by the optical cryocoolers industry, almost 70 % of early adopters have shown their interest in low phonon energy single crystals. Nevertheless, the substantial expenses and constrained design possibilities associated with those materials have generated a need for more adaptable alternatives to enhance the scope of applications. In this context, rare earth (RE) doped silica glasses and glass ceramics (GCs) stand out due to their remarkable attributes, including exceptional stability, robust mechanical and chemical resilience, resistance to high temperatures, moldability, and exceptional purity. Despite its potential benefits, solid-state laser cooling faces a significant challenge due to the high phonon energy of silica and the tendency of RE ions to aggregate at high doping concentrations in oxide glasses. This poses a challenge in achieving maximum cooling efficiency and necessitates better material purification and an increase in the RE ion concentration.

Therefore, the subject of the thesis is focused on ‘Solid-state laser cooling in ytterbium doped oxide glass’.

To counter the aforementioned limitations, the first two publications focused on the creation of a low phonon environment for RE elements within high phonon energy oxide glasses with different host compositions, by using different fluoride nanocrystals. The fluoride nanocrystalline environment offers rare earth ions a low phonon energy environment, superior to that of the oxide vitreous host. Additionally, glass ceramics can be manufactured from glassy materials, making them durable, easily mouldable and inexpensive, thus presenting a viable option for the practical realisation of solid-state laser coolers.

The first publication of the thesis shows how the optical properties of GCs, specifically ytterbium (Yb) doped germanate and aluminosilicate oxyfluoride, can be assessed for their suitability in optical refrigeration applications. These materials were synthesized using the conventional melt quenching technique, with RE ion concentrations ranging from 0.5 to 3.0 mol %. The study reveals that the amount of Yb³⁺ ions significantly impact photoluminescence emission, quantum yield, and consequently, the cooling and heating behaviour of these materials. Using fiber Bragg gratings for

calorimetric measurements, it has been determined that glass-ceramics containing Yb^{3+} concentrations in the range of 1.50-2.00 mol % demonstrate minimal net heating when subjected to excitation at approximately 1030 nm. This finding suggests that these materials hold promise for use in optical refrigeration applications. In the second article, the optical properties of GCs having YF_3 nano crystals (NCs) and YLiF_4 crystals were systematically investigated. A more detailed investigation of the GCs was carried out by modulating the initial composition over time and varying fusion temperatures. Furthermore, a comparison was made between the optical properties of purified and non-purified GCs, revealing that purification enhances photoluminescence (PL) emission intensity and internal quantum yield (iQY) while reducing background absorption. The findings in article 1 and article 2 provide an in-depth understanding of the composition-dependent optical properties of Yb-doped oxyfluoride glass ceramics as a suitable material for laser cooling. Although the use of oxyfluoride glass ceramics led to improved photoluminescence quantum yield and enhanced lifetimes, the fabrication process was restricted by the purity of the material precursors and the glass-making method. As a result, a significant modification to the glass manufacturing process was required.

In the third publication, the modified chemical vapor deposition (MCVD) technique was expanded by introducing alumina to the silica host, thereby increasing the solubility of rare earth elements. This advancement resulted in the creation of a high-Yb-concentration (4×10^{26} ions/ m^3) preform embedded in an oxide glass matrix, facilitating the phase separation of RE components. This innovative approach involves immersing active RE ions within non active RE, establishing a controlled oxide environment with reduced phonon energy, effectively shielding the RE ions from the high phonon energy characteristic of the silica host material. The fundamental constraint on laser-induced cooling of silica glass due to rare earth ion clustering was effectively addressed. Overall, the MCVD approach holds the potential to pave the way for inherently high-purity materials.

The experiments demonstrated cooling of -0.9 K using a 6.5 W pump power at 1029 nm in GAYY glass (aluminum: yttrium: ytterbium oxide glass) at atmospheric pressure. Notably, these initial outcomes were achieved with a suboptimal pump wavelength and restricted pump power. This remarkable achievement was enabled by reducing non-radiative relaxation factors including concentration quenching and background absorption, through meticulous material design.

Consequently, optical properties such as quantum efficiency and lifetime exhibited significant enhancements compared to conventional Yb-doped MCVD SiO₂ glass.

Extensive research was conducted on the temperature change of GAYY glasses to varying wavelengths, and the determination of the global minimum achievable temperature (MAT) for optical cooling applications. In the fourth paper of the thesis, a remarkable achievement was reached as an unprecedented temperature drop of -4 K was attained, starting from room temperature (RT), utilizing a 20 W excitation wavelength of 1037 nm in GAYY glass. Additionally, the same glass demonstrated a noteworthy global MAT of 165 K. A comprehensive study was conducted to investigate the influence of changes in composition on cooling properties. In parallel with the investigation of GAYY glasses, a novel Yb-doped silica glass, referred to as GALY glass, fabricated from lanthano-alumino-silicate was developed and demonstrated cooling in it. The full potential of this glass composition is yet to be fully evaluated.

In short, this thesis investigates the spectroscopic properties of rare earth-doped oxyfluoride GCs and oxide silica glass for solid-state laser cooling. The pioneering research aims to explore the potential of highly RE-doped silica glasses, opening possibilities for novel glass compositions featuring diverse network modifiers and the advancement of radiation-balanced lasers and amplifiers and possibly opening doors to new applications as well.

TABLE OF CONTENTS

DEDICATION.....	III
RÉSUMÉ	V
ABSTRACT.....	VIII
TABLE OF CONTENTS.....	XI
LIST OF TABLES	XV
LIST OF FIGURES	XVI
LIST OF SYMBOLS AND ABBREVIATIONS	XXII
LIST OF APPENDICES	XXIV
CHAPTER 1 INTRODUCTION	1
1.1 The motivation and problem	2
1.2 Objectives.....	4
1.3 Organisation of the thesis.....	6
CHAPTER 2 LITERATURE REVIEW.....	8
2.1 Introduction	8
2.2 Theory	11
2.3 Experimental design considerations for cooling	13
2.3.1 Experimental setups used for solid-state laser cooling.....	13
2.3.2 Crystals	14
2.3.3 Glasses	16
2.3.4 Silica glass optical fibres	17
2.3.5 Semiconductor nanoribbons	18
2.3.6 Techniques to analyse background absorption (αb) coefficient.....	18
2.4 Temperature measurement techniques in solid-state laser cooling.....	20
2.4.1 Thermal imaging.....	20

2.4.2 Photoluminescence (PL) thermometry	21
2.4.3 Temperature measurement using fibre Bragg gratings	21
2.4.4 Thermocouples	22
2.4.5 Photothermal deflection spectroscopy (PTDS)	23
2.4.6 Interferometric technique	23
2.5 Laser cooling materials and properties	24
2.5.1 Crystals	25
2.5.2 Semiconductors	28
2.5.3 Optical fibres	30
2.5.4 Nanocrystalline powders	33
2.5.5 Oxyfluoride glass-ceramics: recent developments in solid-state laser cooling.....	34
2.6 Optical cryocooler devices	43
2.7 Future prospects and conclusions.....	46
CHAPTER 3 GENERAL METHODOLOGY	48
3.1 Methodology of the overall research.....	48
CHAPTER 4 ARTICLE 1: OPTICAL PROPERTIES OF YTTERBIUM DOPED OXYFLUORIDE GLASS-CERAMICS - CONCENTRATION AND TEMPERATURE DEPENDENCE STUDIES FOR OPTICAL REFRIGERATION APPLICATIONS	49
4.1 Introduction	49
4.2 Materials and methods	52
4.3 Results and discussion.....	53
4.3.1 Effect of Yb^{3+} doping in aluminosilicate-oxyfluoride glass-ceramics (SPYb GCs) and identification of a potential composition for laser cooling applications	55
4.3.2 Effect of Yb^{3+} doping in germanate oxyfluoride glass-ceramics (GPYb GCs) and identification of a potential composition for laser cooling applications	62
4.3.3 Prospects of oxyfluoride glass ceramics for laser cooling applications	69

4.4 Conclusions	71
CHAPTER 5 ARTICLE 2: ENHANCING THE OPTICAL PERFORMANCE OF OXYFLUORIDE GLASS CERAMICS BY OPTIMIZING THE OXIDE: FLUORIDE RATIO AND CRYSTALLINITY FOR OPTICAL REFRIGERATION	73
5.1 Introduction	74
5.2 Materials and Methods	76
5.2.1 Sample preparation and characterization	76
5.2.2 Optical measurements	77
5.3 Results and Discussion	78
5.3.1 The thermal stability	79
5.3.2 Optical transmission and refractive index properties	81
5.3.3 Photoluminescence (PL) properties	84
5.3.4 Calorimetry	89
5.3.5 Effect of purification on the optical properties of glasses	91
5.4 Conclusions	93
CHAPTER 6 ARTICLE 3: DEMONSTRATION OF LASER COOLING IN A NOVEL ALL OXIDE GAYY SILICA GLASS	95
6.1 Introduction	95
6.2 Experimental results and discussion	98
6.2.1 Spectral properties of GAYY glasses	100
6.2.2 Laser induced cooling in GAYY glasses	104
6.2.4 Theoretical model and numerical results	106
6.3 Conclusions	110
CHAPTER 7 ARTICLE 4: ANTI-STOKES COOLING IN HIGHLY YTTERBIUM DOPED PHASE SEPARATED ALUMINIUM-YTTRIUM OXIDE GLASS BY 4 K	113
7.1 Introduction	113

7.2 Experimental	116
7.2.1 Materials	116
7.2.2 Structural characterization	117
7.2.3 Experimental setup for temperature measurements.....	117
7.3 Results and discussion.....	118
7.3.1 Laser induced cooling in PS- GAYY glass.....	120
7.3.2 Theoretical model and simulation results	121
7.3.3 Optical cooling in PS-GAYY glasses with different Yb ion concentration.....	126
7.3.4 Optical cooling in PS-GALY glass	127
7.4 Conclusions	129
CHAPTER 8 GENERAL DISCUSSION	131
8.1 Oxyfluoride glass-ceramics for laser cooling.....	131
8.2 Laser cooling in a novel all oxide GAYY silica glass	133
CHAPTER 9 CONCLUSION AND FUTURE PERSPECTIVES	136
REFERENCES	139
APPENDIX.....	159

LIST OF TABLES

Table 2.1: The properties of laser cooled crystals along with the experimental parameters	38
Table 2.2: The properties of laser cooled semiconductors along with the experimental parameters	40
Table 2.3: The properties of laser cooled optical fibers along with the experimental parameters	41
Table 2.4: The properties of laser cooled glasses along with the experimental parameters.	42
Table 4.1: The compositions of investigated GCs along with the terminology used in the text...	53
Table 4.2: Experimental lifetime values of Yb^{3+} ions in SPYb GCs at 920 nm, 980 nm, 1010 nm and 1030 nm.....	58
Table 4.3: The iQY and eQY values for SPYb 2.0 GC sample at room temperature with different excitation wavelengths at a fixed pump power of 300 mW.....	61
Table 4.4: The iQY and eQY values for all germanate glass-ceramics (GPYb GCs) with an excitation at 980 nm and at 1020 nm with a fixed pump power of 300 mW.....	65
Table 5.1: The glass ceramic and parent glass compositions along with the terminology used in the text.....	79
Table 5.2: The measured internal quantum yield (iQY) of all the glasses and glass ceramics using different pump wavelengths.....	86
Table 5.3: PL emission decay time values of Yb^{3+} : $^2\text{F}_{5/2}$ level in all glasses and glass-ceramics.	88
Table 5.4: The extraction efficiency of all glass ceramics at a wavelength of 1030 nm	88
Table 5.5: The background absorption coefficient of all the investigated glass ceramics.....	90
Table 6.1: The Yb ion concentration of investigated glasses along with the terminology used in the text, Al & Y concentration (in atomic percent), the mean fluorescence wavelength (MFW) & quantum yield at RT while exciting with 1029 nm laser with 5 W pump power.	98
Table 6.2: The thermal parameters of GAYY-3 glass.	106
Appendix Table 1: PL emission decay time values of Yb^{3+} $^2\text{F}_{5/2}$ level along with the adjusted R-square values obtained by fitting the curves of Figure 4.7(c) using single exponential function.	160
Appendix Table 2: The concentration of elements Al, Y/La and Yb in PS-GAYY and PS-GALY glass.....	175

LIST OF FIGURES

Figure 2.1: Schematic of laser cooling process in rare earth doped materials.....	11
Figure 2.2: The experimental setup used to measure the cooling of Yb ³⁺ : YAG crystals. Spectra Physics model 3900 s CW Ti: sapphire laser with an excitation wavelength of 1030 nm is used to pump the sample. Source: Adapted from Ref [23].	14
Figure 2.3: Experimental set up used to cool Yb ³⁺ : YLF crystal to 124 K. Source: Adapted from Ref. [61].	15
Figure 2.4: Schematic of mid: IR laser cooling setup of Ho-doped YLF crystals. Source: Adapted from Ref. [62].	16
Figure 2.5: Experimental system for measuring the temperature of the glass sample. Source: Ref. [6].	16
Figure 2.6: Experimental Set up used to cool silica glass. Source: Adapted from Ref. [64].	17
Figure 2.7: Experimental setup used to cool an Yb-doped silica fibre. Source: Adapted from Ref. [65].	18
Figure 2.8: Temperature change at an excitation wavelength of 1040 nm with 110 mW power coupled in the silica fibre. Source: Adapted from Ref. [65].	33
Figure 2.9: Schematic of the solid-state optical cryocooler. Source: Adapted from Ref. [97].	45
Figure 4.1: Schematic of laser cooling process in Yb doped oxyfluoride glass ceramics.....	54
Figure 4.2: (a) The XRD pattern of the glass (SPYb 2G) and corresponding glass-ceramic (SPYb 2GC), (b) The transmission electron microscope (TEM) image of SPYb 2GC. The crystallite size was ~ 20 nm.	56
Figure 4.3: (a) The measured absorption spectra of all SPYb GCs in the near infra-red (NIR) region, (b) The PL emission spectra of all SPYb GCs at an excitation wavelength of 920 nm, (c) The PL emission spectra of SPYb 2.0GC at several excitation wavelengths varying from 920 nm to 1030 nm with a fixed laser power of 300 mW, (d) Lifetime of ² F _{5/2} level of Yb ³⁺ in all the SPYb GCs and corresponding parent glasses at 920 nm and 980 nm excitations with a pump power of 300 mW.....	58
Figure 4.4: The PL emission spectra at different temperatures of SPYb 2.0GC sample using an excitation wavelength of (a) 960 nm and (b) 1020 nm.	59

Figure 4.5: (a) The PL emission spectra at 920, 940, 960, 1010, 1020 and 1030 nm excitation wavelengths with a pump power of 300 mW in different temperatures varying from 25°C to 200°C showing the behaviors of Stokes and anti-Stokes emissions for the sample (a) SPYb 0.5GC, (b) SPYb 1.0GC, (c) SPYb 2.0GC and (d) SPYb 3.0GC. Excitation using 920, 940 and 960 nm give rise to Stokes fluorescence emission. Anti-Stokes fluorescence emission is produced using 1010, 1020 and 1030 nm.....	60
Figure 4.6: The XRD pattern of the glass (GPYb 2G) and corresponding glass-ceramic (GPYb 2GC). The inset shows the TEM image of GPYb 2GC.....	63
Figure 4.7: (a) The PL emission spectra for all GPYb GCs with an excitation of 980 nm and (b) 1020 nm with equal excitation powers of 300 mW, and c) The PL emission decay curves for GC samples corresponding to $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition with an excitation wavelength of 920 nm (experimental values are shown using symbols and fitted curves using solid lines).....	64
Figure 4.8: The PL emission spectra of the GPYb 1.5GC at different temperatures upon laser excitations of 300 mW power of (a) 960 nm and (b) 1020 nm.....	66
Figure 4.9: The PL emission spectra at 300 mW laser power of 920, 940, 960, 1010, 1020 and 1030 nm excitation wavelengths at different temperatures varying from 25°C to 200°C showing the behaviors of Stokes and anti-Stokes emissions for the sample (a) GPYb 0.5GC, (b) GPYb 1.5GC, (c) GPYb 2.0GC and (d) GPYb 2.5GC. Excitation using 920, 940 and 960 nm give rise to Stokes fluorescence emission. Anti-Stokes fluorescence emission is produced using 1010, 1020 and 1030 nm.....	68
Figure 4.10: Anti-Stokes emission intensity of all the investigated oxyfluoride glass ceramics at 1010, 1020 and 1030 nm excitations (constant pump power of 300 mW) at 200°C.	69
Figure 4.11: (a) Temperature changes (ΔT) normalized by absorbed power (P_{Abs}) provided onto the glass-ceramics at various excitation wavelengths ranging from 920 nm to 1030 nm, (b) Temperature changes (ΔT) normalized by power (P_{Abs}) absorbed by the studied GPYb GCs as a function of excitation wavelength, (c) The $(\Delta T) / P_{\text{Abs}}$ behavior as a function of time for the GPYb 1.50 glass-ceramic sample with and without laser excitation at 1029.0 nm and 1480 nm. The minimum temperature was achieved for the GPYb 1.50GC sample.....	70
Figure 5.1: Experimental setup for measuring the temperature change of the G & GC samples.	78
Figure 5.2: DSC curve of the (a) G 65:35:1, (b) G 60:40:1 and (c) YF_3 G 60:40:2.	80

Figure 5.3: The transmission spectra of (a) G 65:35:2 & GC 65:35:2, (b) G 60:40:2 & GC 60:40:2, (c) GC 60:40:1 & GC 60:40:2 and (d) YF ₃ G 60:40:2 & YF ₃ GC 60:40:2.	82
Figure 5.4: The Refractive index values at 532.0, 632.8, 972.0, 1308.0 and 1538.0 nm for (a) all glass samples and (b) for GC 60:40:2, GC 65:35:2 and YF ₃ GC 60:40:2.	83
Figure 5.5: (a) The PL emission spectra of GCs & corresponding parent glasses doped with 1 mol % Yb using a pump wavelength of 980 nm and (b) The PL emission spectra of glass ceramics & corresponding parent glasses doped with 2 mol % Yb at a pump wavelength of 980 nm.	85
Figure 5.6: (a) The PL emission spectra of YF ₃ GC 60:40:2 & GC 60:40:2 with the corresponding parent glasses with a pump wavelength of (a) 980 nm, (b) Comparison of the PL emission spectra of YF ₃ GC 60:40:2 & GC 60:40:2 with a pump wavelength of 1020 nm.	86
Figure 5.7: (a) The temperature variations of all Gs normalized by absorbed power ($\Delta T / P_{\text{Abs}}$) for different pump wavelengths varying from 980 nm to 1040 nm, (b) The temperature variations of all GCs normalized by absorbed power ($\Delta T / P_{\text{Abs}}$) for different pump wavelengths varying from 980 nm to 1040 nm.	89
Figure 5.8: The temperature change as a function of time for the YF ₃ GC 60:40:2 at different pump wavelengths varying from 1000- 1032 nm.	91
Figure 5.9: The PL emission spectra of purified GC 60:40:2 and normal GC 60:40:2 (without purification) with a pump wavelength of 980 nm.	92
Figure 6.1: (a) EPMA analysis of GAYY-2, (b, c) SEM Image of phase separated preform (GAYY-2) at different magnifications, using backscattering electron mode (d) The absorption spectra of all GAYY glasses. The inset shows the highly transparent GAYY-2 preform.	100
Figure 6.2 (a): The anti-Stokes emission in all the GAYY glasses as well as MCVD SiO ₂ glass while exciting with 1029 nm laser with 5 W pump power, (b) The lifetime decay curves of MCVD SiO ₂ glass and GAYY-3 at an excitation wavelength of 920 nm. The inset shows the lifetime values of all glasses.	102
Figure 6.3: The temperature dynamics of (a) GAYY-1, (b) GAYY-2, and (c) GAYY-3 and while pumping with 6.5 W 1029 nm laser.	105
Figure 6.4: (a) The temperature evolution of MCVD SiO ₂ glass while it is exposed to 1029 nm 1 W laser obtained through FLIR thermal camera, (b) ΔT vs. time curve of MCVD SiO ₂ glass while pumping with 1 W at 1029 nm measured using FBG direct contact technique.	106

Figure 6.5: (a) The temperature change as a function of the pump power in GAYY glasses in air. The markers show the experimental results for the pump powers up to 6.5 W, (b) The effect of background absorption and convective heat load in obtaining temperature reduction with a change in pump power in GAYY-3 glass.	109
Figure 6.6: The experimental setup used for temperature measurements in laser cooling experiment. The zoomed-in circle shows GAYY glass placed on the silica optical fibres.	112
Figure 7.1: The temperature measurement setup employed during laser cooling experiments, with an inset image demonstrating the placement of the FBG in contact with the glass for temperature measurement.	118
Figure 7.2: The HAADF TEM image of the GAYY glass	120
Figure 7.3: (a) The experimental (red circles) and simulated temperature change of the glass while exciting with different excitation wavelengths with 20 W of pump power at atmospheric pressure (green line) and in vacuum (blue line), (b) Temperature dynamics of the glass when irradiating with 1037 nm laser radiation obtained using the FBG direct contact technique. The FLIR thermal camera images corresponding to each region is also shown.....	121
Figure 7.4: Temperature change of glass while exciting with 1037 nm laser with different pump powers varying from 300 mw to 20 W in experiment (red circles) along with the predicted temperature change in atmospheric pressure (green line) and in vacuum (blue line) for pump powers up to 800 W in simulations.....	123
Figure 7.5: Contour map of cooling efficiency as a function of temperature and pump wavelength.	126
Figure 7.6: (a) The temperature change of the glasses with different Yb concentrations while exciting with different excitation wavelengths ranging from 1030 to 1080 nm with a 20 W pump power. The optimum pump wavelength to obtain maximum temperature change for each Yb ion concentration is shown in the inset, (b) The temperature dynamics of the GAYY glass with 4×10^{26} ions/m ³ of Yb concentration while exciting with ~20 W of 1035 nm laser measured using FBG direct contact technique.	127
Figure 7.7: (a) Temperature change of the GALY glass while exciting with different excitation wavelengths ranging from 1030 to 1080 nm with 20 W of pump power, (b) Temperature dynamics of the GALY glass when irradiating with ~20 W of 1030 nm laser obtained using FBG direct	

contact technique. The inset shows the thermal image of the glass taken while exciting with laser.

..... 128

Figure 8.1: The comparison of (a) PL emission spectra and (b) PL emission decay curves of $\text{Yb}^{3+} : 2\text{F}_{5/2}$ level obtained by single exponential fitting for purified GC normal GC (without purification) at an excitation wavelength of 920 nm, (c) The ΔT / PABs behavior as a function of time for the purified GC at several excitation wavelengths varying from 1000 nm to 1030 nm.

..... 133

Appendix Figure 1: The room-temperature photoluminescence decay curves of $\text{Yb}^{3+} : 2\text{F}_{5/2}$ level for all aluminosilicate glass ceramics at an excitation wavelength of 980 nm (at a pump power of 300 mW).

..... 159

Appendix Figure 2: Comparison of anti-Stokes emission intensity between different compositions of SPYb GCs at 200°C with 1010, 1020 and 1030 nm excitations at a pump power of 300 mW.

..... 159

Appendix Figure 3: Comparison of anti-Stokes emission intensity between different compositions of germanate glass ceramics at 200°C at 1010 nm, 1020 nm and 1030 nm with constant power of 300 mW..... 160

Appendix Figure 4: The PL emission decay time values of $\text{Yb}^{3+} : 2\text{F}_{5/2}$ level at different temperatures varying from 25°C to 200°C for SPYb 2.0GC, SPYb 3.0GC, GPYb 1.5GC and GPYb 2.0GC at an excitation wavelength of 1020 nm, (b) The PL emission decay curves for SPYb 3.0GC corresponding to $\text{Yb}^{3+} : 2\text{F}_{5/2} \rightarrow 2\text{F}_{7/2}$ transition with an excitation wavelength of 1020 nm at 25°C, 100°C, 150°C and 200°C..... 160

Appendix Figure 5: The X-ray diffraction (XRD) images of GC 60:40:2 and YF_3GC 60:40:2 showing the formation of YLiF_4 and YF_3 phase respectively. 162

Appendix Figure 6: The lifetime decay curves of glass and glass ceramics containing YLiF_4 and YF_3 nanocrystals. 162

Appendix Figure 7: The elemental profiles of the GAYY-2 glass at the bottom and top of the silica tube along with the SEM images. 163

Appendix Figure 8: The transmission of the glasses from VUV to IR region 163

Appendix Figure 9: Cooperative luminescence spectra of MCVD SiO_2 glass and GAYY-3 with 400 mW of absorbed pump power while exciting with 980 nm laser. 164

Appendix Figure 10: The temperature evolution of GAYY 3 glass while it is exposed to 1029 nm 6.5 W laser obtained through FLIR thermal camera.....	164
Appendix Figure 11: The lifetime decay curve along with the single exponential decay fit of GAYY-4 at an excitation wavelength of 920 nm.	165
Appendix Figure 12: Temperature dynamics of the glass when irradiating with 1037 nm laser radiation obtained using the FBG direct contact technique	165

LIST OF SYMBOLS AND ABBREVIATIONS

APCL	Advanced Photonics Concepts Laboratory
ASF	Anti-Stokes Fluorescence
BBS	Broadband Source
BWIMP	Bragg Wavelength Interrogation by Monochromatic Power
CASE	Chelated Assisted Extraction Purification
DLT	Differential Luminescence Thermometry
DSC	Differential Scanning Calorimetry
EPMA	Electron Probe Microscopy Analysis
EQE	External Quantum Efficiency
FBG	Fiber Bragg Grating
FWHM	Full Width at Half Maximum
GAYY Glass	Aluminum: Yttrium: Ytterbium Oxide Glass
GC	Glass-Ceramic
GLTp	Glan-Thompson Polarizer
HAADF	High Angle Annular Dark Field
HWP	Half Wave Plate
iQY	Internal Quantum Yield
IR	Infra-Red
LD	Diode Laser
LED	Light Emitting Diode
LICOS	Laser Induced cooling of Solids

LN2	Liquid Nitrogen
MAT	Minimum Achievable Temperature
MCVD	Modified Chemical Vapour Deposition
MFW	Mean Fluorescence Wavelength
OH	Hydroxyl Ion
OSA	Optical Spectrum Analyzer
PDS	Photothermal Deflection Spectroscopy
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield
PPLT	Pump Probe Luminescence Thermometry
RE	Rare Earth
RI	Refractive Index
RT	Room Temperature
SEM	Scanning Electron Microscopy
SPhPs	Surface Phonon Polaritons
SRV	Servo Motor Controller
TE	Transverse Electric
TEM	Transmission Electron Microscope
T _g	Glass Transition Temperature
TM	Transverse Magnetic
T _p	Peak Crystallization Temperature
T _x	Onset of Crystallization Temperature
XRD	X-ray Diffraction

LIST OF APPENDICES

APPENDIX A- SUPPLIMENTARY INFORMATION.....	159
APPENDIX B- LIST OF PUBLICATIONS AND AWARDS	167

CHAPTER 1 INTRODUCTION

Laser cooling, also referred to as optical refrigeration, is the process of lowering a physical system's temperature using laser light. The basis of optical refrigeration is anti-Stokes fluorescence (ASF), which uses laser light to cool materials by removing phonons as radiation [1]. The technique was developed to deal with the primary issues that cooling methods that are currently available have, such as microphonic vibrations, the requirement for electrical connections, physical heat dissipation, and others. The absence of vibrations other than molecular vibrations, the lack of moving parts, enhanced reliability, the reduced electromagnetic interference, and the prolonged lifetime are just a few of the noteworthy benefits of optical refrigeration.

Pringsheim proposed the concept of solid-state laser cooling based on ASF in 1929 [2]. Initially, it was thought that optical refrigeration violated the 2nd law of thermodynamics, which assert that the overall entropy of an isolated system cannot diminish with time. However, Landau established the groundwork for this phenomenon in 1946 when he assigned entropy to light and demonstrated that the entropy of the radiation field increases during anti-Stokes fluorescence cooling [3].

For solid-state cooling, attaining a fluorescence quantum yield of ~100 % is essential. Due to their exceptional quantum efficiency, Kastler suggested the incorporation of RE-doped ions in transparent solids to observe anti-Stokes cooling [4]. The occupied 5s and 5p outer electron orbitals in these ions provide shielding for the optically active 4f electrons, which limits their engagement with the lattice and minimizing nonradiative decay. The anti-Stokes fluorescence (ASF) radiates concurrently with a thermalization process that extracts vibrational energy from the material, leading to material cooling when the mean fluorescence wavelength (MFW) falls below the pump wavelength. Following this, the ground-state multiplet re-establishes thermal equilibrium [5].

The future of laser cooling is being driven by new developments and trends, with fascinating advances in both theory and applications. However, a significant amount of current optical cooling study has concentrated on substances that are challenging to produce, handle, and incorporate into numerous devices. Consequently, there is a rising need for the creation of substitute materials. One possible field of research is the use of rare earth doped oxyfluoride glass ceramics as a cooling material, first proposed by Nemova G. and Kashyap R. [6]. These materials offer several advantages over conventional laser cooling crystals. The low phonon energy fluoride nanocrystalline environment in which rare earth ions are embedded is preferable for cooling to the

high phonon energy of oxide vitreous hosts. Second, glass ceramics can be produced cheaply and easily because they can be made straight from glassy materials. This offers solid-state laser coolers several significant functional benefits. If these innovative glass materials and glass ceramics are effective in cooling, the cooling of devices with diverse geometries will become more feasible and will pave the way for new laser cooling research.

The MCVD technique also has a significant impact on solid-state laser cooling. This technique of producing silica glass has gained the attention of researchers due to its superior stability, high purity, and low optical loss. Due to the limited solubility of rare-earth ions, silica glass cooling is difficult to accomplish. Some of these obstacles include RE ion clustering, concentration quenching, and the glass's high phonon energy, all of which reduce quantum efficiency and shorten the lifetime of radiative emission. In this thesis, we suggested incorporating network modifiers like aluminum, yttrium, and lanthanum into the silica glass substrate to overcome these restrictions. The Yb^{3+} ions are shielded from the high phonon energy of silica and are given an increase in luminescence efficiency when completely oxidised active RE ions are combined with a non-active RE.

This thesis summarizes the spectroscopic properties of ytterbium-doped silica glasses produced by both conventional melt-quenching and modified chemical vapor deposition (MCVD) techniques, as well as the observation of laser cooling. These findings could prove useful for the development of radiation-balanced fiber lasers and amplifiers.

1.1 The motivation and problem

The optical cooling domain is presently dominated by low phonon energy single crystals [1, 7, 8]. Due to their high cost, complex manufacturing process, challenging handling, and limited integration into various devices, there is an urgent need for the exploration and development of alternative materials. In order to maximize cooling efficiency, the use of low phonon energy materials is necessary. This is due to the fact that phonon-mediated non-radiative relaxation can easily counteract cooling, except if there exists a considerably larger bandgap compared to phonon energy. Additionally, the presence of any background absorption within the substance can result in a large parasitic heat load, significantly decreasing cooling performance. This is why even laser-grade materials of high-gain usually do not suffice for laser cooling purposes. To address this, it

becomes necessary to purify the materials to diminish impurity-induced relaxation and background absorption.

The requirement to expand the scope of laser cooling hosts to encompass oxide glasses has arisen owing to their exceptional mechanical and optical characteristics, their suitability for use with optical fibers, and their ability to retain their properties even after undergoing processes such as heat treatment, molding, cutting, polishing, and so on. However, the high phonon energy of oxide glasses is a significant disadvantage, necessitating additional purification and increased RE ion concentration to improve cooling efficiency.

Therefore, this thesis compiles and details on the spectroscopic investigation and characterization of different rare earth doped silica-based oxide glasses and oxyfluoride glasses. Several solutions for the successful demonstration of laser cooling in silica-based oxide glasses were proposed. The first method is the use of nanocrystals doped with rare earth materials in the form of glass ceramics in a high phonon energy oxyfluoride host. The incorporation of RE ions into fluoride nanocrystalline environments provides a low phonon energy environment, which is much lower than the high phonon energy of oxide glass host. GCs offer several benefits for the effective realization of solid-state laser coolers due to their robustness, ease of moulding, and low cost of production. Moreover, nanocrystals in GCs can produce properties that are different from the parent glass. Additionally, the presence of RE^{3+} ions embedded in the nanocrystals leads to a significant reduction in multi-phonon decay and non-radiative transition probabilities [9]. The use of Ytterbium (Yb^{3+}) offers a range of advantages, including a minimal quantum defect, limited concentration quenching effects, and the absence of excited state absorption [10]. Despite significant advances in glass-synthesizing techniques, attaining a high level of purity remains a challenge. To address this, global research endeavors have been devoted to purifying crystals and glasses through various methods [11]. However, with the current limited facilities, achieving higher quantum yields and lower background absorption is still an obstacle. In this thesis, a particular attention was given to fabricate highly purified oxyfluoride GCs through the chelated assisted extraction purification (CASE) technique in combination with the conventional melt quenching technique. However, the glass fabrication process needed to be fundamentally changed, even though the aforementioned method showed promise (increased quantum yield and lifetime), due to the purity constraints of the initial materials and the glass formation process.

Using the MCVD process, thus, has significant advantages in this critical area. Silica glass made by MCVD has been gaining attention as a potential material for solid-state laser cooling due to its excellent stability, high purity, and low optical loss. However, its low solubility of rare-earth ions makes it difficult to achieve cooling in silica. These challenges include clustering of RE ions and concentration quenching, as well as the high phonon energy of the glass leading to reduced quantum efficiency and shorter lifetime of radiative emission. To overcome these limitations, addition of network modifiers, such as aluminum, yttrium, lanthanum, etc., to the silica glass host was proposed. When active rare-earth ions that are fully oxidized are combined with non-active rare earth ions, it results in the creation of a low phonon solvation layer surrounding the Yb^{3+} ions. This shell acts as a shield, protecting the ions from the elevated phonon energy of silica, thus enhancing their quantum efficiency.

The development of these novel glass ceramics promises to revolutionize optical cooling research, simplifying the process of cooling devices of various shapes and sizes. This thesis presents an overview of the observation of laser cooling in ytterbium doped silica glass, which should aid in the advancement of radiation balanced fiber lasers and amplifiers. It also demonstrates laser cooling in rare earth doped nano crystalline oxide only glasses for the first time. The suggested method to obtain high emission efficiency can also be applied to other RE materials, enabling optical refrigeration via remotely pumped, vibration-free optics. Optical fibers can be easily created from these glasses, which will be a major step forward for photonic applications. This technology can be used to cool optical and electronic devices such as lasers, satellite instrumentations, sensors, etc.

1.2 Objectives

This thesis involves the experimental realization of laser-induced cooling in purified ytterbium doped oxide glasses. Based on the aforementioned problems, we specify four main objectives for the PhD, which are listed below.

- 1. To investigate the photoluminescence (PL) emission characteristics, including quantum yield, lifetime, and anti-Stokes emission, of oxyfluoride GCs and identify the optimal composition for laser cooling.**

The core focus of this investigation revolves around multicomponent germanate and aluminosilicate glass ceramics (GCs). These materials exhibit a diverse range of Yb concentrations, varying from 0.5 to 3 mol%, and feature the incorporation of PbF_2 nanocrystals. The manufacturing process involves the conventional melt quenching technique, with a specific interest in their suitability for optical refrigeration applications.

2. To explore the impact of changes in composition, including Oxide/Fluoride (O/F) ratio, crystallinity, amount of ytterbium and purity of the material for laser cooling applications.

We aim to experimentally uncover four unique factors that play a role in enhancing photoluminescence (PL) and governing the emission characteristics (such as quantum yield, lifetime, etc.) and cooling properties of an oxyfluoride GC with a specific composition: $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-(1-x) YLiF}_4\text{: (x)YbLiF}_4$. Specifically, we aim to investigate the impact of (i) the ratio between oxides and fluorides, (ii) the concentration of ytterbium ions, (iii) the degree of crystallinity, and (iv) glass purity on these properties.

3. To demonstrate laser induced cooling in phase separated oxide only silica glass with different ytterbium ion concentration.

Here we use MCVD technique to fabricate the high purity silica glass preform with the composition yttrium: aluminum: ytterbium (Y:Al:Yb). Our goal is to enhance the solubility of rare earth by adding alumina while encouraging the phase separation of the rare earths in the oxide glass without compromising the lifetime or cooling efficiency. To achieve this, we plan to combine fully oxidized active RE ions with non-active RE ions to create a low phonon solvation layer encircling the Yb^{3+} ions. This shell will protect the RE ions from the adverse effect of high phonon energy silica, thus improving quantum yield. Additionally, we intend to investigate how variations in the Yb ion density affect the optical properties of glass materials.

4. To optimize the maximum achievable temperature reduction in ytterbium doped oxide glass

Here we optimize the maximum achievable temperature reduction in phase separated oxide glasses by optimizing the pump wavelength and power. In addition, the goal is to predict the temperature variations under varying pump wavelengths, both in ambient conditions

and under vacuum, using numerical method and estimate the global minimum achievable temperature (MAT_G) of the glass.

1.3 Organisation of the thesis

A comprehensive literature review [11] on the various topics relevant to my PhD studies is provided in the beginning of this thesis. Section 1 will focus on the review of theoretical concepts of optical cooling. Section 2 discusses the experimental methods employed in laser cooling research, specially for temperature measurements and latest advancements in areas such as optical cooling of crystals, semiconductors, fibres and glasses. Section 3 will cover design aspects for optical cryocooler devices. Lastly, section 4 will provide concluding remarks and outline potential future prospects. Following the literature review the general methodology that is followed in our research and the four articles as the basis for this thesis are presented:

- The first article [12] presents initial investigations of multicomponent germanate and aluminosilicate glasses, which incorporate PbF_2 nanocrystals. These glasses encompass a diverse range of Yb concentrations, varying from 0.5 to 3 mol%, for potential optical refrigeration applications. The article focuses into an analysis of the optical properties, encompassing aspects such as absorption and PL emission spectra. Furthermore, it presents insights into PL lifetimes and internal quantum yields. Additionally, the article offers an in-depth examination of temperature variations, as observed with the assistance of a Fiber Bragg Grating, providing comprehensive insights and discussions.
- The second article [13] discusses four unique factors that play a role in enhancing photoluminescence (PL) and governing the emission characteristics (such as quantum yield, lifetime, etc.) and cooling properties of an oxyfluoride GC such as (i) the ratio between oxides and fluorides, (ii) the concentration of ytterbium ions, (iii) the degree of crystallinity, and (iv) glass purity. Also, compared are the optical properties in glass ceramics (GCs) that incorporate $YLiF_4$ and YF_3 nanocrystals. These nanocrystals are derived from an identical initial composition, which is adjusted through variations in time and fusion temperature to determine the most suitable composition for laser cooling. Furthermore, a comparative analysis was conducted to assess the optical characteristics of purified GCs in contrast to their unpurified counterparts.
- In the third article [14], laser induced cooling in ytterbium doped phase separated oxide glass (GAYY- Aluminum: Yttrium: Ytterbium Glass) fabricated using MCVD technique is demonstrated for the first time. By modifying the MCVD approach, it is possible to produce silica

glass preforms with a high concentration of Yb. Increased solubility of rare earths with the introduction of alumina, while also promoting phase separation of RE ions in the oxide glass is also demonstrated.

- The fourth and last article [15] is a continuation of the third article in which the Yb concentration, excitation wavelength and pump power are optimized. Also predicted the global MAT (minimum achievable temperature) in our glass as well as temperature variations with different excitation wavelengths under both atmospheric pressure vacuum conditions, by numerical simulation.

After presenting these four articles, a comprehensive analysis of the overall research conducted in this thesis will be presented in a general discussion. This discussion is followed by a concluding chapter, which summarizes the key findings of the research and highlights its significance in the field of solid-state laser cooling.

CHAPTER 2: LITERATURE REVIEW

This literature review is based on a published book chapter [11] providing an in-depth analysis of the topic of the current research related to the ‘Solid-state laser cooling in ytterbium doped oxide glass’. It provides an overview of the solid-state laser cooling, including the most recent progress in laser cooling of crystals, semiconductors, glasses and fibres, the experimental techniques and temperature measurement methods. Also, how this research contributes to the development of optical cryocooler devices is discussed. The literature review also highlights gaps in the current research in the field of optical cooling in glasses and suggest directions for further research. However, in the interest of conciseness and aligning with the focus of this thesis, sections that delve into the topics of rare-earth doped oxyfluoride pseudo-binary glasses and glass-ceramics for optical refrigeration are omitted. For readers seeking detailed information on these subjects, Reference [11] is recommended, which provides an in-depth exploration of these areas.

2.1 Introduction

Light matter interaction leads to several fascinating phenomena in interdisciplinary realms of optics to manipulate, heat, or cool objects, which has led to significant applications in materials science, industry, and medicine [16-18]. Among them, laser cooling is of great importance, promising for the development of optical cryocoolers, heat balanced laser system, etc.

Laser cooling or refrigeration generally refers to the temperature decrease of a physical system using laser light exposition. This can be either Doppler cooling, Sisyphus cooling, or anti-Stokes fluorescence (ASF)-based cooling. Doppler cooling, which is based on inelastic interaction of atoms with counter propagating laser beams tuned below resonance, gave rise to the 1997 Nobel Prize in Physics [16]. Later this led to the observation of Bose-Einstein condensation in dilute gas of alkali atoms, a discovery that was awarded a Nobel Prize in Physics in 2001[17]. More recently in 2019, Ashkin received the Nobel prize for his work on manipulation of microparticles with laser light which resulted in the invention of optical tweezers in 1986 [18]. Therefore, three Nobel Prizes were attributed for discoveries related to light-matter interaction that profoundly changed the world! New trends and innovations are emerging rapidly, driving the future of laser cooling to new horizons in both theory and practical applications.

Solid-state laser cooling that depends on ASF was firstly proposed by Pringsheim in 1929 [2]. In the early days this proposal was considered to oppose the second law of thermodynamics (which states that the total entropy of an isolated system can never decrease in time)[19]. Landau in 1946 gave a theoretical framework for this phenomenon by assigning entropy to light [3] and revealed that radiation field entropy should increase while ASF cooling since it is proportional to the beam solid angle as well as the frequency bandwidth. Therefore, in the laser cooling process, the entropy of the system increases by converting low-entropy laser light with a narrow spectral bandwidth into broadband, isotropic luminescence [1, 4, 20].

Fluorescence quantum yield of nearly 100% is a prerequisite to achieving cooling in solids. Kastler put forward the concept of using rare earth (RE)-doped ions in transparent solid materials as a platform for observing anti-Stokes cooling, due to their high quantum efficiency [4]. In these ions, the optically active 4f electrons are protected by the filled 5s and 5p outer electron shells which restrict the interaction with the lattice and therefore reduces nonradiative decay. Also, for temperatures >50 K, the phonon absorption and emission processes in many RE^{3+} excited states occur on ns to ps time scales which leads to the thermal equilibrium [21]. This is faster than that of the μs to ms lifetimes of the RE^{3+} excited states. In case of Yb^{3+} , the subsequent $2\text{F}_{5/2} \rightarrow 2\text{F}_{7/2}$ radiative decay takes place after the thermalization in the $2\text{F}_{5/2}$ crystal-field levels. If the mean fluorescence wavelength (MFW) is shorter than the pump wavelength, ASF emission is accompanied by a thermalization process which removes radiatively the vibrational energy from the material, thus resulting in the cooling of the material. Later thermal equilibrium is re-established in the ground-state multiplet [5].

In 1963, Kushida and Geusic were the first to observe an experimental cooling of a Nd^{3+} doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) crystal using 1064 nm laser. ASF was at 946 nm, in which they observed a lower heating than expected due to the laser cooling [22]. More than 30 years later, in 1995 Epstein et al. demonstrated net cooling from room temperature for the first time using Yb^{3+} doped ZBLANP ($\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF-PbF}_2$) glass [23].

This achievement was made possible thanks to the higher chemical purity and quantum efficiency of fluoride glasses, benefiting directly from the intensive efforts made to develop low loss fluoride optical fibres as an alternative to silica fibres for the telecommunication industry [24]. Since, notable progress has been made in this field by using rare earth ion-doped solids including fluoride glasses ZBLAN [21, 23, 25] BIG [26], oxide crystals $\text{KY}(\text{WO})_4$ [27], Y_2SiO_5 [28], YAG [7, 29]

and fluoride crystals (BaY_2F_8 [8, 30-32], YLF [33, 34] etc. Further developments in the field of laser cooling were achieved by using spontaneous and stimulated Raman scattering [35-38] superradiance [39, 40], nanocrystals [41-45] ferroelectric materials [41] oxyfluoride glasses [6, 46] etc. Electroluminescent cooling [47] as well as radiative cooling by light down conversion were also investigated [48]. Demonstration of radiation-balanced lasers in 1999 was one of the major milestones [49, 50]. Rare earth ion-doped athermal lasers and amplifiers have also been proposed recently [51, 52]. All-fibre approaches to laser cooling have attracted a great deal of attention [6, 53, 54].

The motivations behind the progress in solid state optical refrigeration is to achieve cryogenic temperatures and develop an all solid-state optical cryocooler to be used for cooling of electronic and optical devices, such as sensors, for instance. Recently, the idea of using nanocrystal doped with rare earth ions in the form of glass ceramics proposed by our group has attracted great attention in the area of solid-state laser cooling [6, 46]. Controlled crystallization of parent glasses using appropriate heat treatment makes the formation of transparent glass-ceramics possible [55] and one can observe all the combined properties of glasses and crystals in a single material [56]. These glasses and glass-ceramics possess good mechanical strength and thermal stability. In addition, the low phonon energy of the metal fluorides leads to an increased up-conversion efficiency of the incorporated rare earth ions, which diminishes the nonradiative decay rates, whereas reducing the interionic distance facilitates the energy transfer process [57, 58]. For instance, oxyfluoride glass-ceramics (GCs) containing PbF_2 nanocrystals in vitreous matrices of compositions $50\text{GeO}_2\text{-}30\text{PbF}_2\text{-(}20\text{-x) PbO-xYbF}_3$, with $x = 0.5, 1.5, 2.0, 2.5$ mol% glass composition and $30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-(}29\text{-x)CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-xYbF}_3$ with $x = 0.5, 1.0, 2.0, 3.0$ mol% glass were investigated experimentally for laser cooling applications by our group [59].

The obtained results showed the potential of glass-ceramics in laser cooling with a higher cooling figure of merit than their parent glasses. The unique properties of these materials such as their high thermal and chemical stability, low phonon energy, and higher photoluminescence (PL) quantum efficiency makes them suitable for optical refrigeration applications [60]. Therefore, other purified oxyfluoride glass-ceramic have been investigated over the past few years, with emphasis given to the high chemical purity requested to achieve efficient optical refrigeration effect. Efforts are still ongoing to better exploit the potential of these materials.

This chapter mainly details the recent developments in the field of oxyfluoride glass-ceramics based laser cooling in the Fabulas Laboratory. Section 2.2 discusses the theoretical principles of solid-state laser cooling. The experimental techniques in laser cooling and unique temperature measurement methods are described in Section 2.3. The most recent progress in laser cooling of crystals, semiconductors, and fibres are presented in Section 2.4 whereas the progress in oxyfluoride glass-ceramics are discussed in Section 2.5. The experimental design considerations for optical cryocooler devices are described in 2.6. Last, concluding remarks and future prospects are given in Section 2.7.

2.2 Theory

The laser cooling process (red-shifted photons are absorbed by rare earth ions and blue-shifted photons are then emitted) is illustrated in Figure 2.1. Electrons are excited from the ground state to the excited state (n_0 and n_1 respectively), when photons with frequency ν enter the host material and interact with the rare earth ions. Followed by the thermalization, the electrons in n_1 return to the ground state radiatively. This radiative emission at frequency ν_f leaves the material and the system will be subsequently cooled. Any non-resonant absorption by impurity ions and multi-phonon decay suppresses the cooling process.

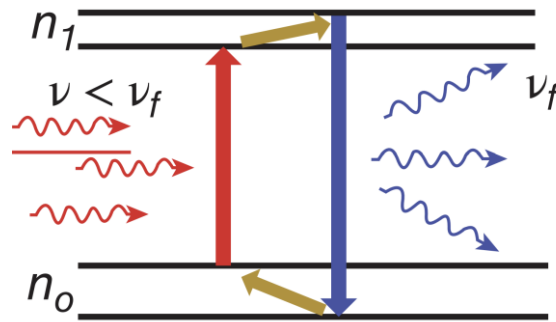


Figure 2.1: Schematic of laser cooling process in rare earth doped materials.

The idealized cooling efficiency can be defined as [61]

$$\eta_c = \frac{h\nu_f - h\nu}{h\nu} = \frac{\lambda}{\lambda_f} - 1 \quad (2.1)$$

which is given by the relation between the energy attained by the phonon absorption and the total pump energy, where $\lambda = \frac{c}{\nu}$ is the wavelength of excitation.

For practical cooling efficiency, both the nonradiative decay and the absorption by parasitic impurities which produce heat need to be taken into account. Considering these facts, at a given pump wavelength λ_p , the theoretical cooling efficiency can be found by using the relation between the absorbed power and the cooling power. It is given by the equation

$$\eta_{cool}(\lambda_p) = \frac{P_{cool}(\lambda_p)}{P_{abs}(\lambda_p)} \eta_{ext} \frac{\alpha_r(\lambda_p)}{\alpha_r(\lambda_p) + \alpha_b} \frac{\lambda_p}{\lambda_f} - 1 \quad (2.2)$$

where η_{cool} , P_{abs} , η_{ext} , α_r are respectively, the cooling power, the absorbed pump power, the external quantum yield, and the resonant absorption coefficient. The α_b , λ_p , and λ_f are the background absorption coefficient, the pump, and the emission wavelengths, respectively. The important parameter in cooling experiments is the temperature change (ΔT). The maximum change in temperature ΔT_{max} directly proportional to P_{cool} for small ΔT . Also, the absorbed power varies accordingly to the pump power P_p for small values of input power. Therefore, the relation between the experimental quantity $\Delta T_{max}/P_p$ and the cooling efficiency can be given by the relation:

$$\frac{\Delta T_{max}(\lambda_p)}{P_p(\lambda_p)} = \frac{P_{cool}(\lambda_p)}{K_{th}} \frac{(1 - e^{-\alpha_T(\lambda_p)L_s})}{P_{abs}(\lambda_p)} = \frac{A_L}{K_{th}} \eta_{cool}(\lambda_p) \quad (2.3)$$

where L_s , A_L , K_{th} , are the sample length, its absorbance ($1 - \exp(-\alpha_T(L_s))$) where $-\alpha_T = \alpha_r + \alpha_b$ and the sample-environment thermal coupling constant, respectively [62]. As we can observe from Eq. (2.1), increasing λ_p results in a higher cooling efficiency. Although at longer wavelengths the resonant absorption coefficient of the material decreases. Therefore, increasing the λ_p is not necessarily a good approach to reach the maximal cooling power, becoming more challenging as the contributions from impurities and multi-phonon relaxation become more significant. However, if these issues can be mitigated, the cooling efficiency will benefit significantly.

The cooling figure of merit Θ_c can be defined by the equation

$$\Theta_c(\lambda_p) = \frac{P_{cool}(\lambda_p)}{P_p(\lambda_p)} = A_L \eta_{cool}(\lambda_p) = K_{th} \frac{\Delta T_{max}(\lambda_p)}{P_p(\lambda_p)} \quad (2.4)$$

The main reason for nonradiative decay of an excited ion is multi-phonon relaxation. For achieving higher cooling efficiency, the band gap of the material should be large compared to the phonon energy. Otherwise, the multi-phonon relaxation can easily bridge the energy gap.

An exponential energy gap law [63] gives the nonradiative relaxation rate (KNR).

$$KNR = \beta_{e1} e^{-(E_g - 2\hbar\omega_{max})\alpha_{e1}} \quad (2.5)$$

where β_{e1} and α_{e1} , E_g , and $\hbar\omega_{max}$ are respectively the electronic factor, energy gap, and the maximum phonon energy of the material.

One of the essential properties of the host material for rare earth ions is its phonon energy, which has to be as low as possible in order to maximize the number of phonons required to nonradiatively de-excite an electron from an excited state. Typically, $h\nu_e \geq 8h\nu_{phonon}$ [2] is desirable to intrinsically achieve more than 90% of the ideal cooling efficiency. This condition comes from the Boltzmann distribution with the probability of de-excitation through nonradiative emission is low enough to induce cooling and restricts the materials that can be used for laser refrigeration. Therefore, the approximate condition for laser cooling [64] is given by:

$$\eta_{ext}\eta_{abs} > 1 - \frac{k_B T}{h\nu_f} \quad (2.6)$$

where η_{ext} and η_{abs} are respectively the external quantum yield and the absorption efficiency; K_B and T are the Boltzmann constant and the lattice temperature, respectively; and $h\nu_f$ is the emitted mean photon energy.

2.3 Experimental design considerations for cooling

Designing an experimental setup with efficient heat management is of great importance to achieve maximum cooling efficiency in laser cooling of different materials. This section is devoted to a review of a few experimental setups used to study optical cooling of crystals, glasses, semiconductors, and fibres. Different methods which have been employed to quantify the amount of impurities present inside a transparent solid material and measuring the exact value of background absorption coefficient are briefly explained. Various temperature measurement tools along with their advantages in using laser cooling measurements are also thoroughly described.

2.3.1 Experimental setups used for solid-state laser cooling

Experimental setups used to study optical cooling of certain crystals, glasses, semiconductors, and fibres are given here.

2.3.2 Crystals

The experimental setup used to measure cooling in Yb^{3+} : YAG crystals at ambient temperature by Epstein et al. is depicted in Figure 2.2 [28].

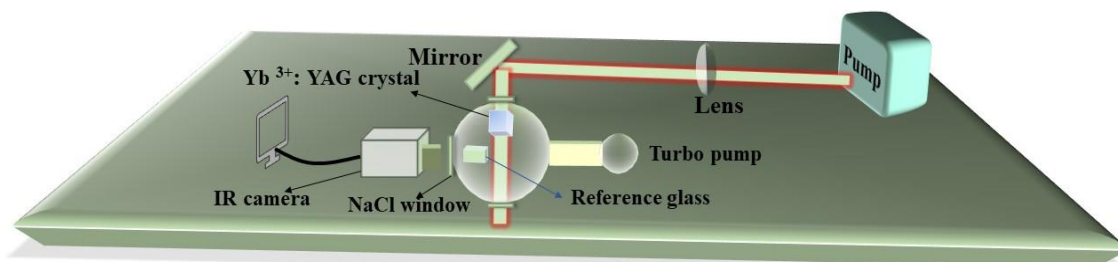


Figure 2.2: The experimental setup used to measure the cooling of Yb^{3+} : YAG crystals. Spectra Physics model 3900 s CW Ti: sapphire laser with an excitation wavelength of 1030 nm is used to pump the sample. Source: Adapted from Ref [28].

The sample was kept on the cover slides inside of a vacuum chamber (10^{-6} Torr pressure) in order to reduce the thermal conduction to the environment. Then, the sample was brought to thermal equilibrium within the chamber. A Ti: sapphire laser with an excitation wavelength of 1030nm (750 mW) was used to pump the sample and dumped at a beam block outside the vacuum chamber. Using thermal camera, the infrared (IR) light intensity difference between the chamber and the crystal was measured. The chamber temperature was higher compared to the crystal due to absorbed fluorescence. Similar measurements were repeated at 1020, 1025, 1030, 1040, and 1050 nm. Since the crystal absorbed only 10% of the laser light in the previously mentioned arrangement, it was placed in an optical cavity constructed between two dielectric mirrors for enhancing the total absorbed power. This arrangement indeed allows multiple passages of the laser beam through the sample and then light can be absorbed more effectively. Starting at room temperature, a net cooling of 8.9 °C was achieved using this method.

The experimental setup used by Melgard et al. to cool Yb^{3+} :YLF crystal to 124 K from room temperature is shown in Figure 2.3 [65]. A Yb^{3+} : fibre laser at 1020 nm was used to pump the crystal which is placed inside of a non-resonant cavity kept in a high vacuum chamber (maintained at a pressure of 10^{-6} Torr). Five round trip passes of the pump light were achieved inside the crystal. The pump light which is not absorbed was dumped externally. The heat load was reduced by decreasing the surface area of the crystal as well as placing the sample into a tightly fitted

copper clamshell coated with a low thermal emissivity material, as illustrated in Figure 2.3. The conductive heat load was minimized by placing the crystal in a holder using six optical fibres. A chilled water loop was used to maintain the clamshell at a constant temperature.

The mid-infrared (mid-IR) laser cooling of holmium-doped YLF crystal was recently achieved by Rostami et al. in 2019. Figure 2.4 depicts the schematic of the setup [66].

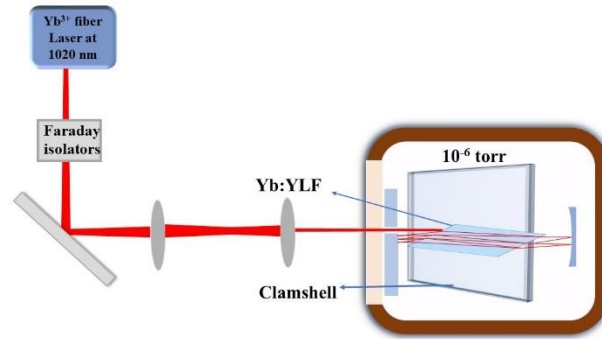


Figure 2.3: Experimental set up used to cool Yb^{3+} : YLF crystal to 124 K. Source: Adapted from Ref. [65].

A mid-IR continuous wave (CW) OPO (tunable pump source) was used for cooling of a Ho^{3+} : YLF(YLiF_4) single crystal. The OPO was pumped at 1070 nm by high-power CW fibre laser (IPG, YLR-500-SM), offering a tuning emission range from 1900 to 2300 nm. The crystal was placed in two low thermal conductivity supports which were kept within the vacuum chamber (10^{-6} Torr). This arrangement helped to reduce the conductive and convective thermal loads. The change in the crystal temperature (ΔT) in various wavelengths was viewed using a thermal camera, from outside the vacuum chamber through a KCl window.

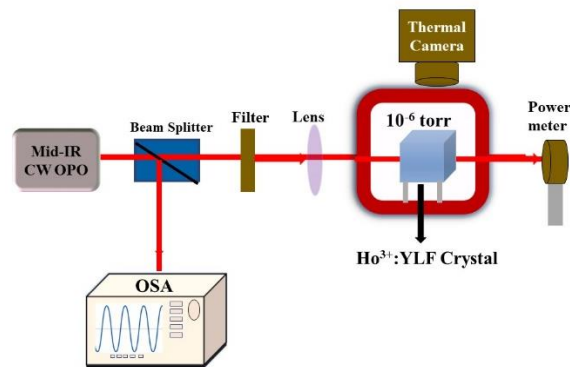


Figure 2.4: Schematic of mid: IR laser cooling setup of Ho-doped YLF crystals. Source: Adapted from Ref. [66].

2.3.3 Glasses

For the cooling experiments performed at the Advanced Photonics Concepts Laboratory (APCL) a single wavelength method (fibre Bragg grating wavelength interrogation by monochromatic power [BWIMP]) was used to monitor the temperature [7, 62, 67]. This is a reliable experimental setup for performing cooling experiments at atmospheric pressure, due to the low thermal mass of the fibre Bragg grating (FBG).

One of the main attractions of this setup is the use of the FBG for contact temperature measurements. For calibration, a broadband source was used along with an optical circulator in which the second port is coupled to the grating (Figure 2.5). The reflection from the FBG is guided to the circulator's third port and analysed by an Ando AQ6317B OSA [7]. The solid sample which has to be cooled is supported by a holder in an aluminium chamber. The holder consists of four silica fibres which are 1 cm long with a 125 μm diameter. The chamber temperature was measured using a thermocouple. The output from the Ti:Sapphire laser was varied by using a half-wave plate (HWP) placed before a Glan-Thompson polarizer (GLTp). The laser output was shaped to the desired diameter by using a pin-hole (PH). To measure the thermocouple (TC), the shutter was controlled with a servo-motor controller (SRV) [7, 62, 67]. This setup was also used to characterize crystals [7].

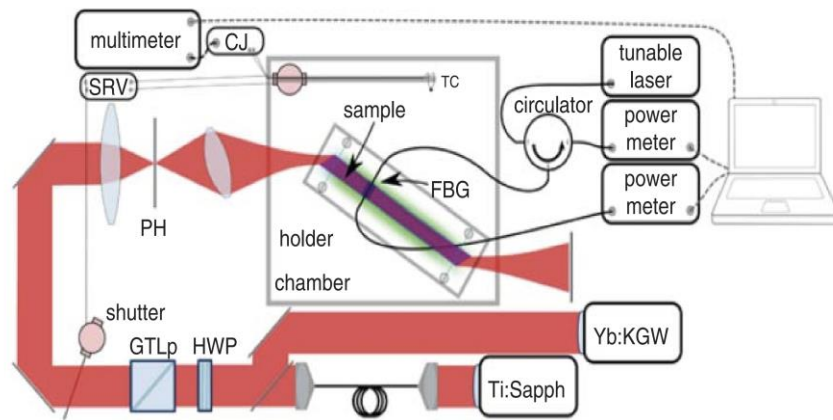


Figure 2.5: Experimental system for measuring the temperature of the glass sample. Source: Ref. [7].

The experimental setup used to cool silica glass at University of New Mexico is shown Figure 2.6 [68]. In order to examine the optical cooling and the cooling efficiency of an Yb-doped silica glass with varying the laser excitation wavelengths, Mobini and co-workers used a method called ‘Laser Induced Thermal Modulation Spectroscopy (LITMos) test’.

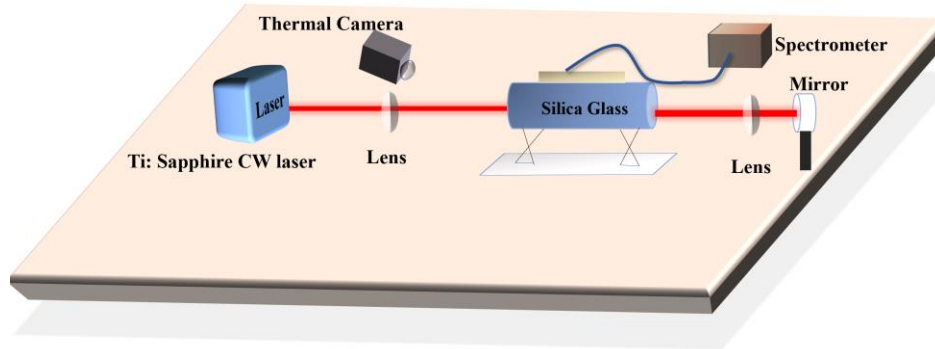


Figure 2.6: Experimental Set up used to cool silica glass. Source: Adapted from Ref. [68].

Using silica fibres, the sample was held inside of a vacuum chamber to avoid the heat load due to conduction and convection on the cooling material. A Ti: Sapphire CW laser with a pump wavelength varying from 980 to 1070 nm was used to excite the samples by focusing into the sample by using a lens having a focal length of 10 cm. As depicted in Figure 2.6 the laser beam travels through the sample twice with the help of an external mirror. A thermal camera and a fibre spectrometer are then used to respectively capture the temperature change and spectral features from the sample perpendicularly to the pumping beam.

2.3.4 Silica glass optical fibres

In 2020 was reported an important result with the first demonstration of cooling at atmospheric pressure of an Yb doped silica fibre. Figure 2.7 depicts the detailed experimental setup [69].

The core of the Yb doped silica optical fibre was pumped at several wavelengths (ranging from 1020 nm to 1070 nm) greater than that of the MFW of the material (1002.5 nm). A FBG sensor (~2 mK resolution) was used to observe the resulting temperature variations. Briefly, the fibre (~10 cm long) is kept in touch with the grating. In order to make two fibres in intimate physical contact, isopropanol is applied in between them. While pumping, the temperature of the fibre varies, and soon both the fibres attain thermal equilibrium. During the temperature variations, the

transmission spectrum of the FBG shifts. When the fibre was pumped at 1020 nm, the energy difference between the pump and the MFW was very small and the energy extracted from the fibre was not high enough to balance heating because of concentration quenching and pump absorption by impurities. In order to increase the energy difference, the fibre was then pumped at 1030 nm and therefore the heat extracted per absorbed pump power was also higher.

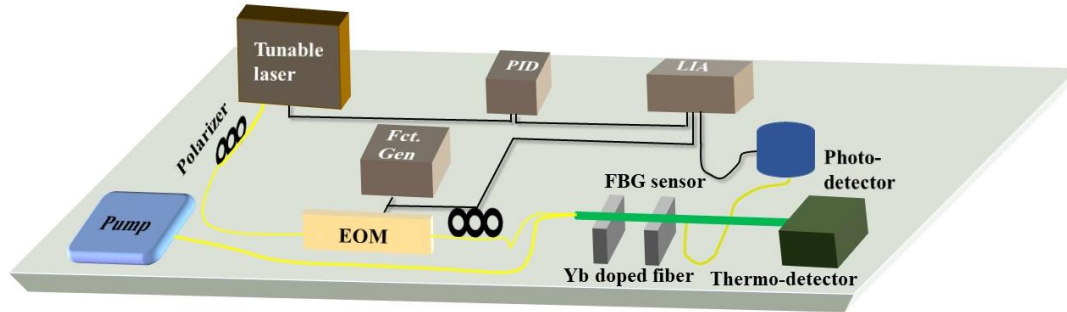


Figure 2.7: Experimental setup used to cool an Yb-doped silica fibre. Source: Adapted from Ref. [69].

2.3.5 Semiconductor nanoribbons

A net cooling of a semiconductor (group II–VI cadmium sulfide nanoribbons) down to ~ 40 K starting from 290 K was achieved by Zhang et al. in 2013 [70]. The experimental details are described below.

The laser cooling experiment was carried out on narrow strips of CdS nanoribbons kept over inverted-pyramid-shaped holes (~ 3 μm wide) on a SiO_2/Si substrate. The cooling material was placed on the cold finger of a continuous-flow microscopy cryostat. In order to cool and obtain the local temperature difference of the nanobelts, a pump–probe luminescence thermometry (PPLT) technique was used. To avoid the laser induced heating, the probe beam power at a wavelength of 473 nm was maintained at low power (20 μW). The pump and probe beams were collimated and focused on the sample by using a 50x objective. A confocal triple-grating spectrometer (Horiba-JY T64000 with a spectra resolution of 0.5 cm^{-1}) in a backscattering configuration was used to collect the spectra.

2.3.6 Techniques to analyse background absorption (α_b) coefficient

Characterizing the material background absorption coefficient is of primary importance in order to determine whether a sample is of cooling grade or not. Indeed, cooling efficiency can be affected by the presence of different extrinsic impurities in the rare earth ions or other starting materials, the presence of hydroxyl groups and other parasitic components (like local variation of material density, local defects, inclusions, etc.). These impurities can absorb or more generally attenuate the excitation light or also play the role of acceptors in energy transfer from excited RE^{3+} ions, emitting IR, and visible up-converted light.

Different methods have been employed to quantify the amount of impurities present inside a transparent solid material by measuring the exact value of background absorption coefficient. First, spectroscopic and elemental chemical analyses can be carried out in order to identify the impurities, to estimate their quantity and to evaluate their impact on cooling efficiencies [71-73]. The impurities can also be found at the primitive phase of the YF_3 , LiF , and YbF_3 starting precursors utilized for synthesizing YLF: Yb [71].

Hehlen et al. showed in their studies that the iron impurities (Fe^{2+} , Fe^{3+}) are the predominant contaminants in the Yb-doped YLF single crystals [71]. Inductively coupled plasma mass spectrometry (ICP-MS) studies showed that the crystal had a $^{56}\text{Fe} + ^{58}\text{Fe}$ concentration of 85 ± 30 ppm, which is almost 97.5% of all 3d transition metals in the sample. Electron paramagnetic resonance (EPR) study of the YLF crystal also identified the presence of Fe^{2+} in the crystal lattice, in agreement with the elemental analysis and the computational results.

During their study, Lieto et al. provided the variations in the cooling efficiency among two equally doped Yb^{3+} :YLF crystals, with the quantity of RE ion impurities contained inside the samples [73]. They investigated the sample PL emission in the green domain (535–560 nm) and in the NIR domain (720–860 nm). The acquired spectra were compared with the spectra from already known sources which led them to conclude that the observed emission in the green region was mainly due to the Erbium and Holmium present as impurities in the crystal. To support these observations, an elemental analysis was performed by using ICP-MS.

A comprehensive purification method based on chelate-assisted solvent extraction (CASE) using ammonium pyrrolidine di-thiocarbamate was reported by Patterson et al. in ZBLAN glasses [74]. A decrease in the transition metal and OH^- impurities was measured directly by using ICP-MS and indirectly by optical refrigeration measurements in ZBLAN glass. The technique was able to

decrease the total impurities in the rare earth concentration from 72 500 to ~ 100 ppb. More processing details on CASE can be found in literature [72].

From the Eq. (1) given in the Section 1 one can notice that a positive cooling efficiency corresponds to a sample cooling, whereas a negative cooling denotes heating. The external quantum yield and background absorption can also be found by plotting the cooling efficiency versus wavelength and fitting these using least squares method [1]. Using this method, a background absorption coefficient of $2 \times 10^{-4} \text{ cm}^{-1}$ ($\sim 1 \mu\text{m}$) was measured in the best cooling solid to date, i.e. the 10 mol% Yb^{3+} :YLF single crystals.

2.4 Temperature measurement techniques in solid-state laser cooling

The temperature measurement of the cooling material is a critical task in optical cooling studies, and several ways have been employed for developing different techniques. We will review a few important tools, such as infrared thermal cameras, photoluminescence (PL) thermometry, fibre Bragg grating (FBG), thermocouples (TC), interferometric method, and photothermal deflection spectroscopy (PDS).

2.4.1 Thermal imaging

The first demonstration of solid-state optical refrigeration in ZBLANP glasses doped with Yb^{3+} was performed by a noncontact temperature measurement using an InSb IR camera [1] having a spectral sensitivity in the range of 3–5 μm . In order to enhance the emissivity, a gold foil (1 mm²) was attached to the glass and painted black on the outside. However, this led to other complications such as fluorescence absorption. During their study, Hoyt et al. imaged the thermal emission of the sample without using the black foil [74]. In addition, temperature measurements using an IR camera were reported for cooling of Yb^{3+} :YAG and Y_2SiO_5 crystals, by Epstein et al. [28, 33] and Seletskiy et al. for Yb^{3+} : ZBLAN glass [75].

IR cameras have been widely used in optical refrigeration experiments [31, 74, 76], sometimes giving rise to problems such as detector saturation [75] obstructing the measurements. Also, the interpretation of the obtained result proved to be difficult because of the different emissivity characteristic to each material. Additionally, one must consider the sample properties such as thickness, surface roughness, and the background temperature, etc.

2.4.2 Photoluminescence (PL) thermometry

Photoluminescence thermometry allows the temperature measurements of materials by interpreting their PL spectral shape, lifetime, or integrated power within a given spectral band [62]. This noncontact temperature sensing method has been used for absolute temperature measurements of rare earth–doped materials, with an accuracy of ± 0.1 °C [77]. The changes in the PL intensity from rare earth ions may not be accurately quantifiable every time, as the crystal-field transitions do not considerably change with temperature. In rare earth–doped materials, the temperature-induced intensity variations in the PL spectra are mainly caused by variation in the Boltzmann distribution of the population of the emitting state [78].

On the other hand, differential luminescence thermometry (DLT) is the most used method in laser cooling experiments. While using at least two bands in DLT, probe power fluctuations cancel. Using a conventional temperature controller by controlling the sample's temperature, the temperature dependence of the PL spectra of the sample is usually measured in advance. DLT can be used during optical pumping, contrary to the opaque contact sensors. In order to detect slight temperature changes in the sample through the change observed in the PL spectrum, Seletskiy et al. implemented a time-resolved technique in 2009 [79]. This technique allows the measurement of the temperature by the time difference in the PL spectra emitted from the sample. A milli-Kelvin sensitivity with a GaAs heterostructure sample was obtained by the use of a monochromator along with a pair of photo diodes. But the sensitivity was only 0.6 K for rare earth–doped materials.

The temperature measurement using DLT does not provide the total averaged temperature but relies on the area of investigation. Other disadvantages of this method are the longer measurement time and the reabsorption of fluorescence depending on the depth of the examined area. Hence, calibration has to be performed with different geometries [62].

In 2009, W. M. Patterson et al. presented a two-band DLT technique that showed ~ 7 mK sensitivity in RE–doped materials [78]. This technique uses two bandpass filters to select regions of the PL spectra that possess distinct temperature dependences. They showed that the net quantum yield can be obtained also with good precision using this technique.

2.4.3 Temperature measurement using fibre Bragg gratings

Soares de Lima Filho et al. implemented and demonstrated a monolithic temperature sensor using a FBG to measure the temperature range between ambient to liquid nitrogen temperatures [80]. They showed that the nonlinear thermal sensitivity of the gratings originates from the nonlinearity of thermo-optic and thermal expansion coefficients, permitting reliable modelling of gratings at lower temperatures. Conventional silica fibres are transparent from 300 to 2000 nm, and they are appropriate for temperature sensing even in the presence of intense fluorescent light, in cooling experiments. They exhibit a negligible heat load with 125 μm radius, that can be even further minimized when the fibre diameter reduces to 14 μm [81]. Moreover, it is possible to write gratings even inside the cooling material. They are not affected by the electromagnetic noise and are inert to a vast range of chemicals.

The Bragg reflection wavelength λ_B , the spatial period of refractive index (RI) modulation, Λ and the effective mode index in the fibre n_{eff} can be related by $\lambda_B = 2n_{eff}\Lambda$ [62]. The Bragg wavelength changes with temperature as:

$$\Delta\lambda_B = \lambda_B \xi \Delta T \quad (2.7)$$

where the wavelength shift of the Bragg wavelength is, $\Delta\lambda_B$, for a temperature change of ΔT and ξ , is the temperature coefficient of wavelength change. The FBG used in our laser cooling experiments at the APCL was prepared by using a frequency quadrupled Q-switched Nd:VO₄ laser [82] employing a Talbot interferometer [83].

2.4.4 Thermocouples

Kushida et al. were the first to use thermocouples (TCs) for temperature measurements in optical cooling of Nd³⁺-doped YAG crystal in 1968 [22]. TCs were used in several optical refrigeration experiments [21, 25, 76, 84].

The working principle of the TC relies on the Seebeck effect. TCs consist of two different metal wires that are connected together at one junction where is measured the temperature. The temperature variation indeed results in a voltage variation in the joint metal wires.

Thermocouples have some intrinsic drawbacks when used in cooling experiments. During their studies, Edwards et al. used TCs glued to the Yb³⁺:ZBLAN glass [21]. They realized that absorption of intense fluorescence and heat conduction along the TC wires create undesired heating and distort the measurements. In addition, the need of a stable reference with the desired

resolution, the size of the sensor and fragility increases the complications. Later, improvements were made by reducing the diameter of the TC wires, enabling their use in cooling experiments by Thiede et al. [76].

2.4.5 Photothermal deflection spectroscopy (PTDS)

When the pump laser beam heats or cools a sample, its refractive index is changed. By measuring this refractive index variation using a probe beam, it is possible to correlate the beam deflection to the optical absorption of the material. By chopping the pump laser beam and determining the signal magnitude and angular deviation (deflection) δ of the probe beam, one can then find out the relative cooling and heating of the sample [85]. This method has been used in several laser cooling experiments [1, 28].

There are two different types of PTDS. One is collinear with photothermal deflection, in which the refractive index gradient is created and analysed within the material. The second type is transverse with photothermal deflection, in which the probing of the refractive index gradient is achieved within the thin layer near to the sample. The later method is suitable for less-transparent materials and for bad optical quality samples [85].

It is important to differentiate the effect of laser-induced population modifications in the ground and excited levels, since this alters the absorption and therefore the refractive index [86] for several important applications such as laser design [87]. This technique allows a rapid way to assess the temperature change of samples [1]. However, it also has the disadvantage that the absolute value of the temperature is difficult to measure.

2.4.6 Interferometric technique

Similar to PTDS where the temperature change alters the material refractive index, it can also alter the length, therefore affecting the phase of the laser light which passes through the material. The optical path length of the laser light relies on material temperature [88]. In order to quantify the path length change, the sample has to be placed in one arm of an interferometer and the phase shift among the beam passing through the sample and the reference beam can thus be observed. This technique is useful to measure the temperature of the bulk sample.

Investigation of laser heating/cooling in Yb^{3+} :YAG crystal using Mach-Zehnder interferometric technique can be found in the literature [89]. Farley et al. used a rectangular configuration of Mach-Zehnder interferometer using an Ar^+ laser (514.5 nm) beam to make interference fringes. The Ti:Sapphire laser beam at 915 nm was the pump. The crystal was introduced in one arm of the interferometer while the pump and probe laser beams were collinear to the Yb^{3+} : YAG but propagating in opposite directions. The fringes shift when the sample temperature changes and the variation in optical path length is measured from the number of fringes shifted. Even though no cooling was observed during their experiments, they demonstrated that the Mach-Zehnder interferometer can be simultaneously used to study laser heating as well as optical cooling of solids. The variation will only be in the direction of fringe movement. The main prerequisite condition is that both the pump and probe laser beams should overlap in the sample.

2.5 Laser cooling materials and properties

This section briefly discusses the properties and features of several materials that have been used for optical refrigeration applications. The active ions in laser cooling materials require high quantum yield at high energy to absorb photons from the pumping laser and re-emit them as fluorescence. Since the 5s and 6s electron shells shield the optically active 4f shell in RE ions, nonradiative decay is suppressed leading to narrow optical transitions and high quantum yields. Rare earth ions other than Ce^{3+} and Yb^{3+} have many 4f electronic states creating additional nonradiative processes which can cause heating. The Ce^{3+} ion is not a preferred choice, because the pump wavelength is near $\sim 4.5 \mu\text{m}$, which is currently not common. On the other hand, Yb^{3+} ion can be easily excited with commercial laser sources, making it a very practical and suitable rare earth ion for solid state laser cooling. It is generally desirable to use materials that possess low phonon energy for cooling, because this governs the rate of the multi-phonon relaxation rate [64]. The host material's chemical purity is also a critical criterion to be considered since quenching of excited ions by impurities can create unwanted heating in the solid. Impurities can be extrinsic species that absorb at the pump wavelength, vibrational impurities such as hydroxyl ion (OH^-) or metal ion impurities. A recent study in Yb^{3+} :YLF crystal by Hehlen et al. shows that Fe^{2+} trace metal ions have strong absorption at the optical cooling wavelength and can reduce the cooling efficiency [71]. They suggest chelate assisted solvent extraction for purification of starting materials.

Rare earth ion concentration is another important factor that can affect the quantum efficiency. When the active ion concentration increases, ion–ion interaction also increases. Energy migration among different ions increase the chance for reaching the excitation at the impurity where it decays nonradiatively and heats the material. Due to concentration quenching, the rare earth ion concentration has to be optimized in each sample. The thermal and mechanical properties of materials, chemical durability, and refractive index are also important for designing an optical cryocooler [64].

Fortunately, recent advances in the fabrication, material process conditions, and purification methods have improved the material quality to be used for cooling applications. Research avenues in the area of solid-state laser cooling using several potential materials such as crystals, semiconductors, optical fibres, nanocrystalline powders, glasses, and glass-ceramics will be described in Section 2.5.1–2.5.6.

2.5.1 Crystals

A major breakthrough in the area of optical refrigeration emerged with the perception that the cooling efficiency enhancement can be easily obtained in RE-doped crystalline hosts [90] in comparison with amorphous material hosts of same purity. The advantage of having long-range order in the crystalline materials helps to reduce the inhomogeneous broadening of the crystal-field transitions compared with glasses. Therefore, the peak absorption cross section at the Stark-level resonances sustains and leads to an enhancement of the absorption efficiency. One of the necessary requirements to achieve cooling in a RE doped material is a near-unity quantum yield, therefore, an as low as possible multi-phonon emission due to nonradiative transition probabilities. This condition is satisfied in low-phonon energy crystals. Along with these intriguing features, significant improvements in the crystal growth technologies and the innovative pumping schemes has led this to a promising technology.

Optical cooling experiments done by Bowman and Mungan on $\text{KY}(\text{WO}_4)_2$ and $\text{KGd}(\text{WO}_4)_2$ crystals in 2000 confirmed the potential of crystalline materials for anti-Stokes optical cooling [27]. They mentioned that because of the high cross-sections, the $\text{KY}(\text{WO}_4)_2$ and $\text{KGd}(\text{WO}_4)_2$ crystals have 20 times bigger cooling figure-of-merit than that of the ZBLANP glass. The first report of anti-Stokes cooling in crystals was based on 3.5% Yb-doped $\text{KGd}(\text{WO}_4)_2$ crystals. Later, the first demonstration of net optical refrigeration in crystals was achieved in 2001 in a 2.3%

Yb^{3+} :YAG crystal with a temperature drop of 8.9 °C from room temperature using 1.8 W of 1030 nm laser light [28]. This crystal has high thermal conductivity (13 W (m K)^{-1}) and ruggedness, making it a promising material for use in optical refrigerators. YAG has a phonon energy of $\sim 630 \text{ cm}^{-1}$. But the refractive index of this material is higher (1.93 at around $1 \mu\text{m}$) in comparison with ZBLAN glass (1.5). The higher refractive index is not desirable, since it can cause radiation trapping and fluorescence reabsorption.

Still in 2001, the KPb_2Cl_5 crystal was studied as a promising material because of its very low phonon energy of 203 cm^{-1} , its non-hygrosopicity, high chemical stability, and rare earth ions solubility [91]. Internal laser cooling in Yb^{3+} : KPb_2Cl_5 crystals was experimentally demonstrated by Mendioroz et al. in 2002 [92]. They achieved a room-temperature cooling efficiency of 0.2% in a $\sim 5 \times 10^{19} \text{ ions cm}^{-3}$ of Ytterbium-doped sample.

The theoretical and experimental cooling efficiencies of Yb^{3+} : BaY_2F_8 (BYF) crystals were reported by Bigotta et al. in 2006. A temperature drop of 4 K was measured with a cooling efficiency of 3% by pumping the crystal with 3 W of laser radiation at 1025 nm in a single pass configuration [8]. Those crystals were grown using the Czochralski technique. Even though crystalline BaY_2F_8 does not possess good mechanical properties, in particular thermal conductivity and hardness, the optical properties such as a wide transparency range ($0.125\text{--}12 \mu\text{m}$), low refractive index (1.51 at $1 \mu\text{m}$), and low phonon energy (420 cm^{-1}) can effectively compensate for these drawbacks. This material is less affected by the radiative heat loading compared to the fluoride glasses and oxide crystals due to broader transparency range in the infrared (up to $12 \mu\text{m}$). ASF optical cooling was also observed in Erbium-doped crystals. The first demonstration of ASF cooling in the single crystals of non-hygrosopic Er^{3+} : KPb_2Cl_5 were achieved by utilizing photothermal deflection measurements and time evolution of the average temperature of the sample obtained with an infrared camera [93]. The cooling efficiency was found to be about 0.4%. The first optical-cooling investigation of Yb^{3+} :YLF crystal was done in 2007 by Bigotta et al. [94]. This is a popular laser material with highest phonon energy of $\sim 450 \text{ cm}^{-1}$ and a thermal conductivity of 6.3 W (m K)^{-1} . A comprehensive study of Yb^{3+} :YLF was performed by Bensalah et al. in 2004 to determine the Yb energy levels in this host [95]. The ground state in Yb^{3+} :YLF has a crystal-field splitting of 485 cm^{-1} which is low compared with the Yb^{3+} :BYF (546 cm^{-1}), helping thus to reach lower temperatures.

The 5% Yb^{3+} :YLF crystal was grown using Czochralski furnace at a pulling rate of 1 mm h^{-1} at 845°C . The temperature was reduced to 6.3 K with an approximate cooling efficiency of $\sim 2\%$ after pumping the crystal with 2.6 W at 1026 nm in single-pass configuration placed in the vacuum-chamber. Later in 2008, Seletskiy et al. introduced a cavity-enhanced resonant absorption method [86]. They were able to achieve $\sim 89\%$ incident pump light absorption inside the 5% Yb^{3+} -doped YLiF_4 crystal by placing it inside of a Fabry-Perot cavity. The temperature was dropped down to 69 K from ambient temperature, while pumping the crystal using a Yb^{3+} :YAG disk laser at a wavelength of 1030 nm. Their measurements showed that 5% Yb^{3+} :YLF had a minimum achievable temperature (MAT) of $170 \pm 10 \text{ K}$.

Shortly thereafter, using an actively stabilized cavity, cooling in Yb^{3+} :YLF crystal was achieved with a temperature drop of 150 K [96]. Later, optical cooling of the same crystal with a temperature drop of $\sim 155 \text{ K}$ along with a cooling power of 90 mW was obtained in 2010 when pumping near the E4–E5 crystal-field transition [90]. This was a major breakthrough in the area of solid-state laser cooling. The same team presented the first demonstration of cooling a payload in 2010. This surpassed the performance of a standard thermoelectric cooler. They achieved cooling of a GaAs/InGaP double heterostructure ($2 \mu\text{m}$ thickness) of 165 K from ambient temperature [97]. These results were constrained due to the lower pump power and by the shortest wavelength of the tunable Yb:YAG pump laser (1023–1040 nm). Later in 2011, MAT of $\sim 110 \text{ K}$ was obtained in a Yb:YLF crystal with an excitation wavelength of 1020 nm [87]. The external quantum yield and background absorption values were $\eta_{\text{ext}} = 0.995 \pm 0.001$ and $\alpha_b = (4.0 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$, respectively. The results were obtained through two band differential spectrometry pump-probe technique.

The laser cooling efficiency model predictions were validated using a pump–probe technique in which local cooling to $\sim 110 \text{ K}$ at 1020 nm was achieved [98]. The studies reveal that the background absorption remains as the main barrier for obtaining sub-100 K working temperatures of the optical cryocoolers. Another potential promising candidate for optical refrigeration was presented by Zhong et al. in 2014 [99]. They prepared an Yb^{3+} -doped LuLiF_4 crystal and demonstrated a maximum temperature reduction down to 228 K by pumping at 1019 nm. A temperature reduction of $\sim 2 \text{ K}$ from ambient temperature was obtained. Even though the cooling performance of Yb^{3+} -doped LuLiF_4 crystal was not better than Yb^{3+} -doped YLiF_4 crystal at present, it has numerous advantageous such as low crystal lattice aberration, low internal stress

contributing to good optical quality and surface properties. Later a 5 mol% $\text{Yb}^{3+}:\text{LuLiF}_4$ crystal was cooled down with a temperature drop of 11 K by the same group in 2016 [100]. The cooling power and efficiency of the sample was ~ 14.5 mW and $\sim 1.9\%$, respectively.

As above mentioned, one of the major breakthroughs in the area of solid-state optical cooling was the first ever laser refrigeration of a payload in 2018 [101]. An $\text{Yb}^{3+}:\text{YLiF}_4$ single crystal was used to cool a HgCdTe sensor within a Fourier transform spectrometer.

2.5.2 Semiconductors

The distinct advantage of semiconductors in comparison with RE-doped materials is their capability for obtaining temperatures of ~ 10 K and lower by virtue of the ground state populations difference in the two systems. Due to Boltzmann statistics, the population at the top of the ground state decreases dramatically during the temperature decrease below 100 K in a RE-doped system. Semiconductors, which obey Fermi-Dirac statistics, maintain the lower energy valence band populated even at absolute zero.

The cooling efficiency, $\eta_c(h\nu, T)$ in semiconductors is given by [102, 103].

$$\eta_c(h\nu, T) = \eta_{exe}\eta_{abs} \frac{v_f(T)}{\nu} - 1 \quad (2.8)$$

where ν is the frequency of the pump laser, T is the sample absolute temperature, $v_f(T)$ is the mean fluorescence frequency, h is the Planck's constant, and η_{exe} is the external quantum yield, given by:

$$\eta_{exe} = \frac{\eta_e w_{rad}}{\eta_e w_{rad} + W_{nr}} \quad (2.9)$$

where η_e is the luminescence extraction efficiency and w_{rad} and W_{nr} are the radiative and nonradiative recombination rates, respectively; and $\eta_{abs} = [1 + \frac{\alpha_b}{\alpha(\nu, T)}]^{-1}$ is the absorption efficiency, where α_b is the background absorption coefficient and $\alpha(\nu, T)$ is the semiconductor absorption coefficient. A net optical cooling requires $\eta_c(h\nu, T) > 0$, which can be obtained in three different routes: possessing a large energy difference $\Delta E = h\nu_f(T) - h\nu$; having η_{exe} near unity; and obtaining η_{abs} near unity through the reduction of the background absorption [70].

Considerable progress has been made in the field of optical cooling of semiconductors during the past years from both theoretical and experimental points of view. Most of the experimental works were focused on the measurement of the external quantum efficiency and on developing sensitive noncontact probes of the localized sample temperature [104-107]. Theoretical works highlighted the importance of exciton-phonon coupling [102, 107, 108].

The first tentative experiment for semiconductor optical cooling was reported by Gauck et al. in 1996. They tried to cool a direct band gap semiconductor, GaAs, using a dome lens scheme with a tunable Ti:Sapphire laser source [105]. A GaAs heterostructure was kept among a sapphire piece and a transparent ZnSe dome lens. However, no net cooling was obtained, a reduction in heating was observed while tuning the laser wavelength below the MFW. An external quantum efficiency of $\eta_{\text{ext}} \sim 96\%$ was measured by using a bolometric calibration technique.

Gfroerer et al. attempted to cool an InGaAs/InP structure in 1998 by using an integral parabolic reflector [109]. They developed an accurate technique in order to measure the external quantum yield of LEDs with unknown emission profiles. The spontaneous emission was centred at 1620 nm with an external radiative efficiency of $\sim 63\%$.

Net cooling of group II–VI cadmium sulfide nanoribbons or nanobelts from room temperature by 40 K was achieved in 2013 [70]. A pump laser at 514 nm was used to achieve 1.3% of cooling efficiency with a cooling power of 180 microwatts. At 100 K, 532 nm pumping led to a net cooling of ~ 15 K with a 2.0% cooling efficiency.

In 2015, Sun et al. experimentally investigated the potential cooling of wide-band gap polar III–V semiconductor, namely GaN, by excitation below the band gap. Phonon-assisted anti-Stokes PL was observed, but the quantum efficiency was not high enough to drive net cooling [110]. Chen et al. analytically showed that engineering the photonic density of states (DoS) can help to achieve spontaneous Raman cooling by enhancing the anti-Stokes quantum efficiency beyond the natural optical absorption of the material and reducing the effect of Stokes emission [38]. Later, their study presented a precise expression for analysing the anisotropic DoS in a photonic-engineered system and evaluating the impact of anisotropic DoS on Raman scattering [111].

ASF was observed for CdSe quantum dots dispersed in solid PMMA polymer and in liquid toluene at room temperature [112]. Although a possible 2.3 °C cooling sign was observed for the toluene samples due to the absorption of 2LO phonons of CdSe, the comparatively low 80% quantum yield suggests that bulk cooling of the sample cannot, in fact, occur.

In 2017, Nemova and Kashyap proposed the idea of optical refrigeration of solids under the influence of surface phonon polaritons (SPhPs) [113]. Two samples can theoretically be brought close enough together in a way that their near-field thermal radiative modes are coupled. For example, one sample can be a rare earth–doped laser-cooled crystal and the other could be a slab of silicon carbide (SiC), such that surface waves evanescently tunnel from one to the other. It was shown that for short sample distances, when SPhPs propagate in the optically cooled material and in the nearby material supported at room temperature, the cooling can reduce considerably. The effect of coupled SPhPs on the refrigeration process in samples which differ in sizes and with distinct distances between them was investigated.

A net cooling of 23.0 K has recently been demonstrated in 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) along with the 58.7 K in 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) directly from ambient temperature [114]. The strong photoluminescence up conversion and near unity external quantum yield make these materials appropriate for net laser cooling.

A method to improve the efficiency of laser cooling in GaAs using single LOP-assisted transitions in band-tail absorption has been proposed and analysed theoretically during the past years [115, 116]. Band gap engineering can be used by introducing donor–acceptor pairs, which alter the DoS and could create a higher energy difference. However, the main difficulty of this method is to simultaneously optimize the doping density and binding energies of donors and acceptors [115]. The high refractive index, surface recombination, Auger decay, and parasitic background absorption are the major obstacles for optical refrigeration in semiconductors. Efforts have focused on obtaining photoluminescent cooling of quantum dots and electroluminescent cooling of light-emitting diodes [47, 48].

2.5.3 Optical fibres

Optical cooling of fibres have several advantages over bulk materials since light can be guided in long distances. Moreover, the miniature size of the fibre can be useful for spot cooling of micro-electronic devices. The Yb^{3+} :ZBLAN glass is one of the mostly investigated candidate for optical refrigeration applications [84, 117]. An Yb^{3+} :ZBLAN in the form of 6 g weight glass rod was cooled from ambient temperature to 240 K in 1999 [21]. Then, Gosnell optically cooled a fibre of the same material to 236 K in 1999 [118]. Using a more powerful pump laser and an improved cooling chamber, a cylinder of Yb^{3+} :ZBLAN was recently cooled down to 208 K [76].

A comprehensive model of optical cooling in Yb^{3+} :ZBLAN glass was introduced by Hehlen et al. in 2007 [119]. Their goal was to examine the upper concentration limits for impurities presented in the fibre. They found that Cu^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and OH^- are the most detrimental impurities for cooling process. For a practical optical cryocooler able to work at 100–150 K using this material, its Cu^{2+} concentration needs to be lower than 2 ppb, whereas the Fe^{2+} , Co^{2+} , Ni^{2+} , and OH^- need to be minimized to 10–100 ppb. Such trace levels are very low, even for high-quality optical materials, making very challenging the production of ZBLAN-based cryocoolers.

Tm-doped tellurite fibres have also been proposed for laser cooling. Temperature reduction of 30 °C from ambient temperature was attained with an excitation at 1943 and 1949 nm wavelengths (1.2 and 2.5 W, respectively) under vacuum [52]. All the metal impurities concentrations in the fibre were lower than 1 ppm.

However, the optical cooling of a fibre at atmospheric pressure was first demonstrated only in 2019 by Knall et al. [120]. With the maximal input power, 5.2 mK and 0.65 K cooling from ambient were measured in a 1% YbF_3 : ZBLAN single-mode fibre and 3% YbF_3 :ZBLAN multimode fibre, respectively. While analysing the performance of those fibres, it was evident that the observed cooling scales with core size and is strictly limited in the single-mode fibre (core size $\sim 3 \mu\text{m}$). Nearly ~ 67 times larger temperature change was observed in the multimode fibre due to the large core size. These results were consistent with the comprehensive model presented by Knall et al., which showed that for low-loss fibres, the maximum heat that is able to be extracted by ASF is proportional to the core radius and doped area [121].

In 2017, our research group proposed and fabricated new fibre material in the form of oxyfluoride glass ceramics for optical refrigeration applications. Single-index optical fibres made of oxyfluoride $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CdF}_2\text{-PbF}_2\text{-YF}_3$ glass and glass-ceramics (GCs) doped with 2 mol% Yb^{3+} were fabricated and characterized [122]. In order to produce the nano-crystallized GC fibres, the parent glass fibre was heat treated above its glass transition temperature (460 °C for 20 hours) after drawing directly from the crucible. Using the conventional glass fibre drawing technique from the preform did not allow to control the crystallization process to obtain a uniform crystalline size and distribution in the fibre. A notable enhancement of the Yb^{3+} PL intensity and higher photoluminescence quantum yield (PLQY) (95%) were observed for the nano crystallized GC-fibre upon 940 and 975 nm laser excitation wavelengths in comparison with the glassy (crystal-free) fibre. From the simulation, it was shown that the GC-fibre can demonstrate laser cooling

effect if the segregation ratio of Yb^{3+} ions inside the fluoride nanocrystals is $\sim 95\%$ to achieve high enough PLQY. The presence of impurities, such as unwanted Er^{3+} and Tm^{3+} ions has been detected in these fibres, which inhibit cooling.

Recently, Yb-doped ZBLAN fibres have been recommended as a gain medium for radiation-balanced lasers (RBL) [123]. A multimode 1% YbF_3 :ZBLAN fibre (300 μm core diameter and 430 μm cladding diameter) which was supported by two glass fibres was pumped using a tunable Ti:Sapphire laser in a double-pass configuration. A thermal camera was used to assess the temperature change. In order to determine the cooling efficiency and the resonant and parasitic absorption properties of the fibre at each wavelength, Peysokhan et al. used LITMoS test and the ‘Measuring the Absorption Coefficient via Side Light Analysis’ (MACSLA) method [124]. Simulations were done while considering the cooling parameters such as wavelength dependent cooling efficiency, resonance absorption coefficient, background absorption coefficient, and the external quantum yield with the aim of designing such lasers with negligible heat generation. It was found that the 10-fold reduction in parasitic background absorption can significantly decrease the heating in the system.

Although Yb^{3+} : ZBLAN glass has proven itself as a feasible material for cooling, the fibres made from these fluoride glasses are difficult to handle, and producing an all-fibre integrated optical cooling system based on these fibres would be a challenging task.

Therefore, Yb^{3+} doped oxide fibres are currently considered for laser cooling applications because of their versatility, ease of handling, and mature technique of fabrication (i.e. the modified chemical vapour deposition technique used to produce ultra-low-loss telecom fibres). Laser cooling was first demonstrated in a silica optical fibre in 2020 [69]. The fibre core (21 μm diameter) was doped with 2.06 wt.% of Yb^{3+} and co-doped with Al_2O_3 and fluorine. Using an excitation wavelength of 1040 nm, a maximum cooling of 50 mK at atmospheric pressure was achieved from room temperature with an absorption per unit length of 0.33 W m^{-1} . An FBG sensor with ~ 2 mK resolution was used to assess the temperature variation. The temperature change at an excitation wavelength of 1040 nm with 110 mW power coupled in the silica fibre is shown in Figure 2.8.

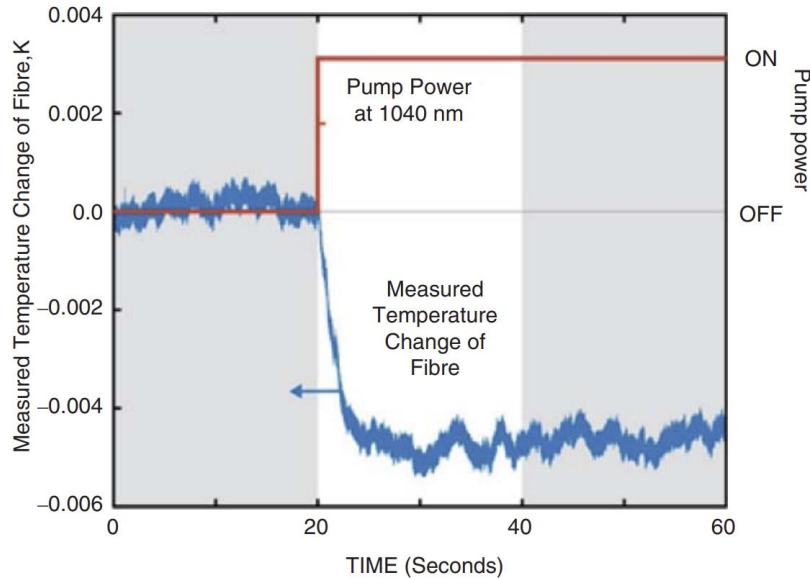


Figure 2.8: Temperature change at an excitation wavelength of 1040 nm with 110 mW power coupled in the silica fibre. Source: Adapted from Ref. [69].

These important results contribute towards the realization of radiation-balanced silica-based fibre lasers.

2.5.4 Nanocrystalline powders

Interestingly, optical refrigeration was initially predicted to be more readily achieved in rare earth–doped nanocrystalline powders than in bulk single crystals [125]. Enhanced laser cooling of Yb^{3+} : Y_2O_3 nanocrystalline powders was predicted and compared with the bulk material of same composition by Ruan et al. in 2006. Light can be localized easily in the powder due to multiple scattering. Also, the smaller size (few nanometres) of the crystalline powder affects the phonon distribution in a manner that the long wavelength tail of this distribution is enhanced in comparison with its bulk crystalline counterpart [126].

Using energy transfer theory, the material dopant concentration was optimized which gave rise to higher electron number and an enhancement in cooling power. In addition, due to photon localization, the cooling performance was enhanced in the nanocrystalline powders in comparison with the bulk material. Theoretical studies relying on the Maxwell equations revealed that, when the particle size reduces to the order of the pump wavelength, recurrent scattering effects lead to

the photon localization in the powder. Therefore, the photon density is enhanced, giving rise to an enhancement in absorptivity. The phonon DoS size effect was also explored. Molecular dynamics simulations were also employed as well as the Fourier transform of the velocity autocorrelation function. Using a second-order quantum mechanical calculation, the rate of phonon-assisted transition was obtained. Based on the pumping wavelength used, this process can enhance or diminish the cooling performance. In the practical cooling range (exciting at 1020–1030 nm), more enhancement was shown rather than temperature reduction.

Local internal and laser refrigeration of Nd-doped potassium lead chloride (KPb_2Cl_5) bulk crystals and nanocrystalline powders were reported by Garcia-Adeva et al. in 2010. Moreover, they also validated the predictions of Ruan and Kaviny [126]. The nano-powder which was excited at 855 nm (0.5 W) was cooled by $\sim 1.1^\circ\text{C}$. On the other hand, the bulk crystal which was excited with more power (1.2 W) was cooled only by $\sim 0.6^\circ\text{C}$.

The optical properties of Yb^{3+} doped YLiF_4 nanocrystalline powders with varying dopant concentration and different nanocrystal sizes were investigated for optical refrigeration applications by Soares de Lima Filho et al. in our group in 2015 [127]. No enhancement in quantum efficiency or absorption was observed in the nanocrystals when compared with the bulk crystal. The presence of rare earth impurities such as undesired thulium, erbium, and holmium was detected which is harmful for cooling. From the lifetime measurements, it was shown that at 15 mol% concentration, the emission of the nanocrystalline samples was strongly quenched. The shorter lifetimes of Yb^{3+} in the nanocrystals in comparison with the bulk single crystal showed that the quantum yield of the former is very low to obtain cooling.

2.5.5 Oxyfluoride glass-ceramics: recent developments in solid-state laser cooling

Rare earth-doped glass-ceramics have been extensively investigated during the past decades due to their excellent optical properties for developing optical amplifiers, lasers, display devices, medical sensors, etc. [128-131]. Owing to the low phonon energy and nanostructured environment of the RE (incorporated into fluoride nanocrystals) that results in enhanced PL quantum yield, oxyfluoride glass-ceramics were recognized as promising candidates for anti-Stokes optical refrigeration [67, 132]. They are unique materials obtained using glass synthesis technique and thermally activated crystallization of nanoparticles. They therefore possess the properties of all

their components, glasses, and crystals. An appropriate combination of oxide and fluoride constituents in the mixed parent glass indeed allows one to obtain by suitable heat-treatment fluoride-based nanocrystals embedded within the oxide-based glass matrix. Oxyfluoride glass-ceramics have the capability of accommodating relatively large amounts of activating dopants with uniform distribution within the crystalline phase. One of the unique properties of oxyfluoride glass-ceramics compared with fluoride single crystals and glasses is their ability to stabilize metastable fluoride crystalline phases that are difficult to prepare by conventional methods and protect at room temperature [133]. This is due to the fact that the nanoparticles are created in a highly non-equilibrium process, and the growth of crystallizing phases happens according to Ostwald's step rule, i.e. during the crystallization, 'the thermodynamically unstable phases occur initially, followed by the thermodynamically stable step' [134].

Mortier and Dantelle [135] well described the processes for the synthesis of transparent oxyfluoride glass-ceramics (GCs) containing PbF_2 , CdF_2 , CaF_2 , and LaF_3 nanocrystals. The comparison of thermal and optical properties of these GCs with those of their respective parent glass reveals the distinct spectral luminescence features of GCs. Usually, the RE fluoride dopants play the role of nucleating agent and reduce the thermal stability of the glass towards crystallization [136]. During the thermal treatment of these glasses, these RE fluoride components form the initial crystalline nanophases [137] as a constituent of a more complex fluorite-type structure and behave as activators, especially in luminescent materials. Wang and Ohwaki reported for the first time the fabrication of oxyfluoride glass-ceramics containing ErF_3 and YbF_3 [138]. Later, Kawamoto developed transparent oxyfluoride glasses of composition $50\text{SiO}_2-(50-x)\text{PbF}_2-x\text{ErF}_3$ ($x = 4$ and 5 mol%) and heat-treatment of these glasses at their first temperature of crystallization permitted transparent glass-ceramics to be formed, showing dispersion of $\beta\text{-PbF}_2\text{:Er}^{3+}$ crystallites within the glass matrix [139]. Since the Er^{3+} ions in the glass-ceramics strongly coupled to the phonon mode at 930 cm^{-1} , the multi-phonon relaxation rate was very small compared with the glass.

The rare earth dopants are indeed preferentially incorporated in the low phonon energy site of the fluoride nanocrystals (e.g. 270 cm^{-1} for $\beta\text{-PbF}_2$ crystals) and shielded from the high phonon energy of the oxide glass host, providing favourable conditions for the anti-Stokes laser cooling process. In addition, the fluoride crystals with low phonon energy contribute to lower the nonradiative relaxations and enhance the quantum yield of the radiative emission with respect to a high phonon energy oxide environment.

Our research group has proposed and investigated different types of oxyfluoride glass-ceramics for optical refrigeration applications during the past years. The characterization of GCs for optical refrigeration was first conducted by Soares de Lima Filho et al. in 2015 [140]. Ytterbium-doped oxyfluoride glasses of the composition $2\text{YbF}_3\text{:}30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-}27\text{CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3$ (mol%) were synthesized and characterized for three different crystallization levels. The cooling figure-of-merit was found to be depend on the crystallization level of the glass. Glass-ceramic samples had lower background absorption and higher quantum yield than the parent glass sample. It was also shown for the first time that glass-ceramics could be used as a reference for quantum efficiency measurements.

In 2016, oxyfluoride glasses of the composition $30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-(}29\text{-}x\text{)CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-}x\text{YbF}_3$, $x = 2, 5, 8, 12, 16$, and 20 mol% were prepared and their optical and thermal properties studied [46]. The aim of the study was to optimize the Yb^{3+} ion concentration to achieve high PL quantum yield and low background absorption. The presence of luminescence quenching for Yb^{3+} concentration higher than 2 mol%, was evident from the absolute PL spectra of the samples collected with a pump wavelength of 920 nm as a function of Yb^{3+} concentration. This was because of an increment in the energy transfer and reabsorption by the Yb^{3+} ions. The interaction among the Yb^{3+} ions were significantly reduced at lower concentrations. The highest quantum yield was attained for the GC containing 2 mol% of ytterbium. Due to concentration quenching effect, further increments in the Yb^{3+} concentration resulted in a reduction of the quantum yield. Moreover, the lifetime (τ) of the $\text{Yb}^{3+}\text{:}^2\text{F}_{5/2}$ excited state shortened from 1.52 to 0.19 ms in the studied glasses when increasing the Yb^{3+} concentration from 2 to 20 mol%. The authors mentioned that lifetime quenching may result from multi-phonon relaxation. Therefore, the 2 mol% Yb^{3+} -doped oxyfluoride glass which possess higher quantum yield among the studied compositions, associated with the low maximum phonon energy and low background absorption observed in all studied samples, was selected as the most promising candidate for laser cooling. Nevertheless, no cooling has been experimentally demonstrated so far in these glass-ceramics, essentially because of the large content of impurities.

The structural, thermal, and luminescence properties of Yb^{3+} -doped $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-CaF}_2$ oxyfluoride glasses and transparent GCs were also studied by our group [141]. The OH^- amount was reduced in the glasses to improve the optical properties. The formation of CaF_2 nanocrystals of 10 nm size was evidenced using x-ray diffractometry studies. While increasing the thermal

treatment temperature, transparency in the UV-Vis to the NIR region was reduced in GCs in comparison with the parent glass. The absolute PLQY was ~ 0.59 for the base glass prepared and 0.71 for the GC-650 (GC obtained from the parent glass by heat treatment at 650 °C). The PLQY decreased from 0.71 to 0.22 while increasing the heat treatment temperatures from 650 °C to 725 °C, because of larger nanocrystals size, as verified by the XRD measurements. The CaF_2 nanocrystals size, the Yb^{3+} ions concentration, and the amount of the Yb^{3+} ions incorporated into the nanocrystals were the crucial parameters for the optical refrigeration process in these GCs. The temperature-dependent PL spectra of the GC-650 sample revealed that PL intensity decreases when the temperature decreases at short wavelengths, but at longer wavelengths the intensity increases, due to the effect of Boltzmann distribution. While increasing crystallization temperature, the MFW also increased from the parent glass to the GC725 sample.

Recently, we studied the structural and optical properties of $50\text{GeO}_2\text{-}30\text{PbF}_2\text{-(}20\text{-x)PbO-xYbF}_3$, with $x = 0.5, 1.5, 2.0, 2.5$ mol% glass-ceramics for laser cooling [132]. The glass-ceramics doped with 1.5 and 2.5 mol% have the highest PL quantum efficiency under laser 1011 nm excitation, with anti-Stokes PL emission, which is essential to achieve laser cooling. In 2018, the optical properties of synthesized germanate glass-ceramics doped with 2 mol% of ytterbium were characterized as a function of crystallization temperature by our group [67]. The annealing temperatures were 330 °C, 350 °C, and 370 °C for five hours in order to obtain transparent GCs. The GC produced by heat-treatment for five hours at 350 °C has the highest PL efficiency and near infrared PL emission centred at ~ 1016 nm. The temperature measurement studies revealed that the GC heat-treated at 350 °C was the best sample which had a net heating near to zero with a pump wavelength of 1030 nm. The $\beta\text{-PbF}_2$ crystals which have a phonon energy of 270 cm^{-1} has a significant role in the cooling effect in this germanate oxyfluoride glass matrix. The net cooling was hindered due to radiation trapping and background absorption.

Along with the oxyfluoride glass-ceramic systems with PbF_2 nanocrystals, YLiF_4 crystals embedded glass-ceramics are also attracting interest in a variety of ways such as display devices and lasers, as recently shown by Deng et al. [142, 143]. In order to optimize the material properties for cooling applications, we studied the effect of optimization of the oxide:fluoride ratio in oxyfluoride glass-ceramics with the composition $(\text{SiO}_2\text{-Al}_2\text{O}_3)_{(100-x)}(\text{YLiF}_4)_x\text{: (YbF}_3)_1$ ($x = 35$ and 40 mol%) [144]. The thermal stability against crystallization of the material (corresponding to the difference between the onset of crystallization T_x and glass transition T_g temperatures) was found

to be 184 and 189 °C, respectively, which is considered to be excellent for shaping and fibre production. It is indeed assumed that having a difference between those characteristic temperatures equal or higher than 100 °C make the glass promising for thermal shaping without suffering from uncontrolled crystallization. The near IR PL emission was centred at ~1010 nm in both the glass-ceramics and the highest PL emission occurred for the GC with 40% of fluoride content. Depending on the oxide: fluoride ratio, the PL quantum efficiency changes between 99% and 64%, with the sample with 40% of fluoride content (lower oxide: fluoride ratio) as the most efficient under 980 nm excitation. The studies based on the optimization of lanthanide concentration and fluoride ratio in these glass-ceramics are still in progress.

A summary of potential laser cooling materials (crystals, semiconductors, fibres, and glasses) along with their properties and laser parameters used for cooling are given in Tables 2.1 to 2.4.

Table 2.1: The properties of laser cooled crystals along with the experimental parameters

Type of material	Final temperature (T) or ΔT	Pump wavelength (λ_p) with Pump power (P_p)	Background absorption coefficient(α_b), external quantum efficiency (η_e)	Sample dimension	Temperature measurement tool	Year	Reference
Crystals							
5 % Yb: LuLiF ₄	$\Delta T = 11$ K	1020 nm with 3W		3×3×5 mm ³ Brewster cut	Thermal IR camera	2016	[100]
7 % Yb: YLF	T= 130 K	1020 nm with 12 W	$\alpha_b = 3.0 \times 10^{-4}$ cm ⁻¹ $\eta_e = 99.5$ % at 1μm	2× 2× 2 mm ³ Brewster Cut	Differential luminescence thermometry (DLT)	2014	[145]
10 % Yb: YLF	T= 93 K	1020 nm with 54 W	$\alpha_b = 2.0 \times 10^{-4}$ cm ⁻¹ $\eta_e = 99.6$ % at 1μm	1.2 cm length, Brewster cut	Differential luminescence thermometry (DLT)	2014	[146]

5 % Yb: YLF	T= 123 K	1020 nm with 40 W	$\alpha_b = 4.6 \times 10^{-4}$ cm^{-1} $\eta_e = 99.5 \%$ at $1 \mu\text{m}$	1.2 cm length, Brewster cut	Differential luminescence thermometry (DLT)	2013	[147]
3 % Yb: YAG	T = 8.8 K	1029 nm with 4.2 W	$\alpha_b = 2.89 \times 10^{-4}$ cm^{-1} At 1550 nm $\eta_e = 99.14 \%$ at $1 \mu\text{m}$	Square cross section of edge d = 1 mm, 10 mm long, Brewster-cut	Fiber Bragg gratings (FBG) direct contact technique	2013	[7]
0.5 % Er: K ₂ Pb ₂ Cl ₅ (KPC)	$\Delta T = 0.7$ K	870 nm with 1.9 W	$\eta_e = 100.34 \%$ at 870 nm	4.5×6.5×2.7 mm^3	Infrared (IR) thermal camera	2012	[148]
5 % Yb: YLF	T= 155 K	1023 nm with 9 W		3× 3× 11 mm^3 Brewster Cut	Differential luminescence thermometry (DLT)	2010	[97]
5 % Yb: YLF	ΔT = 69 K	1030 nm with 45 W		Brewster Cut	Differential luminescence thermometry (DLT)	2008	[149]
1.2 % Tm: BaY ₂ F ₈ (BYF)	$\Delta T = 3.2$ K	1855 nm with 4.4 W	$\alpha_b = 2.0 \times 10^{-4}$ cm^{-1} $\eta_e = 98.0 \%$ at 1850 nm	5.5 cm, 1.5 cm diameter	Micro- bolometer camera	2008	[32]
2.5 % Yb :	$\Delta T = 4$ K	1025 nm with 3 W		3× 4× 10 mm^3	Thermal Camera,	2006	[31]

BaY ₂ F ₈ (BYF)				Monoclinic crystalline structure	Fluorescence intensity ration technique		
Yb: KPb ₂ Cl ₅	T= 150 K	1010 nm	$\eta_e = 100.2 \%$	4.6x 4x 3.3 mm ³ 2 cm in diameter	Photothermal deflection technique (PDT)	2002	[93]
2.3 % Yb:Y ₃ A l ₅ O ₁₂ (YAG)	ΔT =8.9	1030 nm with 1.8 W	$\alpha_b = 2.2 \times 10^{-4}$ cm ⁻¹ $\eta_e = 98.8 \%$ at 1 μ m	Cubic crystal structure	Photothermal deflection technique (PDT)	2001	[28]

Table 2.2: The properties of laser cooled semiconductors along with the experimental parameters

Type of material	Final temperature (T) or ΔT	Pump wavelength (λ_p) with Pump power (P_p)	external quantum efficiency (η_e) at 1 μ m	Temperature measurement tool	Year	Refer ence
Semiconductors						
CdSe/ ZnS quantum dots	ΔT = 2.3 K	647 nm with 27 mW	$\eta_e = 80 \%$	Thermocouple	2016	[112]
3D CH ₃ NH ₃ PbI ₃ (MAPbI ₃) and 3D CH ₃ NH ₃ PbI ₃ (MAPb)	T= 23 K And 58.7 K	785 nm with 0.66 mW	η_e = 99.8 %	pump–probe luminescence thermometry (PPLT) technique	2016	[114]

Group II–VI cadmium sulfide (CdS) nanoribbons or nanobelts	$\Delta T = 40\text{ K}$ at 514 nm $\Delta T = 40\text{ K}$ at 532 nm	514 nm/ 532 nm	$\eta_e = 99\%$	pump–probe luminescence thermometry (PPLT) technique	2013	[70]
GaAS/GaInP double heterostructure		888 nm	$\eta_e = 96\%$		1996	[105]

Table 2.3: The properties of laser cooled optical fibers along with the experimental parameters.

Type of material	Final (T) or ΔT	Pump wavelength (λ_p) with Pump power (P_p)	Fiber dimension	Temperature measurement tool	Year	Reference
Fibers						
2.06 mol % Yb doped Silica Optical fiber	$\Delta T = 50\text{ mK}$	1040 nm with 110 mW	Core diameter- 21 μm , Numerical aperture (NA)- 0.070, outer diameter- 125 μm	Fiber Bragg grating (FBG) sensor	2020	[69]
2 % Tm doped germanate fiber	$\Delta T = 30\text{ K}$	1943 nm with 1.2 W/ 1949 nm with 2.5 W	30 mm length, core/cladding diameter sizes of 25/250 micron	High precision NTC MF51E thermistor	2011 , 2012	[52, 53]
	$\Delta T = 13\text{ K}$	1015 nm at 85 mW	40 mm length,	Photo thermal	2001	[150]

Multimode Yb ³⁺ doped ZBLAN fiber			total diameter - 250 μm , core diameter - 170 μm	deflection spectroscopy (PDS)		
Multimode Yb ³⁺ doped ZBLAN fiber	T= 236 K $\Delta T = 65$	1015 nm	7 mm length, total diameter-250 μm , core diameter-170 μm	Luminescence spectroscopy	1999	[118]
Multimode Yb ³⁺ doped ZBLAN fiber	$\Delta T = 16$ K	1015 nm at 77 mW	10 mm length, 250 μm Core diameter	Luminescence spectroscopy	1998	[151]

Table 2.4: The properties of laser cooled glasses along with the experimental parameters.

Type of material	Final (T) or ΔT	Pump wavelength (λ_p) with Pump power (P_p)	Sample dimensions	Temp measurement tool	Year	Reference
Glasses						
Yb doped silica glass	$\Delta T = 0.6$ K	1053 nm with 10.4 W		Infrared (IR) thermal camera	2019	[68]
Yb: ZBLANP glass	$\Delta T = 6$ K	1027 nm with 6 W	2×2×3 mm ³	Luminescence spectroscopy	2004	[152]
Tm: ZBLANP glass	$\Delta T = 19$ K	1900 nm with 3.5 W	4×4×8 mm ³	Pyroelectric thermal camera/ Micro bolometer thermal camera	2003	[74]

2 mol % Tm: ZBLANP glass	$\Delta T = 2 \text{ K}$	1900 nm with 2.72 W	$3 \times 3 \times 10 \text{ mm}^3$	Pyroelectric thermal camera/ Micro bolometer thermal camera	2003	[74]
Yb: ZBLANP glass	$\Delta T = 1.25 \text{ K}$	1857 nm with 3 W	$5 \times 5 \times 9 \text{ mm}^3$	Thermal IR camera	2000	[153]
Yb: ZBLANP glass	$\Delta T = 1.20 \text{ K}$	1900 nm with 3W	$5 \times 5 \times 9 \text{ mm}^3$	Thermal IR camera	2000	[154]
Yb: ZBLANP glass	$\Delta T = 0.3 \text{ K}$	1015 nm	$2.5 \times 2.5 \times 6.9 \text{ mm}^3$	IR thermal camera & Photothermal deflection spectroscopy (PDS)	1995	[1]

2.6 Optical cryocooler devices

The most important characteristics of solid-state laser cooling are the absence of mechanical vibrations, the reliability, low electromagnetic interference, and the very long lifetime of the system. In general, the technology attempts to cool a payload such as sensors. This technology also finds a vast range of applications such as in satellite instrumentations, biomedical sensing, geophysical sensors, etc.

The performance of a solid-state cryocooler is governed mainly by two parameters such as the cooling power P_{cool} , and the heat load on the cooling material P_{load} [21]. The temperature evolution of the cooling materials can be written as:

$$C(T) = \frac{dT}{dt} = -P_{cool} + P_{load} \quad (2.10)$$

where C is the heat capacity of the material. There are mainly three types of heat loads: convective, conductive, and radiative. Contributions from the first two can be reduced by keeping the cooling element inside a vacuum chamber and by reducing the contact area between the sample and holder. The radiative load has the maximum contribution and can be expressed as:

$$P_{rad} = \frac{\sigma \varepsilon_s A_s}{1 + \chi} (T_c^4 - T^4) \quad (2.11)$$

where σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W (m}^2 \text{ K}^4)^{-1}$), $\chi = (1 - \varepsilon_s) \varepsilon_s A_s / \varepsilon_c A_c$ with ε_s and A_s the thermal emissivity and the surface area of the sample, respectively; ε_c and A_c are the thermal emissivity and the surface area of the chamber, respectively. P_{rad} can be minimized

by maximizing χ which can be accomplished for small ε_c and A_c . A tight-fitting clamshell chamber surrounding the cooling sample with a low-emissivity coating can help to satisfy these conditions.

Even though observation of cooling has been demonstrated by several research groups, only few did thermally link the samples to the practical heat loads in ways that attain the desired temperatures. For practical applications, simply linking the payload with the laser-cooling element is not viable, since it absorbs the strong fluorescence that leaves the material and heats up. Designing a thermal link for preventing the fluorescence from exposing the payload is therefore important. At the same time, the designed thermal link should offer an excellent thermal conductivity among the laser-cooling element and the payload. Thus, the proper design of the thermal link demands a suitable selection of the optical geometry and materials used to connect the different elements.

A numerical model of the cooling process along with the design of an optical cryocooler for a focal plane cooling application was introduced by Mills et al. in 2001 [154]. Their design concept consists of a cooling element that is bonded directly to the focal plane structure for absorbing the heat. A heat sink having high absorption at the emitted fluorescence wavelength is used to absorb the fluorescence. A low thermal conductivity material in the form of folded tube is used to support the cooling material and focal plane. Using an optical fibre, pump laser light is transmitted and focused to the cooling material. Their particular design consists of 20 W diode laser package to make 400 mW heat lift at 80 K when the laser heat sink is kept at 300 K.

Different types of thermal link models such as a cascaded mirror design, a kinked waveguide, a hemispherical design, and a tapered waveguide were theoretically and experimentally presented by Parker et al. in 2009 [155]. Thermal link made of sapphire (thermal conductivity of 32–35 W cm⁻²) with a right-angle kink is another attractive design choice [156]. Sapphire presents good thermal conductivity, and the 90° kink eliminates the unwanted fluorescence which enters into the link. The residual fluorescence that reaches the attached payload can be blocked by using an additional metal coating at the link end face.

The first optical refrigeration of a payload connected to a cooling element was achieved in 2018 by researchers at Los Alamos National Laboratory and the University of New Mexico [101]. The cooling element was Yb³⁺:YLiF₄ crystal which has been previously been cooled down to 91 K

[157]. This was kept in a Herriott cell and excited using a linearly polarized CW fibre laser of 1020 nm (47 W laser wavelength) to refrigerate a mercury cadmium telluride (HgCdTe) IR sensor.

The optical cryocooler design which they used is schematically shown in Figure 2.9. The sensor which has to be cooled is connected using a cold finger, a mirror, and the thermal link to the Yb^{3+} : YLiF₄ crystal. A support element and closely fitting clamshell are used to mount the whole assembly.

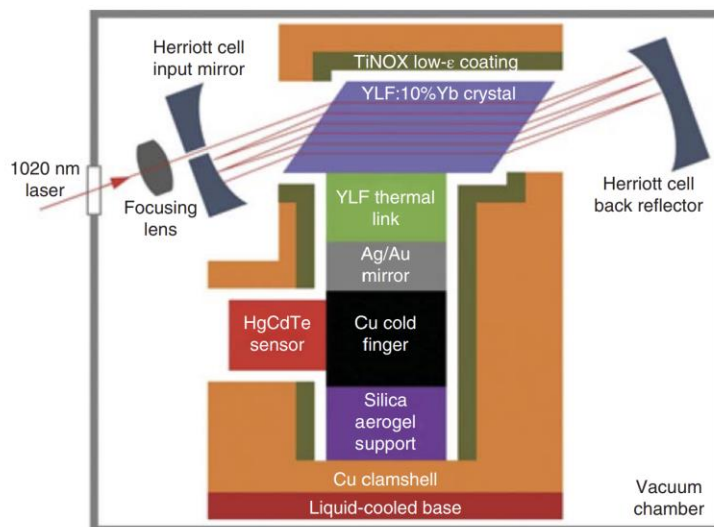


Figure 2.9: Schematic of the solid-state optical cryocooler. Source: Adapted from Ref. [101].

There were mainly four stringent requirements that led towards the efficient operation of all-solid-state optical cryocooler. First, a suitable material (Yb^{3+} : YLF crystal) with low background absorption and high external quantum yield, enabled sufficient cooling of the payload. Secondly, the use of a copper cold finger contributed enough design flexibility needed to integrate the payload, support element, and diagnostic components. Thirdly, the hydrophobic silica aerogels used were mechanically reliable to support the laser-cooled assembly and provided good thermal insulation. Next, they avoided unnecessary heating by bonding the Yb^{3+} : YLF crystal and thermal link using Van der Waals bonds.

Nowadays, along with identifying and preparing high purity materials, research, and development in solid-state laser cooling technology is devoted to make use of the optical cryocooler devices for cooling of satellites and space-based remote sensor systems. Moreover, it is also expected that cryocooler devices will find new applications various domains, like defense and security, etc.

2.7 Future prospects and conclusions

Solid-state laser cooling technology is progressing quickly with a strong potential for utilization in radiation-balanced lasers, aerospace applications, and sensors. The current cooling techniques use mechanical refrigerators, which have practical complications like microphonic vibrations and thermal noise. Laser-induced cooling of solids (LICOS) effectively overcomes these drawbacks as thermal energy is removed optically.

Different materials such as crystals, semiconductors, optical fibres, nanocrystalline powders, and glass-ceramics have been introduced as efficient cooling materials within the past 15 years since the first demonstration of cooling in ZBLAN glasses. New reliable temperature measurements methods have been proposed and implemented over the years. Material purifying methods such as chelated assisted extraction of precursor materials have been introduced to reduce the background absorption coefficient and enable efficient cooling. The optical refrigerator based on $\text{Yb}^{3+}:\text{YLiF}_4$ crystals recently developed by researchers at the University of New Mexico has now surpassed the cryogenic barrier. The first demonstration of cooling of a payload (HgCdTe sensor as a part of Fourier transform infrared spectrometer) in 2018 was another major milestone.

The main challenging issues to address are the requested chemical purity and the radiation trapping in the cooling optical materials. Therefore, new materials having low phonon energy as well as purification and fabrication processes to ensure ultra-high purity need to be developed in order to fully explore the possibilities of solid-state laser cooling phenomena. Recent studies are devoted to high purity material alternative fabrication methods, effective removal of waste fluorescence, reducing the heat load by designing effective thermal links, designing optimal cooling cavities which allows multi-pass configuration, etc.

Demonstrating highly efficient laser cooling with oxyfluoride glass-ceramics would be a major breakthrough. This allows the implementation of laser cooling in a robust material which is cheap and easy to produce and shape. Successful cooling within these novel glasses and glass-ceramics will open new avenues in laser cooling research, making it easier to cool devices with any geometry. These glass-ceramics can be used in a heat balanced (radiation balanced) laser system and would be more efficient allowing higher power extraction without any thermal damage. Recent results on the optimization of Ytterbium doping level and crystallization temperature of the glass gave new insights on selecting suitable candidates for cooling. The advantages of low phonon energy crystals and low background absorption make those glass-ceramics suitable for laser

cooling. These glasses and glass-ceramics can also be drawn into optical fibres, opening new possibilities for research.

Acknowledgements

The authors acknowledge Natural Sciences and Engineering Research Council of Canada (NSERC), Government of Canada's Canada Research Chairs program (CRC) and Canadian Excellence Research Chair program (CERC) on Photonic Innovations, Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT), Canada Foundation for Innovation (CFI). Dr. Wonji Park and Dr. Emeline Baudet are acknowledged for their help on investigating the pseudo-binary $\text{SiO}_2\text{-PbF}_2$ glasses and glasses-ceramics.

CHAPTER 3 GENERAL METHODOLOGY

This chapter describes the methodology employed during the course of the research.

3.1 Methodology of the overall research

This thesis studies the spectroscopic properties of rare earth doped oxyfluoride glass ceramics made by conventional melt quenching technique and oxide silica glass made by MCVD for solid-state laser cooling applications.

At first the glasses are fabricated using different techniques such as conventional melt quenching technique, modified chemical vapour deposition technique combined with solution doping etc. Then the structural and optical properties are characterised and if satisfactory, used for laser cooling experiments. The structural characterization of the produced glasses was done through X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe microscopy analysis (EPMA) and transmission electron microscope (TEM) measurements. The glass stability was studied using differential scanning calorimetry (DSC) technique. The aforementioned characterizations were done at center of optics, photonics and lasers (COPL), University of Laval, Canada.

The optical properties of the glasses were studied by measuring the transmission spectra, refractive index, photoluminescence (PL) emission, PL lifetime, quantum efficiency etc. Later the best candidates were selected for laser cooling experiments. A tunable Ti: Sapphire Laser (900-1040 nm), Pharos laser (1029 nm) and high power fiber laser (1030-1080 nm) were used for laser cooling experiments. The temperature change of the glasses upon laser irradiation was measured using fiber Bragg grating (FBG) direct contact technique. An Infra-red camera was also used for temperature measurements.

The aforementioned techniques and processes will be thoroughly discussed in the following chapters across four articles. Due to the detailed procedures provided therein, I will refrain from reiterating them here.

CHAPTER 4 ARTICLE 1: OPTICAL PROPERTIES OF YTTERBIUM DOPED OXYFLUORIDE GLASS-CERAMICS - CONCENTRATION AND TEMPERATURE DEPENDENCE STUDIES FOR OPTICAL REFRIGERATION APPLICATIONS

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Published in: Journal of Luminescence, June 10, 2021

Oxyfluoride glass-ceramics (GCs) doped with lanthanides have recently attracted much attention as a novel optoelectronic material candidate for optical refrigeration. In this study, the optical properties of highly transparent ($\sim 90\%$ in the near infrared region) ytterbium doped germanate and aluminosilicate oxyfluoride glass ceramics with different rare earth ion concentrations varying from 0.5 to 3.0 mol % synthesized by the conventional melt quenching technique have been investigated to determine and compare their potential for optical refrigeration applications. The photoluminescence (PL) emission spectra at different temperatures (25°C - 200°C) were measured using different excitation wavelengths varying from 920 nm to 1030 nm in order to understand the behaviour of Stokes and anti-Stokes emission in all the glass-ceramics. The influence of ytterbium content is studied and found to substantially affect the PL emission and quantum yield and thus affect the cooling/heating characteristics. The highest intensity of anti-Stokes emission from the GC samples was observed in the composition containing 1.5 mol % or 2.0 mol % of Yb^{3+} . Experiments monitoring the sample temperature at varying excitation wavelength between 1020 and 1030 nm demonstrates that the 1.5 mol % or 2.0 mol % Yb^{3+} concentrations are the most suitable for laser cooling applications.

Keywords: Ytterbium; oxyfluoride glass-ceramics; photoluminescence; quantum yield; anti-Stokes emission; fiber Bragg grating

4.1 Introduction

Optical cooling based on anti-Stokes emission has been attracted a great deal of interest during the past few years focusing on several applications such as sensors and satellite instrumentations which require mechanical vibrations-free operation, no moving parts and high reliability [101, 158].

Ever since the first experimental demonstration of solid-state laser cooling in 1995 by Epstein *et al.* [1], a series of experiments on different types of materials include crystals, semiconductors, optical fibers and glasses have been proposed and demonstrated as potential candidates for optical refrigeration [7, 29, 65, 68-70, 114, 152].

Among them, lanthanide (Ln^{3+}) doped oxyfluoride glass-ceramics have received great attention recently since they are mouldable and are easier to manufacture into complex structures such as optical fibres, using standard techniques in the glass industry [67, 132, 144].

The size of the crystal and crystallinity can be easily manipulated with controlled heat treatment [67, 159-161]. Concomitant with these properties, one of the significant advantages of glass ceramics is the presence of low phonon energy nanocrystals, which is essential for optical cooling. The nanocrystals in the GCs can enhance or provide completely new properties than those of the parent glass. Further the multi-phonon decay and non-radiative transition probabilities become very small in these materials since Ln^{3+} ions are incorporated in the nanocrystals [133]. In addition, the presence of Ytterbium (Yb^{3+}) provides the advantage of a low quantum defect, weak concentration quenching effect and no excited state absorption, making it suitable for laser cooling applications [10].

Although the glass synthesizing techniques have achieved considerable progress, it remains challenging to attain a high level of purity and near unity quantum yield which is essential for achieve cooling [140, 141, 162]. Great concerns about rare earth impurities and other parasitic components have stimulated intensive worldwide efforts, which have focused on purification of crystals and glasses through different techniques [71, 72]. However, it is still a challenge to obtain higher quantum yield and low background absorption which is essential for laser cooling with limited facilities.

In recent years our group explored a series of purified oxyfluoride glass ceramics focusing on laser cooling applications [11, 46, 67, 132, 140, 144, 162]. Oxyfluoride GCs consisting of PbF_2 nanocrystals were first studied experimentally for laser cooling applications by Soares de Lima Filho *et al.* in 2015 [140]. Their results showed that compared to parent glasses, GCs possess a

higher cooling figure-of-merit. The low phonon energy of these glasses along with the high PL quantum yield between 85 % and 98 % makes them a good candidate for laser refrigeration applications [162]. Over the ensuing two years, a significant effort has been undertaken to both understand and further improve the optical performance of these materials, particularly in terms of optimization of material host and purity [11]. The maximum phonon energy of the host that governs the non-radiative relaxation rate strongly influences the photoluminescence quantum yield of Ln^{3+} doped solids, and hence, the laser cooling effect. Therefore, other GCs oxyfluoride matrices must be good candidates for laser refrigeration, and further scientific investigations in this area must be carried out, particularly on the identification of other new matrices. To achieve significant heat mitigation, it is paramount to choose a suitable combination of RE ion and host composition that improves the quantum efficiency and reduces the background absorption. Therefore in the present study, we explored germanate and aluminosilicate GCs containing PbF_2 nanocrystals of compositions $50\text{GeO}_2\text{-}30\text{PbF}_2\text{-(}20\text{-x) PbO-xYbF}_3$, with $x = 0.50, 1.50, 2.00, 2.50$ mol % and $30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-(}29\text{-x)CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-xYbF}_3$ with $x = 0.50, 1.00, 2.00$ and 3.00 mol % for laser cooling applications. The absorption and PL spectra, together with the lifetime and the internal quantum yield of the PL were measured. Also, the temperature variations detected by means of the fiber Bragg grating technique [80] are presented and discussed. The ytterbium was doped into aluminosilicate and germane-silicate glass principally being manufactured for laser cooling purposes and fiber drawing.

The temperature-dependent optical properties such as luminescence intensity/lifetime in these GCs were also explored in this study. So far, studies of optical refrigeration in solids have concentrated on cooling them from room temperature to lower temperatures with the aim of making optical cryocoolers, radiation balanced lasers etc. Maintaining a stable temperature is also an important application of optical refrigeration which can be beneficial for microelectronic devices and light emitting diodes which requires quick dissipation of heat to prevent malfunction. The Yb^{3+} effective absorption cross-section in oxyfluoride glasses relies on the phonon occupation number in the material and can be increased by raising the medium temperature [163]. Thus, it is possible to enhance the phonon assisted anti-Stokes emission in these materials and make use of solid materials to maintain them at a stable temperature above RT. In addition to this, the anti-Stokes emission is the basis of numerous fundamental studies such as laser cooling [101] cavity quantum electrodynamics [164], bioimaging [165], Raman spectroscopy [166] etc. These applications

require the study of anti-Stokes emissions at different temperatures and are of great important for the selection/design of new material candidates for diode-pumped lasers and amplifiers [167]. Therefore, our detailed photoluminescence studies enable the way to efficiently design and optimize the Yb^{3+} doped oxyfluoride GCs for all aforementioned optoelectronic applications.

4.2 Materials and methods

Conventional melt-quenching process was used to synthesize the glasses with the following compositions in mol %: $50\text{GeO}_2\text{-}30\text{PbF}_2\text{-(}20\text{-x)PbO-xYbF}_3$ with $x = 0.50, 1.50, 2.00$, and 2.50 mol % and $30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-(}29\text{-x)CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-xYbF}_3$ with $x = 0.50, 1.00, 2.00$ and 3.00 mol %. After mixing the high purity precursors rigorously in an agate mortar, it was kept in a platinum crucible inside a glove box. In order to remove hydroxyl groups, the powders were dried under a pure N_2 flow at 460°C for 12 h and then melted at 900°C for 1 h in a resistive furnace integrated into the glove box. The melts were cooled using a stainless-steel mold pre-heated to near the glass-transition temperature. Then, GC samples were produced by heat treatment at 360°C for 3 hours and cut and polished for optical measurements [67, 132, 140].

X-ray diffraction (XRD) measurements were performed using an X-ray Bruker D8 Advance ($\text{CuK}\alpha 12$ radiation) equipped with a Vantec-1 linear detector over the $10\text{--}70^\circ 2\theta$ range (with a 0.0245° step, 4 s per step counting time). A Philips CM20 microscope was used for Transmission electron microscope (TEM) imaging.

Temperature dependent PL measurements were made using a temperature-controlled stage (HP Photonics- PID controlled with programmable features) and Ti: Sapphire laser (Spectra-Physics 3900S, pumped by Millennia 5SJSPG with 5 W) tunable laser (920 nm-1040 nm) was used to excite the samples. The PL emission was collected using an ocean optics mini spectrometer (USB 4000- UV-IR).

Ti: Sapphire laser at various excitation wavelengths were used to measure the photoluminescence emission (PL) spectra and quantum yield (QY) of the GCs with ~ 2.5 mm-thickness at room temperature. The emitted light was collected using an integrating sphere (2" Thorlabs IS200-4) coupled to a multimode optical fiber and an optical spectrum analyzer (Ando AQ6317B) which works in the range of 800-1600 nm.

The lifetimes of the $\text{Yb}^{3+} {}^2F_{5/2}$ level were measured by using a Thorlabs SM05PD1B photodiode with a resolution of $10 \mu\text{s}$ [13]. A bench top transimpedance amplifier (Thorlabs PDA200C) was used to amplify the signal and was read with a Tektronix TDS2012C 100MHZ 2GS/s digital storage oscilloscope. A ThorLabs MC100A mechanical chopper with two slotted blades operating at a frequency of 20.0 Hz was used to modulate the signal. In order to block the pump wavelength, a wavelength selective edge filter was used.

Finally, calorimetric measurements were performed using a fiber Bragg grating (FBG) direct contact technique [7, 67]. An Ando AQ6317B optical spectrum analyzer (OSA) which works in the range of 800-1600 nm was used to observe the shift in the FBG reflection spectra.

4.3 Results and discussion

In order to determine the potential use of different Yb-doped oxyfluoride GCs for optical refrigeration applications, a series of glasses were prepared using the melt quenching method and converted into GCs by post-heat treatment approach [67, 132, 140]. The compositions of the investigated GCs are given in Table 4.1. Each GCs examined was found to exhibit unique PL emission characteristics, enabling an optimum sample selection for laser cooling applications.

Table 4.1: The compositions of investigated GCs along with the terminology used in the text.

GCs composition	Terminology	GCs composition	Terminology
$30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-}27\text{CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-}0.5\text{YbF}_3$	SPYb 0.5GC	$50\text{GeO}_2\text{-}30\text{PbF}_2\text{-}9.5\text{PbO}-0.5\text{YbF}_3$	GPYb 0.5GC
$30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-}27\text{CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-}1\text{YbF}_3$	SPYb 1.0GC	$50\text{GeO}_2\text{-}30\text{PbF}_2\text{-}18.5\text{PbO}-1.5\text{YbF}_3$	GPYb 1.5GC
$30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-}27\text{CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-}2\text{YbF}_3$	SPYb 2.0GC	$50\text{GeO}_2\text{-}30\text{PbF}_2\text{-}18\text{PbO}-2\text{YbF}_3$	GPYb 2.0GC
$30\text{SiO}_2\text{-}15\text{Al}_2\text{O}_3\text{-}27\text{CdF}_2\text{-}22\text{PbF}_2\text{-}4\text{YF}_3\text{-}3\text{YbF}_3$	SPYb 3.0GC	$50\text{GeO}_2\text{-}30\text{PbF}_2\text{-}17.5\text{PbO}-2.5\text{YbF}_3$	GPYb 2.5GC

The PL emission characteristics (quantum yield, lifetime, anti-Stokes emission) of all the investigated glass ceramics were studied and compared to each other to find the most suitable composition for optical refrigeration. The PL properties of rare earth ions in the inorganic glasses rely on the chemical composition of the host glass, the rare earth ion concentration, the phonon energy and the excitation power [168]. In order to demonstrate laser induced cooling in solid materials, the active ions (Yb^{3+}) in glass require quantum yield near to unity to absorb photons from the laser source and re-emit them as anti-Stokes fluorescence.

A schematic diagram of the laser cooling principle in glass ceramics is given in Figure 4.1. For the oxyfluoride glass ceramic system doped with Yb^{3+} ions, laser cooling process occurs via absorbing the red photons by the Yb ions from the laser (low pump energy monochromatic source) via resonant absorption and then more energetic blue shifted photons are emitted via anti-Stokes fluorescence. The LHS of Figure 4.1 shows the oxyfluoride GC system. Yb-doped low phonon energy fluoride nanocrystals are grown within the oxide glass matrix by controlled heat treatment [165]. Through resonant absorption electrons are excited from the ground state to the excited state when photons with frequency ν enter the glass host and interact with Yb ions. Then, by phonon annihilation more energetic photons leave the material via radiative emission (with frequency ν_f) and material is cooled. Impurity ions absorption, multi phonon decay and other forms of parasitic interactions suppress the optical cooling process and cause unwanted heating of the glass [11].

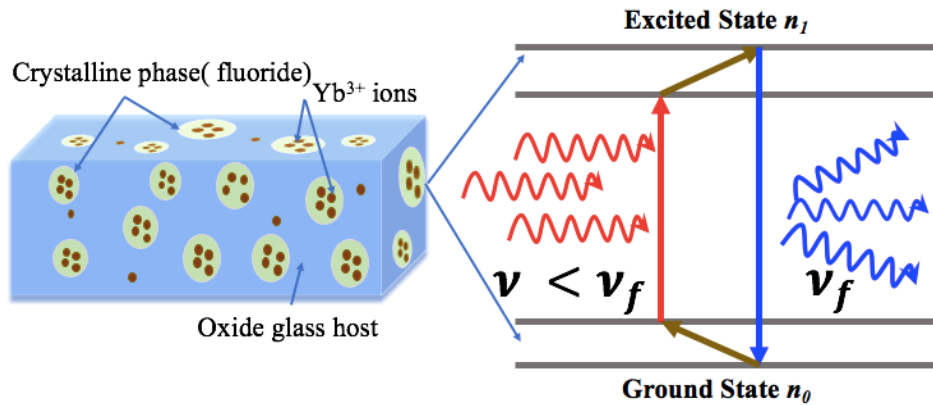


Figure 4.1: Schematic of laser cooling process in Yb doped oxyfluoride glass ceramics.

Therefore, the chemical purity of the glass is an important factor to consider while designing a material for laser cooling applications. The concentration of RE ions is another important factor

that can influence quantum efficiency. As the concentration of active ions increases, the RE ion-ion interaction also increase. Due to energy migration between different ions, the probability of reaching the excitation at the impurity becomes very high, from where it decays non-radiatively and heats the material. Because of concentration quenching, the RE ion concentration in each sample must be optimized [11]. In the present study we optimized the ytterbium ion concentration while measuring the PL emission intensity, quantum yield and lifetime.

4.3.1 Effect of Yb^{3+} doping in aluminosilicate-oxyfluoride glass-ceramics (SPYb GCs) and identification of a potential composition for laser cooling applications

The structural characterization of the produced GCs was done through X-ray diffraction (XRD) and transmission electron microscope (TEM) measurements. The XRD performed on samples of SPYb 2GC and corresponding parent glass (SPYb 2G) are provided in Figure 4.2 (a). It is evident from the figure that the parent glass is amorphous in nature and GC shows relevant sharp diffraction peaks related to the existence of cubic $\beta\text{-PbF}_2$ nanocrystalline phase [140]. The crystallite size of the PbF_2 nanocrystals was evaluated by using Scherrer's formula from the XRD peak widths and was found to be ~ 20 nm. The transmission electron microscope (TEM) images of the samples provided in Figure 4.2 (b) also shows that the nanocrystals are sized at ~ 20 nm which corresponds to the average value determined by XRD measurements and are dispersed homogeneously in the glass matrix. More detailed studies focussing on the crystallisation kinetics of aluminosilicate glasses are available in Ref. [122].

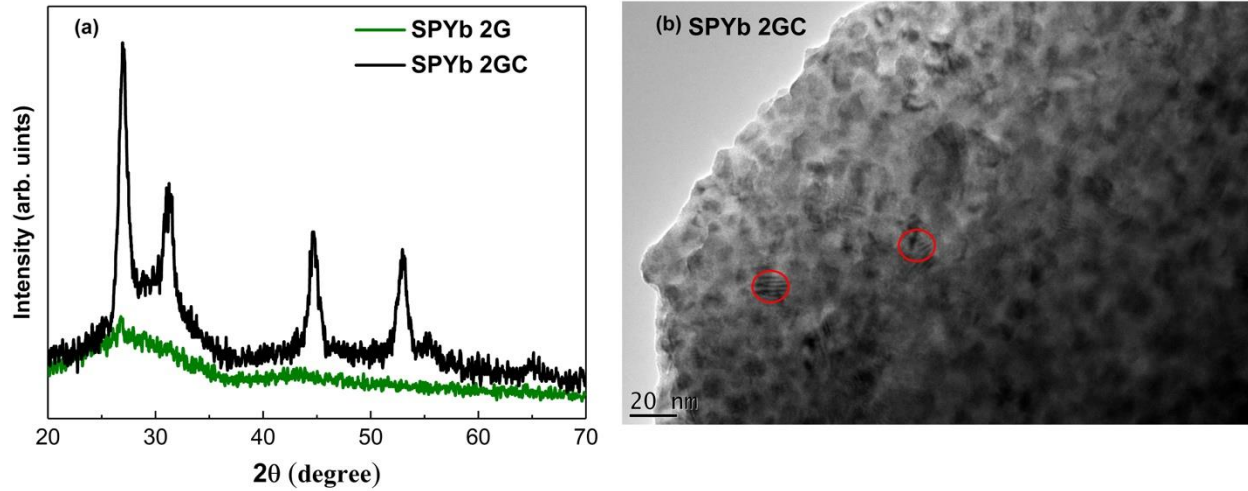


Figure 4.2: (a) The XRD pattern of the glass (SPYb 2G) and corresponding glass-ceramic (SPYb 2GC), (b) The transmission electron microscope (TEM) image of SPYb 2GC. The crystallite size was ~ 20 nm.

The absorption spectra of aluminosilicate GCs in the NIR region with different Yb^{3+} concentration is provided in Figure 4.3 (a). One can clearly observe an increase in the absorption band intensity centered at 978 nm which is related to the increase in the Yb content from 0.50 to 3.0 mol % in the GCs. The Yb^{3+} ion has a broad absorption band ranging from 870 to 1060 nm which can be attributed to the ground ($^2F_{7/2}$) and the excited ($^2F_{5/2}$) stark sublevels electronic transitions together with the strong electron-phonon interaction ascribed to the glassy host [167]. In the wavelength range of 920-1030 nm, which is typically used to excite the samples, the absorption cross-section increases with increasing temperature. This happens because of the change in the population of the starting Stark level with temperature and an increase in phonon occupation number in the host matrix [163].

The photoluminescence (PL) emission spectra of aluminosilicate GCs with different Yb^{3+} concentration at an excitation of 920 nm (with laser power of 300 mW) collected using an integrating sphere method, as depicted in Figure 4.3 (b). Increasing concentrations from 0.5 mol % to 3 mol %, shifts the emission maximum to longer wavelengths due to the reabsorption of the emission and nonradiative energy transfer to Yb^{3+} ions [169]. Also, the PL emission intensity is increased with increasing the Yb^{3+} concentration from $x = 0.50$ to $x = 2.00$ mol %. However, for $x = 3.00$ mol % a reduction in PL intensity was observed compared to $x = 2.00$ mol % due to reabsorption, Yb^{3+} ion-ion interaction or the radiation trapping effect. Due to these reasons, we

shifted our focus mainly onto SPYb 2.0 GC as it exhibits a high PL intensity compared to other investigated GCs. The PL emission spectra shape remained the same at several excitation wavelengths for the SPYb 2.0GC as shown in Figure 4.3 (c). PL emission measurements were performed for all samples with similar experimental conditions (Temperature, sample position, laser wavelength etc.) with a constant pump power of 300 mW (due to the availability of limited pump power).

The emission behaviour may change if we increase the pump power and the excited volume in all samples. Previous pump power dependence studies in oxyfluoride glass ceramics have shown a linear increase in the PLQY and a decrease in the lifetime with an increase in the pump power [46]. Therefore, in the present study we expect an increase in PL emission intensity and quantum yield with the use of high pump powers which cause bleaching and thus reduce the reabsorption. The experimental values of the luminescence lifetime (τ) associated with the $\text{Yb}^{3+}: {}^2F_{5/2}$ level for all SPYb GCs and corresponding parent glasses at 920 and 980 nm excitations with a constant pump power of 300 mW is depicted in Figure 4.3 (d). The luminescence lifetimes of GCs were higher than that of parent glasses as expected. Since the article mainly focuses on the luminescence properties of GCs, we have not included further optical properties of glasses here. The room-temperature photoluminescence decay curves of $\text{Yb}^{3+}: {}^2F_{5/2}$ level for all aluminosilicate glass ceramics at an excitation wavelength of 980 nm (at a pump power of 300 mW) are provided in Appendix Figure 1. It was observed that as the Yb^{3+} concentration increases from 0.50 mol % to 3.0 mol %, the fluorescence lifetime, τ , increases from 1.96 to 2.94 ms. A similar behavior was observed for excitations at 920, 1010 nm and 1030 nm (Table 4.2). This increase in lifetime is attributed to radiation trapping, in agreement with the work of Dai *et al.* [170] on Yb^{3+} doped phosphate glasses.

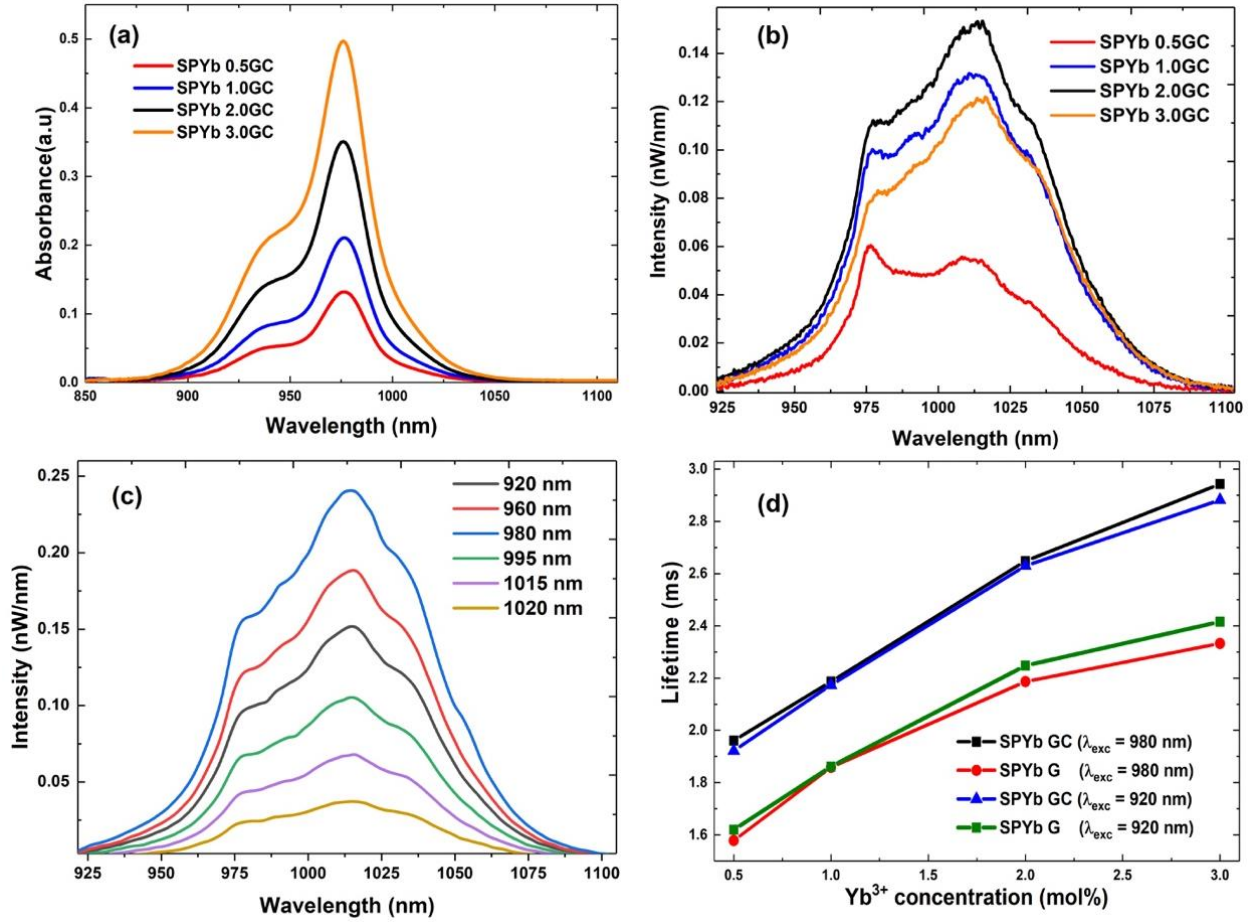


Figure 4.3: (a) The measured absorption spectra of all SPYb GCs in the near infra-red (NIR) region, (b) The PL emission spectra of all SPYb GCs at an excitation wavelength of 920 nm, (c) The PL emission spectra of SPYb 2.0GC at several excitation wavelengths varying from 920 nm to 1030 nm with a fixed laser power of 300 mW, (d) Lifetime of $^2F_{5/2}$ level of Yb^{3+} in all the SPYb GCs and corresponding parent glasses at 920 nm and 980 nm excitations with a pump power of 300 mW.

Table 4.2: Experimental lifetime values of Yb^{3+} ions in SPYb GCs at 920 nm, 980 nm, 1010 nm and 1030 nm

Sample	Lifetime (ms)			
	920 nm	980 nm	1010 nm	1030 nm
SPYb 0.5GC	1.922 ± 0.001	1.961 ± 0.002	2.005 ± 0.001	2.106 ± 0.002
SPYb 1.0GC	2.174 ± 0.001	2.187 ± 0.002	2.192 ± 0.001	2.414 ± 0.002

SPYb 2.0GC	2.630 ± 0.002	2.648 ± 0.002	2.494 ± 0.002	2.459 ± 0.002
SPYb 3.0GC	2.882 ± 0.001	2.943 ± 0.003	3.037 ± 0.003	2.911 ± 0.002

The fluorescence emission spectra of all the SPYb GCs using different excitation wavelengths at different temperature (25°C- 200°C) were evaluated to understand the behavior of Stokes and anti-Stokes emission. The obtained fluorescence spectra for sample SPYb 2.0GC at temperatures varying from 25°C to 200°C using 960 and 1020 nm excitation wavelengths with a constant pump power of 300 mW are given in Figure 4.4 (a) and Figure 4.4 (b) respectively. The most important observation in these figures is that the Stokes emission intensity decreases as we increase the temperature (Figure 4.4 (a)) while the anti-Stokes emission intensity increases (Figure 4.4 (b)). It is note-worthy to mention that the anti-Stokes emission intensities are enhanced while increasing the temperatures without changing the peak positions of the emissions. On the other hand, below 960 nm excitation, the Stokes emission profile changes significantly with increase in temperature. It is revealed that the peak tail at around 1010 nm disappears with increase in temperature. This indicates that the reabsorption is reduced significantly with increase in temperature.

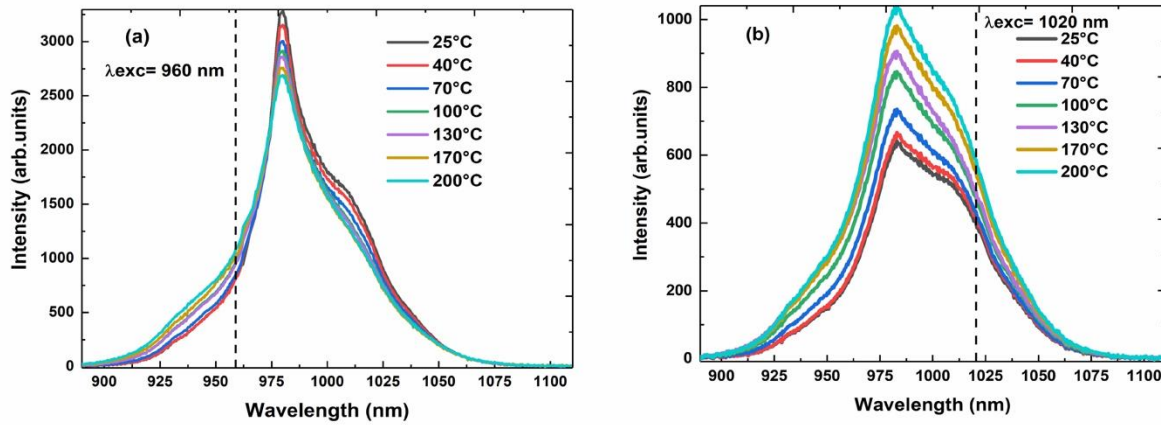


Figure 4.4: The PL emission spectra at different temperatures of SPYb 2.0GC sample using an excitation wavelength of (a) 960 nm and (b) 1020 nm.

The experimental results demonstrated in Figure 4.4 (b) reveals a ~ 1.6 -fold enhancement in the anti-Stokes PL emission intensity of SPYb 2.0GC as the temperature was increased from 25° to 200°C at an excitation wavelength of 1020 nm. Here the population of Yb^{3+} ions is obtained via

multi-phonon assisted anti-Stokes excitation. To compensate for the energy mismatch of $\sim 396.08 \text{ cm}^{-1}$ ($\lambda_{\text{exc}} = 1020 \text{ nm}$ (9803.92 cm^{-1})) and the energy gap of the $2F_{7/2} \rightarrow 2F_{5/2}$ transition of the Yb^{3+} ions ($\sim 10200 \text{ cm}^{-1}$), the involvement of optical phonons is necessary. Using 1030 nm excitation wavelength ~ 2.1 -fold enhancement was observed due to the large energy difference. Along with the thermal population of the highest stark sublevels, the increase in the Yb^{3+} absorption cross section through multi-phonon absorption also contributes towards the enhancements in the anti-Stokes emission [171]. The emission spectra were also broadened for anti-Stokes emission, as shown in Figure 4.4 (b). Furthermore, we discern that the rates of change in intensity with respect to temperature for the PL emission spectrum of different samples are dissimilar and dependent on the Yb^{3+} ion concentration and the excitation wavelength (Figure 4.5 (a-d)).

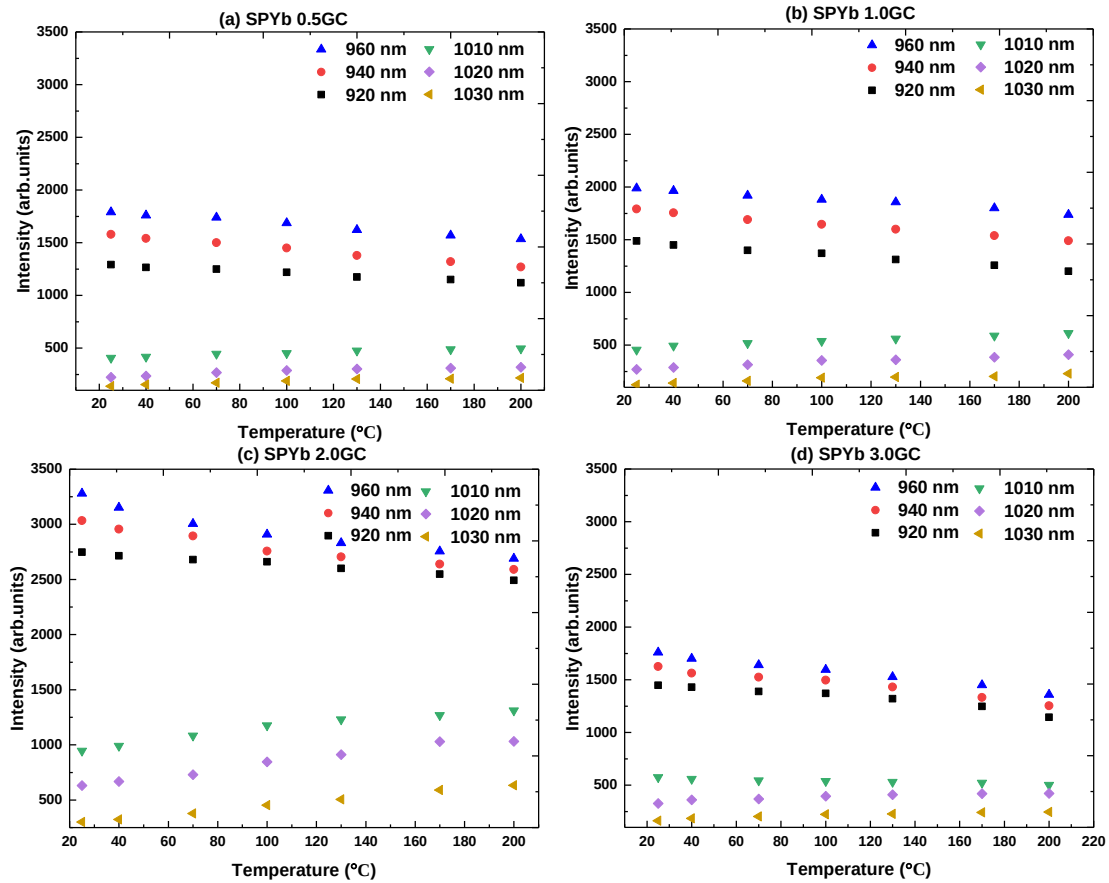


Figure 4.5: (a) The PL emission spectra at 920, 940, 960, 1010, 1020 and 1030 nm excitation wavelengths with a pump power of 300 mW in different temperatures varying from 25 °C to 200 °C

showing the behaviors of Stokes and anti-Stokes emissions for the sample (a) SPYb 0.5GC, (b) SPYb 1.0GC, (c) SPYb 2.0GC and (d) SPYb 3.0GC. Excitation using 920, 940 and 960 nm give rise to Stokes fluorescence emission. Anti-Stokes fluorescence emission is produced using 1010, 1020 and 1030 nm.

Since our primary focus is restricted to the anti-Stokes emission, we further examined the impact of Yb^{3+} concentration (0.50, 1.00, 2.00 and 3.00 mol %) on the enhancement of the anti-Stokes emission intensity using 1010, 1020 and 1030 nm excitations as shown in Figure 4.5 (a-d). Here, the temperature dependent PL emission intensity change is controlled by the phonon-assisted anti-Stokes excitation and multi-phonon non-radiative relaxations [163]. With a pump power of 300 mW, the maximum anti-Stokes emission was observed for SPYb 2.0GC, compared to the other samples (Appendix Figure 2). Due to concentration quenching and reabsorption, the emission intensity decreased for SPYb 3.0GC. As we mentioned earlier, the bleaching at high pump powers can reduce the reabsorption, leading to an increase in PL emission intensity. The detrimental effect of reabsorption in oxyfluoride glass ceramics imposes a restriction on access to higher PL emission intensity, and as a consequence limits their further applications in laser cooling.

Table 4.3 provides the internal as well as external quantum yields (iQY and eQY, respectively) values for the SPYb 2.0GC at RT. It was measured by using an integrating sphere method as described in Ref. [46, 140].

The iQY was determined by calculating the ratio of the number of emitted photons to the number of absorbed photons and the eQY by the ratio of the number of emitted photons to the number of exciting laser photons [46, 67, 140].

A detailed procedure can be found in the appendix. The iQY changes between 70 % and 99 % at various excitation wavelengths and the eQY changes from 5 % to 19 %. Ostensibly, all these results lead to conclude that the GC sample with 2 mol % appears to be promising for optical refrigeration and should be studied in detail.

Table 4.3: The iQY and eQY values for SPYb2.0 GC sample at room temperature with different excitation wavelengths at a fixed pump power of 300 mW

λ_{exc} (nm)	iQY (%)	eQY (%)
920.0	99.1	13.0
960.0	88.7	19.4
1000.0	92.5	17.7
1005.0	94.4	15.3
1015.0	79.1	11.6
1020.0	76.0	8.3
1030.0	70.0	4.9

The maximum phonon energy of the host that governs the non-radiative relaxation rate has significant impact on the photoluminescence quantum yield (PLQY) of RE doped solids [172]. Due to their low phonon energy, oxyfluoride glass ceramics are thus excellent hosts for achieving higher PLQY. In our case, the RE ions are preferentially encapsulated inside the PbF_2 low phonon energy ($\sim 250 \text{ cm}^{-1}$) nanocrystals [173] and is shielded from the high phonon energy of the oxide glass host. As a result, the multi-phonon decay and non-radiative transition probabilities become small and influences significantly the cooling characteristics [174]. The maximum phonon energy of the germanate and aluminosilicate oxyfluoride glass matrix corresponds to $\sim 900 \text{ cm}^{-1}$ and 1100 cm^{-1} respectively [174, 175] and it plays an important role in removing heat from the glassy system during laser illumination [175].

4.3.2 Effect of Yb^{3+} doping in germanate oxyfluoride glass-ceramics (GPYb GCs) and identification of a potential composition for laser cooling applications

The structural characterization of the produced GCs was done through X-ray diffraction (XRD) and transmission electron microscope (TEM) measurements. From the XRD analysis provided in Figure 4.6, the presence of PbF_2 (JCPDS #77-1866) crystalline phases were detected in GPYb 2GC [67, 176]. The crystallite size of the PbF_2 nanocrystals was calculated by using the Scherrer's formula from the XRD peak widths and was found to be less than 15 nm. The transmission electron

microscope (TEM) images of the GC provided in inset of Figure 4.6 also shows that the nanocrystals are sized at ~ 15 nm.

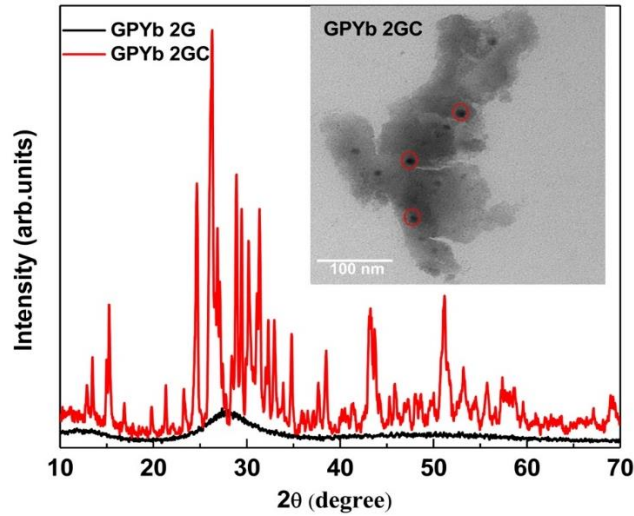


Figure 4.6: The XRD pattern of the glass (GPYb 2G) and corresponding glass-ceramic (GPYb 2GC). The inset shows the TEM image of GPYb 2GC.

To frame the scope of GPYb GCs for laser cooling applications, we optically characterized PL emission, quantum efficiency, lifetime etc. Here we chose only samples having 0.1, 1.5, 2.0 and 2.5 mol % of ytterbium because for higher concentrations energy transfer and reabsorption of the emission can occur. The GPYb GC doped with 3 mol % of ytterbium was not available for the present study. The PL emission spectra of all GCs were recorded using the integrating sphere method at an excitation of 980 nm (Figure 4.7 (a)) and 1020 nm (Figure 4.7 (b)) with equal excitation powers of 300 mW [67, 140].

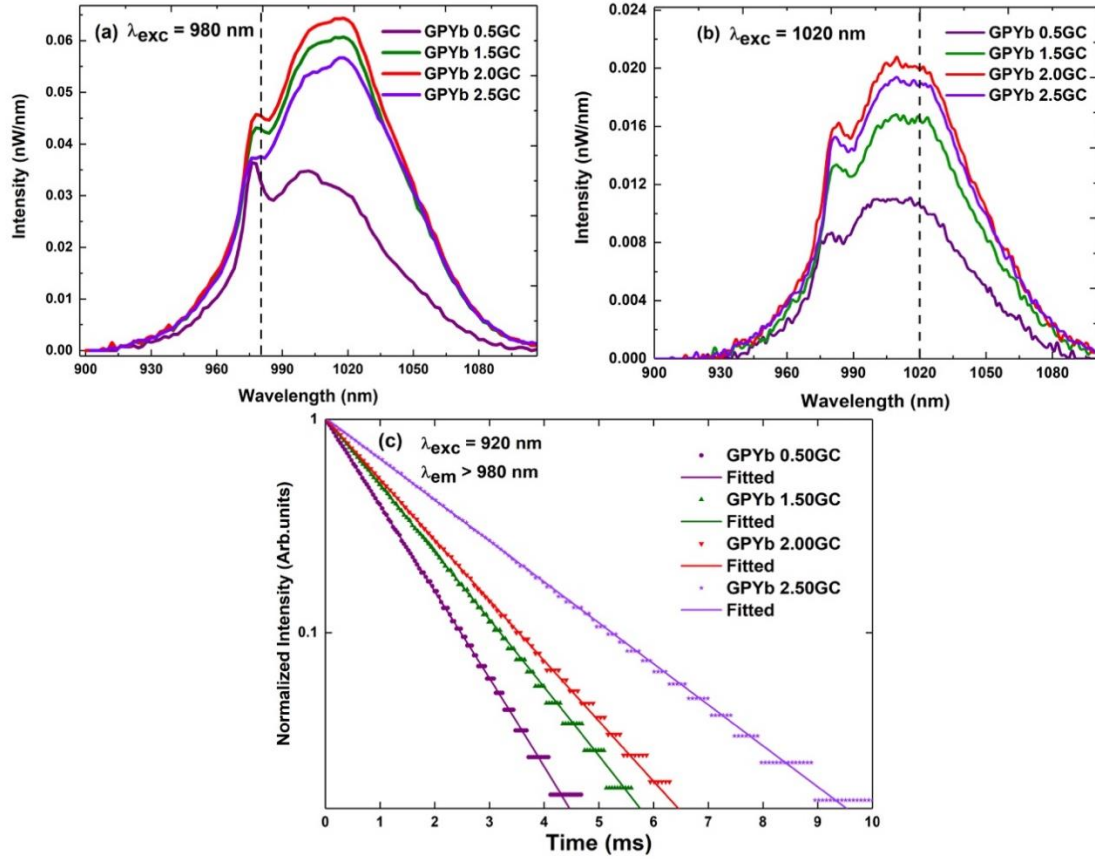


Figure 4.7: (a) The PL emission spectra for all GPYb GCs with an excitation of 980 nm and (b) 1020 nm with equal excitation powers of 300 mW, and c) The PL emission decay curves for GC samples corresponding to $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition with an excitation wavelength of 920 nm (experimental values are shown using symbols and fitted curves using solid lines).

Similar to SPYb GCs, the PL emission intensity of GPYb GCs was observed to increase with changing the Yb^{3+} concentration ($x = 0.50$ to $x = 2.00$ mol %) but was reduced for $x = 2.50$ mol % due to Yb^{3+} ion-ion interaction, reabsorption or the radiation trapping effect. Similar behavior was observed for Yb^{3+} doped transparent oxyfluoride glasses, where the PL emission intensity at room temperature using an excitation of 980 nm increased with the increase in Yb^{3+} concentration in the material. Nevertheless, due to concentration quenching, it decreased substantially at 4.0 mol % Yb^{3+} concentration [177, 178].

In our samples, depending on the Yb^{3+} concentration the PL spectra was broadened and redshifted due to reabsorption effects and nonradiative energy transfer to Yb^{3+} ions [132]. The PL spectral shapes were remained same under excitation at 1020 nm (Figure 4.7(b)).

Table 4.4 provides the internal as well as external quantum yields values for the GPYb GCs. The iQY changes from 70 % to 85 %, with a maximum for $x = 1.50$ and 2.50 mol % sample under excitation at a pump power of 300 mW of 980 nm laser. But the eQY increases from 10 % to 19 % from $x = 0.50$ to $x = 2.00$ mol % and reduces to 14 % for $x = 2.50$ mol %. Nonetheless, the highest iQY was achieved for $x = 2.50$ mol % sample, under excitation at 1020 nm. The eQY, was increased from $x = 0.50$ to $x = 2.50$ mol %. All these results lead us to conclude that samples with 1.50 mol % and 2.00 mol % appear to be promising for optical refrigeration and should be studied in detail.

Table 4.4: The iQY and eQY values for all germanate glass-ceramics (GPYb GCs) with an excitation at 980 nm and at 1020 nm with a fixed pump power of 300 mW.

Sample code	λ_{Exc} (nm)	iQY (%)	eQY (%)
GPYb 0.50 GC	980	70	10
GPYb 1.50 GC	980	84	15
GPYb 2.00 GC	980	79	19
GPYb 2.50 GC	980	85	14
GPYb 0.50 GC	1020	67	4
GPYb 1.50 GC	1020	74	7
GPYb 2.00 GC	1020	71	9
GPYb 2.50 GC	1020	73	10

The experimental values of the luminescence lifetime (τ) associated to the $\text{Yb}^{3+}: {}^2F_{5/2}$ level for all GPYb GC samples with an excitation at 920 nm (300 mW) are shown in Figure 4.7(c). The lifetime increases from 1.08 ms for 0.50 mol % to 2.29 ms for 2.50 mol % in our glass-ceramic samples owing to radiation trapping. Probably due to low-phonon energy associated with low Yb^{3+} concentration, the multiphonon relaxation process and energy transfer among the Yb^{3+} ions were limited. The lifetime values determined under excitations at 980, 1010 and 1030 nm wavelengths were similar to those obtained at 920 nm, as can be seen in appendix Table 1. A similar trend was observed previously in YAG crystals [179] and in glasses [46] doped with Yb^{3+} . At low Yb^{3+} concentration radiation trapping was clearly evident.

A previous report on aluminosilicate oxyfluoride glass doped with 2 mol % of Yb^{3+} ions show a lifetime of ~ 1.57 ms [46]. The present work reports a lifetime of 1.53 ms. The authors mentioned that energy transfer among the rare earth ions and multi-phonon relaxation are the primary mechanisms responsible for lifetime quenching, particularly for Yb^{3+} concentrations higher than 5 mol %. The iQY and eQY determined under excitation at 1020 nm (Table 4.4) have good correlation to the lifetime increase shown in appendix Table 1. Having an iQY value close to unity is perquisite for efficient cooling.

We studied the temperature dependence of the luminescence properties with a focus on understanding the nature of Stokes and anti-Stokes emission in these glass-ceramics. The obtained PL emission spectra of GPYb 1.5GC at different temperatures using 960 nm and 1020 nm excitation wavelengths (300 mW) are given in Figure 4.8(a) and Figure 4.8(b) respectively.

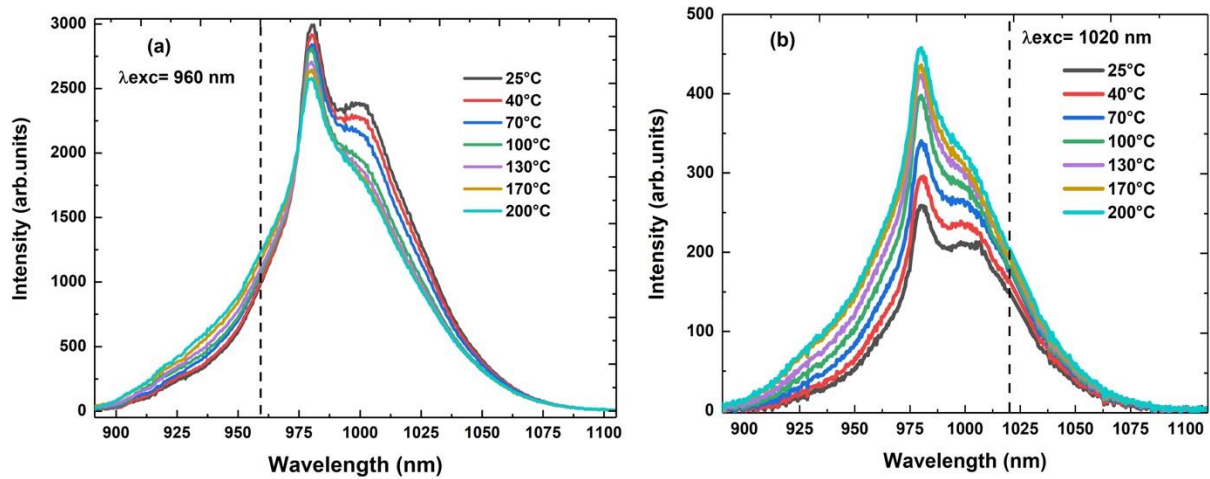


Figure 4.8: The PL emission spectra of the GPYb 1.5GC at different temperatures upon laser excitations of 300 mW power of (a) 960 nm and (b) 1020 nm.

Similar to SPYb 2GC, the Stokes emission intensity decreases (Figure 4.8(a)) and the anti-Stokes emission intensity increases (Figure 4.8(b)) while varying temperatures from 25° to 200°C of sample GPYb 1.5GC. We could observe a ~ 1.4 fold enhancement in the anti-Stokes PL emission intensity as the GPYb 2.0GC temperature was increased from 25° to 200°C at an excitation wavelength of 1020 nm. Using 1030 nm excitation wavelength ~ 1.7 fold enhancement was observed due to the large energy difference between the excitation and emission wavelengths.

The fluorescence intensity was measured as a function of temperature for all four Yb³⁺ concentrations of GPYb GCs using 920, 940, 960, 1010, 1020 and 1030 nm for comparing the Stokes and anti-Stokes emission intensity changes as shown in Figure 4.9(a-d).

It is noticeable that when we increase the temperature of germanate glass-ceramics in the 0.5, 1.5, 2.0 and 2.5 mol % doped ytterbium samples, the Stokes emission intensity decreases and the anti-Stokes emission intensity increase similar to alumino-silicate glass-ceramics. Among all germanate glass ceramics, with a maximum pump power of 300 mW, GPYb 2.0GC possessed higher anti-Stokes emission intensity at 200°C (appendix Figure 3). Due to reabsorption, the emission intensity was decreased for GPYb 2.5GC, but is expected to increase with the pump power [46]. In order to avoid concentration quenching and reabsorption, the doping level of ytterbium has to be kept relatively low (≤ 2 mol %) to ensure an optimal separation between the rare earths to prevent parasitic interaction.

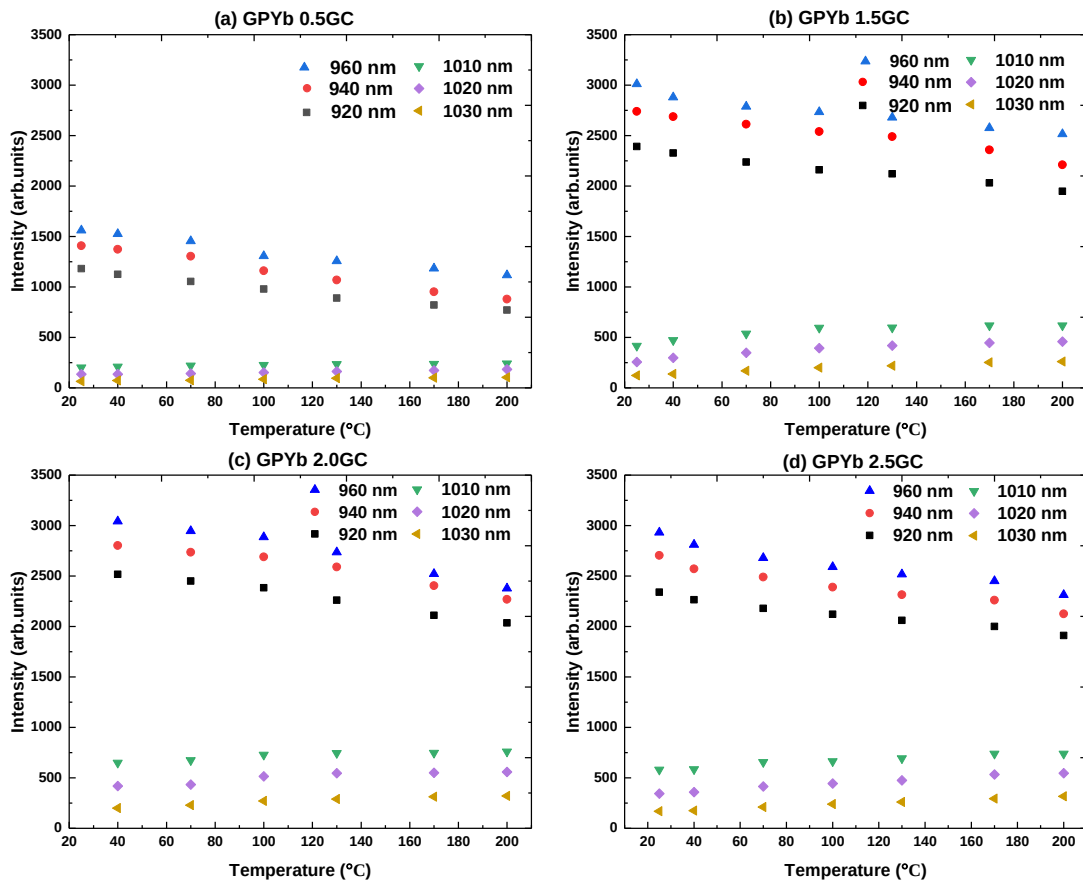


Figure 4.9: The PL emission spectra at 300 mW laser power of 920, 940, 960, 1010, 1020 and 1030 nm excitation wavelengths at different temperatures varying from 25°C to 200°C showing the behaviors of Stokes and anti-Stokes emissions for the sample (a) GPYb 0.5GC, (b) GPYb 1.5GC, (c) GPYb 2.0GC and (d) GPYb 2.5GC. Excitation using 920, 940 and 960 nm give rise to Stokes fluorescence emission. Anti-Stokes fluorescence emission is produced using 1010, 1020 and 1030 nm.

While comparing the anti-Stokes emission intensity of all the investigated oxyfluoride glass ceramics (SPYb GCs and GPYb GCs) at 1010, 1020 and 1030 nm excitations (300 mW) at 200°C, SPYb 2.0GC was found to be the best sample which possess higher anti-Stokes emission intensity compared to others (Figure 4.10). This unique and important result originates from optimizing both the host composition and optimized ytterbium doping level in this GC. Overall, these novel family of ytterbium doped aluminosilicate and germanate oxyfluoride glass-ceramics opens a new avenue through optimizing the host composition and ytterbium doping level to enhance and tune the photoluminescence emission, anti-Stokes emission and quantum efficiency for relevant future laser cooling applications.

The findings in Figure 4.10 are also beneficial for LEDs & other microelectronic devices operating at elevated temperatures. This provides an option to further exploit the potential of these glass ceramics which exhibits a significant increase in emission cross-sections and anti-Stokes emission at elevated temperatures and make use of these for temperature stabilization applications.

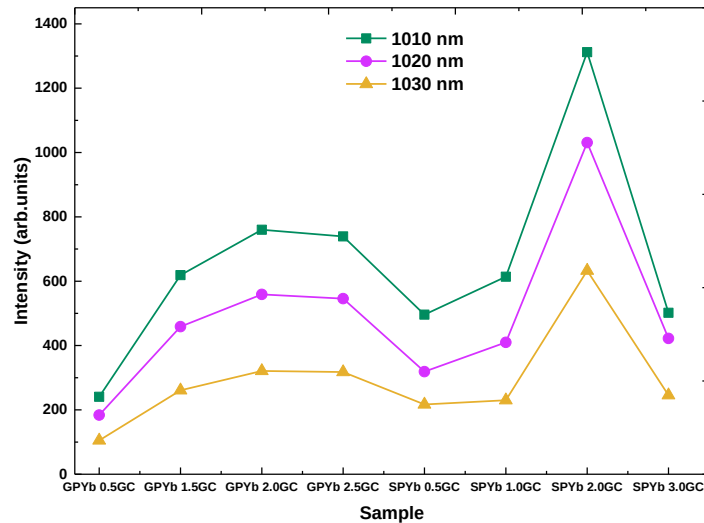


Figure 4.10: Anti-Stokes emission intensity of all the investigated oxyfluoride glass ceramics at 1010, 1020 and 1030 nm excitations (constant pump power of 300 mW) at 200°C.

To gain additional insight into the enhanced anti-Stokes emission process at elevated temperatures we examined the lifetime of $\text{Yb}^{3+} {}^2\text{F}_{5/2}$ level at an excitation wavelength of 1020 nm. The lifetimes at each stabilized temperature were measured and compared with those at room temperature. The results show that the lifetime of SPYb GCs is longer than that of GPYb GCs and this is attributed to the effect of host composition and low phonon energy environment. The observed increase in anti-Stokes PL intensity is in line with the increase in PL lifetime observed for all the glass ceramics in this temperature regime (appendix Figure 4(a)). Since the lifetime of ${}^2\text{F}_{5/2}$ level of Yb^{3+} is proportional to the quantum efficiency we could expect an equal increment with the temperature. The PL emission decay curves for SPYb 3.0GC corresponding to $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition with an excitation wavelength of 1020 nm at 25°C, 100°C, 150°C and 200°C is provided in appendix Figure 4(b). The lifetime increases from 2.94 ms to 3.30 ms when increasing the temperature from 25°C to 200°C.

Overall, the results obtained from these Yb^{3+} doped oxyfluoride glass-ceramics look promising for the applications of optical cooling, although each has its own individual properties.

4.3.3 Prospects of oxyfluoride glass ceramics for laser cooling applications

The excellent optical properties, such as higher quantum efficiency and anti-Stokes emission led us to investigate the temperature change of the all the glass ceramics samples at different excitation wavelengths. Using a fiber Bragg grating (FBG) direct contact technique [7, 80] temperature measurements of the aluminosilicate glass samples at different excitation wavelengths were performed. The glass-ceramics (10x2x2mm² cross-section) polished with parallel facets were excited using a continuous wave Ti: Sapphire laser at various wavelengths ranging from 920 nm to 1030 nm. Figure 4.11(a) presents the temperature change normalized by absorbed power delivered to the studied samples as a function of excitation wavelength. It can be observed that > 1000 nm, the heating process decreases progressively, approaching near zero between 1020 and 1030 nm for all the glass samples. Moreover, higher heating processes are observed for higher Yb^{3+} concentration in the glass-ceramic. From the temperature measurements, using an excitation

wavelength of 1030 nm (pump power of 300 mW), SPYb 2.0GC was found to be the best sample among all aluminosilicate glass ceramics that have been investigated. This can be changed at higher pump powers, since bleaching can reduce the reabsorption in highly ytterbium doped samples.

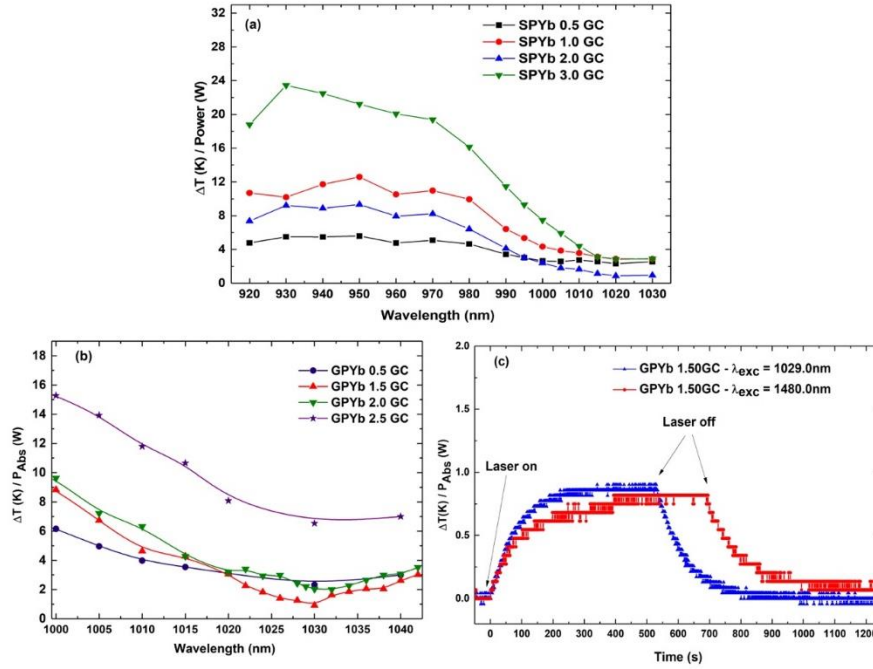


Figure 4.11: (a) Temperature changes (ΔT) normalized by absorbed power (P_{Abs}) provided onto the glass-ceramics at various excitation wavelengths ranging from 920 nm to 1030 nm, (b) Temperature changes (ΔT) normalized by power (P_{Abs}) absorbed by the studied GPYb GCs as a function of excitation wavelength, (c) The (ΔT) / P_{Abs} behavior as a function of time for the GPYb 1.50 glass-ceramic sample with and without laser excitation at 1029.0 nm and 1480 nm. The minimum temperature was achieved for the GPYb 1.50GC sample.

The Figure 4.11(b) illustrates the temperature reduction in germanate glass ceramics by increasing the excitation wavelength to longer than 1000 nm. From the results one can observe that the heating effect decreases almost linearly when increasing the excitation wavelength, while heating per absorbed power becomes higher as the Yb^{3+} concentration increases, except for 1.50 mol % which has a minimum between 1020 and 1030 nm, with maximum temperature reduction at ~1029 nm.

This behavior can be correlated with the change in iQY measured under excitation at 980 nm and 1020 nm (Table 4.4) for all Yb³⁺ concentrations, and the lifetime values (appendix Table 1).

To better understand these behaviors, we measured the change in temperature per absorbed power as a function of time for GPYb 1.50GC when the laser is on and off under excitations at 1029.0 nm or 1480.0 nm wavelength, as plotted in Figure 4.11(c). When laser is on, the sample presented a maximum of 0.9 K/W under excitation at 1028.8 nm, and 0.8 K/W under excitation at 1480.0 nm. Note that the difference is only 0.1 K/W being equal to the error bar. The background absorption coefficient (α_b) of GPYb 1.5GC was found to be 0.118 m⁻¹ using a calorimetric technique [7]. Radiation trapping, impurities in the precursors and convection from sample to air hinders the observation of net-cooling. Our on-going studies focus on the reduction of background absorption through better glass production methods. Especially, purifying the starting materials instead of using them in the same condition. Improved sample quality may address these issues and provide more direct evidence of the laser cooling. However, our observations provide a starting point from which to explore the rare earth doped glass ceramics that are mechanically and chemically stable, cost-effective, and scalable material for laser cooling applications.

4.4. Conclusions

In conclusion, this study demonstrated that the Yb³⁺-doped glass-ceramics of 50GeO₂-30PbF₂-(20-x)PbO-xYbF₃ composition, with x = 0.50, 1.50, 2.00, and 2.50 mol % and 30SiO₂-15Al₂O₃-(29-x)CdF₂-22PbF₂-4YF₃-xYbF₃ with x = 0.50, 1.00, 2.00 and 3.00 mol % are promising candidates for laser cooling applications. Photoluminescence measurements revealed the near IR PL emission due to the Yb³⁺: ²F_{5/2} – ²F_{7/2} transition, with the intensity and peak shape relying on the host composition and Yb³⁺ concentration. Due to the ion-ion interaction, reabsorption and radiation trapping, the PL emission intensity starts to decrease as the Yb³⁺ concentration reaches a critical value of 2 mol % (power and volume excitation limited). Based on the Yb³⁺ concentration and excitation wavelength the PL internal quantum yield varies between 70 % and 99 %. Calorimetric measurements performed on glass-ceramics using fiber Bragg gratings demonstrated that GCs containing 1.50 – 2.00 mol % of Yb³⁺ have a net heating near to zero at ~1030 nm excitation revealing their potential for optical refrigeration applications. Also, SPYb 2.0GC sample was found to possess higher anti-Stokes emission intensity at elevated temperatures compared to all other GCs investigated, due to the optimized host composition and ytterbium doping level in

this glass-ceramic. Our results show a promising approach for exploring the optical properties of Yb^{3+} doped oxyfluoride glass ceramics at elevated temperatures to harness it toward the realization of practical temperature stabilization applications. These GCs could be also useful to calibrate an integrating sphere as they revealed the iQY close to unity. With the expected high quantum efficiency and operating stability, Yb doped oxyfluoride glass-ceramics also show potential for applications in solid state lasers and optical amplifiers.

Acknowledgements

The authors thank Mr. Frederic Monet for the fabrication of the FBGs used for the temperature sensor. The authors thank Mr. Thomas Meyneng for the TEM measurements. The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC), Canadian Excellence Research Chair program (CERC) on Photonic Innovations, Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT), Merit scholarship program for foreign students (PBEEE Quebec-India) and Canada Foundation for Innovation (CFI) and Brazilian Agencies: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) - Finance Code 001, and Fundação de Amparo à Pesquisa do Estado de Goiás (FAPEG).

CHAPTER 5 ARTICLE 2: ENHANCING THE OPTICAL PERFORMANCE OF OXYFLUORIDE GLASS CERAMICS BY OPTIMIZING THE OXIDE: FLUORIDE RATIO AND CRYSTALLINITY FOR OPTICAL REFRIGERATION

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Published in: Journal of Non-crystalline Solids- X, February 16, 2023

The optimization of the oxide and fluoride content, crystallinity and rare earth ion concentration in oxyfluoride glass ceramics (GCs) are of great importance in obtaining high photoluminescence quantum yield (PLQY) for optical refrigeration applications. Presented herein are the important advancements in the development of a novel oxyfluoride GCS of the composition $(\text{SiO}_2\text{-Al}_2\text{O}_3)_{(100-a)}(\text{YLiF}_4)_b(\text{YbF}_3)_b$ ($a = 35$ and 40 ; in mol %, $b = 1$ and 2 mol %) with the corresponding parent glasses with an in-depth investigation on enhancing the optical performance for laser cooling. Depending on the oxide/fluoride (O/F) ratio and ytterbium content the internal quantum yield (iQY) varied between 70 to 99 % in glass ceramics at several excitation wavelengths. The optical properties of GCs containing YLiF_4 and YF_3 nanocrystals obtained from the same initial composition (modulated by time and fusion temperature) were compared to find the optimal composition for optical refrigeration. Low fluorine content led to the generation of YLiF_4 as a major phase after ceramization and high fluorine content helped in the generation of the YF_3 phase. An increase in the radiative lifetime of YF_3 GCs compared to YLiF_4 GCs has been found to coincide with the enhancement of the PLQY, which is beneficial for laser cooling. The temperature change (ΔT) change measured using a fiber Bragg grating (FBG) in the glass and glass-ceramic samples with different pump wavelengths showed significant heat mitigation near ~ 1030 nm. The observed enhanced PL intensity, iQY and lifetime after purification of YLiF_4 glasses imply that the purity of the material plays a paramount role in lowering the background absorption and enhancing the quantum yield. Looking ahead, we see a bright future for oxyfluoride GCs in applications requiring the ultimate levels of thermal, mechanical and optical performance, especially for the development of cryocooler devices, which are still technologically challenging

and expensive. The usage of GCs will open up new possibilities in optical cooling technology, enabling cooling devices of any size and shape.

Keywords: oxyfluoride glass ceramics, photoluminescence quantum yield, laser cooling

5.1. Introduction

Solid-state laser cooling has emerged as an exciting research area recently driven by the rapidly increasing demand for cryocooler devices, sensors and satellite instruments, radiation balanced lasers etc. requiring low mechanical vibrations, no mechanical components and enhanced reliability [101, 154]. To meet the requirements of the aforementioned applications, new innovative materials with higher quantum efficiency and low background absorption is of great significance. Although the solid-state laser cooling technique was proposed more than a century ago [2], the enormous interest in optical properties of crystals and glass ceramics has arisen only after 65 years with the observation of laser cooling in ZBLAN glasses [1] thanks to the advances in purification required for the fabrication of high quality optical fibers. Lately, many materials with unprecedented properties have been proposed and studied [22, 27, 42, 90, 180]. Among them, the oxyfluoride glass ceramics (GCs) represent a class of promising materials due to their specific advantages relative to crystals and a range of other unique and important properties. Many ground-breaking experiments have already shown the great potential of glasses for laser cooling [88, 180, 181]. Furthermore, GCs offer advantages compared to crystals and semiconductors, they enable the control of the shape and size, which can be explored for producing optical fibers. Higher optical transparency, thermomechanical strength and easy moulding make glass a preferred photonic platform material [138, 182-185].

In the past decade, oxyfluoride glass ceramics with different hosts consisting of nano-crystals of PbF_2 , LaF_3 , BaF_2 , BaYF_5 , NaYF_4 , etc. with interesting optical properties have become of great interest [139, 186, 187]. In recent years, the development and applications in solid state laser cooling have been widely explored by our group owing to its near unity quantum yield and the excellent mechanical and thermal stability [6, 11, 46, 67, 132, 140, 141, 144, 188, 189]. The transparent GC is fabricated by applying thermal treatment to the parent glass [139]. The multi phonon decay as well as non-radiative transition probability in such materials are lower since RE ions are predominantly distributed in low phonon energy nanocrystals making it a promising

material for laser cooling [11]. For efficient cooling it is of great importance to choose the RE ion and host matrix that offers a near-unity quantum efficiency along with higher purity. Therefore, in the current work, we explored GCs containing YLiF₄ and YF₃ nanocrystals and studied the structural and optical properties of those glasses with different compositional variations. The RE-doped glass ceramics containing YLiF₄ nanocrystals have been studied by several groups for display devices, lasers and other opto-electronic applications [142, 189, 190]. But a detailed study of their optical properties is absent in the literature and those glasses have not yet been explored for laser cooling. Recently YLiF₄ nanocrystals embedded transparent glass–ceramics were fabricated by controlled heat-treatments of LiF-YF₃-Al₂O₃-SiO₂ glass by Suzuki *et al* [190]. Their studies were focused on incorporating RE ions such as Er³⁺ and Eu³⁺ into YLiF₄ nanocrystals in the glass–ceramics. It is already known that YLiF₄ crystals are ideal matrices for trivalent Yb ions which can substitute the Y³⁺ ions as a dopant [143, 191]. Similarly, YF₃ crystals also possess a low phonon energy ($\sim 358\text{ cm}^{-1}$) and the Y³⁺ ion sites can be easily replaced by trivalent Yb³⁺ ions. Therefore, it is highly desirable to utilize them as an optical cooling material.

A highly purified glass is the most demanding challenge in demonstrating cooling in GCs [11, 140]. Owing to the undesirable impurities and other detrimental components, it is challenging to achieve lower background absorption. This has led to enormous attempts around the world in the synthesis of highly pure glass by various processes and purification techniques [71, 72]. Nevertheless, using limited handful facilities, obtaining near unity quantum yield and minimizing background absorption which are essential for optical refrigeration, remain as significant challenges. Along with the purity, optimizing the oxide: fluoride content in oxyfluoride glass ceramics is paramount to maximizing the quantum yield that will ultimately set the optical performance limits of GC for optical cooling.

In this work, we experimentally separate or unveil four mechanisms that contribute to the PL enhancement and govern the PL emission properties (quantum yield, lifetime etc.) and cooling characteristics of oxyfluoride glass ceramic namely, (i) the oxide: fluoride ratio, (ii) ytterbium ion concentration, (iii) amount of crystallinity and (iv) the purity of the material. First, we address the impact of the O/F ratio on GCs and corresponding parent glasses by comparing different samples (See Table 5.1). In the quantum yield and lifetime measurements we note a strong dependence of the emission properties on the O/F ratio and thus the cooling characteristics. Second, we address the impact of ytterbium ion concentration (in mol %) as we compare the PL emission from samples

doped with 1 mol % to 2 mol % of ytterbium. The GC doped with 2 mol % was found to be most suitable for cooling applications. Thirdly, the optical properties of GCs containing YF_3 NCs and YLiF_4 NCs obtained from the same initial composition (modulated by time and temperature of the fusion) were compared to find the optimal composition for optical refrigeration. GCs with YF_3 crystals having a higher fluorine concentration and higher crystalline fraction benefiting from the low phonon energy were found to be most suitable for laser cooling compared with the one having a low fluorine concentration and lower crystalline fraction. Finally, we compared the optical properties of purified GCs with that of not purified GCs and found that the purification helps to enhance the PL emission intensity and iQY along with lowering the background absorption.

5.2. Materials and Methods

5.2.1 Sample preparation and characterization

The selected Gs and GCs pertinent to the following chemical composition in mol %: $(\text{SiO}_2\text{-Al}_2\text{O}_3)_{(100-a)}(\text{YLiF}_4)_b(\text{YbF}_3)_b$ ($a = 35$ and 40 ; in mol %, $b = 1$ and 2 ; in mol %) were made by the conventional melt quenching technique. Calculated amounts of precursor materials were mixed in an agate mortar in a glove box in a dry nitrogen atmosphere, and thereafter heated up to the melting temperature of 1530°C in a platinum crucible for 10 minutes. Afterward, the melt was poured into a preheated brass mold at 520°C followed by annealing at the glass-transition temperature for 2 h, to relieve cooling stresses. GCs containing YF_3 crystals were prepared at a fusion temperature of 1430°C for 10 minutes inside of a platinum DPH (expand) crucible, under a dry argon atmosphere. The melt was then cast in a stainless steel mould that had been preheated to 520°C , and annealed for two hours [192]. The GCs containing YLiF_4 nanocrystals were fabricated by using a heat treatment using 600°C for 4 hours. Ceramization of GCs containing YF_3 phase was performed at 580°C for 4 hours in a Nabertherm L-092S3RN3 under ambient air atmosphere.

A differential scanning calorimeter (Netzsch DSC, 404 F3 Pegasus) equipped with a liquid nitrogen cooling unit and a type S thermocouple sensor was used to measure the glass transition (T_g) and onset of crystallization (T_x) temperatures of both glass samples, at a heating rate of $10^\circ\text{C}/\text{min}$ in platinum pans up to 1000°C under inert atmospheric conditions. To determine accurately their heat capacity at room temperature, the same apparatus was employed using helium as flowing gas, a more sensitive type E thermocouple sensor, a heating rate of $4^\circ\text{C}/\text{min}$ from -50°C to 100°C , uncovered aluminium sample pans and reference materials (sapphire).

The elemental analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 8800 – ICP MS. 100 mg of samples were digested in lightly heated nitric acid. Concentration of iron (Fe) was measured with the calibration of 10 standards from 0.1 ppb to 500 ppb.

5.2.2 Optical measurements

Ultraviolet - visible - near infrared (UV-Vis-NIR) transmission spectra (resolution of 2.0 nm) of the samples (~2.0 mm-thick) were measured using an Agilent Cary 5000 double-beam spectrophotometer. An M prism coupler (Metricon 2010) was used to measure the linear refractive index (RI) of the samples.

The photoluminescence (PL) emission spectra and quantum yield (QY) of the samples were measured using a Ti: Sapphire laser (Spectra-Physics 3900S) at pump wavelengths of 920 nm, 980 nm, and 1020 nm. An integrating sphere (Thorlabs IS200-4) connected to a multimode optical fibre to an Ando AQ6317B optical spectrum analyzer (OSA) was used to collect the emitted light. The PL lifetime (τ) values ascribed to the $\text{Yb}^{3+}: 2F_{5/2}$ level were obtained using a fast oscilloscope (Tektronix). A Thorlabs SM05PD1B photodiode along with a benchtop trans impedance amplifier was used to record the signal. To modulate the external signal, a Thorlabs MC100A chopper (frequency of 20.0 Hz) was employed. The pump wavelength was eliminated using an edge filter. The steady-state temperature change of glasses and glass ceramics were measured while exciting with different pump wavelengths (980- 1040 nm) from a the Ti: sapphire laser. Figure 5.1 shows a schematic representation of the experiment.

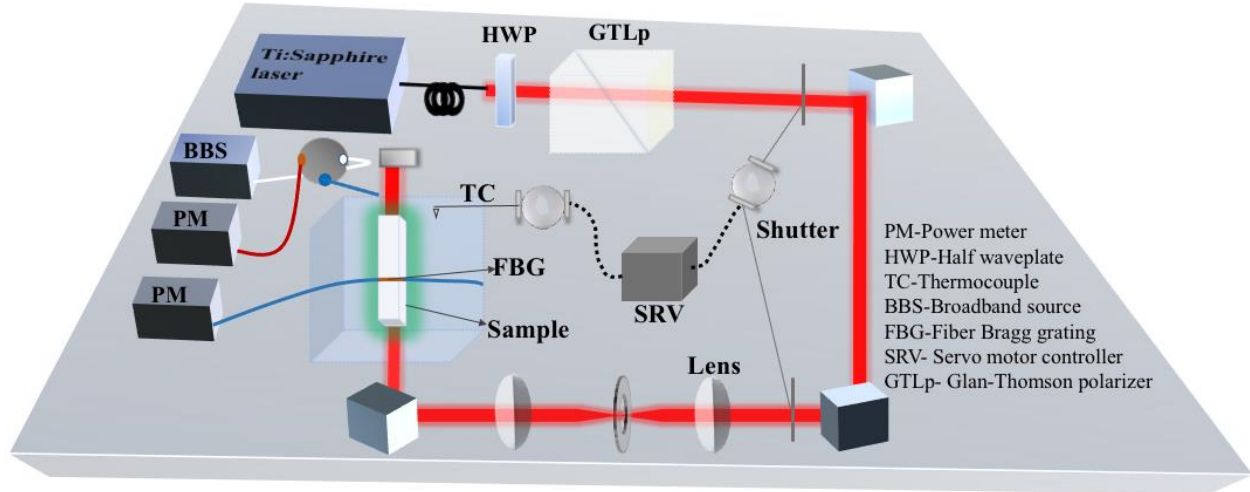


Figure 5.1: Experimental setup for measuring the temperature change of the G & GC samples.

The samples were placed on a couple of silica optical fibres that were mounted on a stainless-steel holder, to reducing the heat load on the glasses. A fiber Bragg grating (FBG) contact method [80] was used for temperature measurements. A broadband source and an optical circulator with the second port connected to the grating were employed for calibration. The reflection from the FBG is collected through the circulator's third port, where it is analyzed by an optical spectrum analyzer (Ando AQ6317B). A combination of half-wave plate (HWP) and Glan-Thompson polarizer (GLTp) was used to adjust the laser output power.

The background absorption coefficient (α_b) was determined using calorimetric technique while exciting the samples with 3 W at 1550 nm from an IPG ELR-70-1550-LP ytterbium-erbium fiber [11, 140].

5.3. Results and Discussion

For our study, we chose aluminosilicate oxyfluoride glass as a host matrix for several reasons: First, the embedded nanocrystals enable the full exploitation of the PL properties towards various optoelectronic applications. Moreover, the presence of low phonon energy nanocrystals (YLiF₄ and YF₃) within the glass matrix can be exploited towards enhancing and manipulating the PL properties of GC and thus the cooling characteristics. Finally, the silicate glass has a glass transition temperature of $\sim 550^\circ\text{C}$, which is enough for fiber production. The compositions of investigated glasses and glass ceramics are listed in Table 5.1. In the terminology used to describe

the samples, the first number represents the fluoride ratio followed by the oxide ratio and ytterbium ion concentration.

A very interesting feature of this composition is the fluorine concentration of the final glass which was modulated by the time and fusion temperature [192]. A lower fluorine content led to the generation of YLiF_4 as a major phase after ceramization, on the other hand, a higher fluorine content led to the generation of YF_3 .

Table 5.1: The glass ceramic and parent glass compositions along with the terminology used in the text.

Glass-ceramics composition	Terminology	Parent Glass composition	Terminology
$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{65}\text{-(YLiF}_4)_{35}\text{: (YbF}_3)_1$	GC 65:35:1	$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{65}\text{-(YLiF}_4)_{35}\text{: (YbF}_3)_1$	G 65:35:1
$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YLiF}_4)_{40}\text{: (YbF}_3)_1$	GC 60:40:1	$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YLiF}_4)_{40}\text{: (YbF}_3)_1$	G 60:40:1
$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{65}\text{-(YLiF}_4)_{35}\text{: (YbF}_3)_2$	GC 65:35:2	$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{65}\text{-(YLiF}_4)_{35}\text{: (YbF}_3)_2$	G 65:35:2
$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YLiF}_4)_{40}\text{: (YbF}_3)_2$	GC 60:40:2	$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YLiF}_4)_{40}\text{: (YbF}_3)_2$	G 60:40:2
$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YF}_3)_{40}\text{: (YbF}_3)_2$	$\text{YF}_3\text{GC 60:40:2}$	$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YF}_3)_{40}\text{: (YbF}_3)_2$	$\text{YF}_3\text{G 60:40:2}$

5.3.1 The thermal stability

The glass transition temperature T_g , onset crystallization temperature T_x , and the peak crystallization temperature (T_p) determined by DSC for GC 65:35:1 and GC 60:40:1 is depicted in Figure 5.2 (a-b). T_g was obtained from the inflection point on the enthalpy curve. For the parent glasses used to prepare the GC 65:35:1 and GC 65:35:2 samples, the glass transition temperature T_g was 581°C . For GC 60:40:1 and GC 60:40:2 it was 569°C . The onset crystallization temperature T_x was 765°C and 758°C , respectively. The Hruby parameter ($\Delta T = T_x - T_g$) was used to determine the glass thermal stability vs crystallization. The parent glass of composition

$(\text{SiO}_2\text{-Al}_2\text{O}_3)_{65}\text{-(YLiF}_4)_{35}\text{: (YbF}_3)_1$ has a ΔT value of 184. For $(\text{SiO}_2\text{-Al}_2\text{O}_3)_{60}\text{-(YLiF}_4)_{40}\text{: (YbF}_3)_1$, it was 189° C. The high stability of both the glass shows their potential for shaping and fiber production. The glass transition temperature T_g , onset crystallization temperature T_x and the peak crystallization temperature (T_p) evaluated by DSC for $\text{YF}_3\text{GC } 60:40:2$ was 531° C, 670° C, and 695° C (Figure 5.2(c)).

The thermal properties of glasses were significantly influenced by the fluoride content. The specific heat capacity (C_p) at 300 K for sample GC 65:35:1 was 0.73 J/K/Kg. The increase of fluorine ratio in sample G 60:40:1 resulted in a decrease of the T_g and a decrease of specific heat (0.68 J/K/Kg) accompanying the glass transition region. Since fluorine is a powerful network disrupter, it replaces the oxygen ions from the glass matrix and thus increases the chance for YLiF_4 crystallization in the glass [133]. Also due to the shifting of the initial ceramization temperature to lower temperatures, the stability against the crystallization parameter ($\Delta T = T_x - T_g$) is increased. In short, all the investigated glasses exhibit good thermal stability which is good for fiber production. Our findings are in good agreement with the previous works on aluminosilicate, and silicate-based glasses which contain fluorine [193, 194].

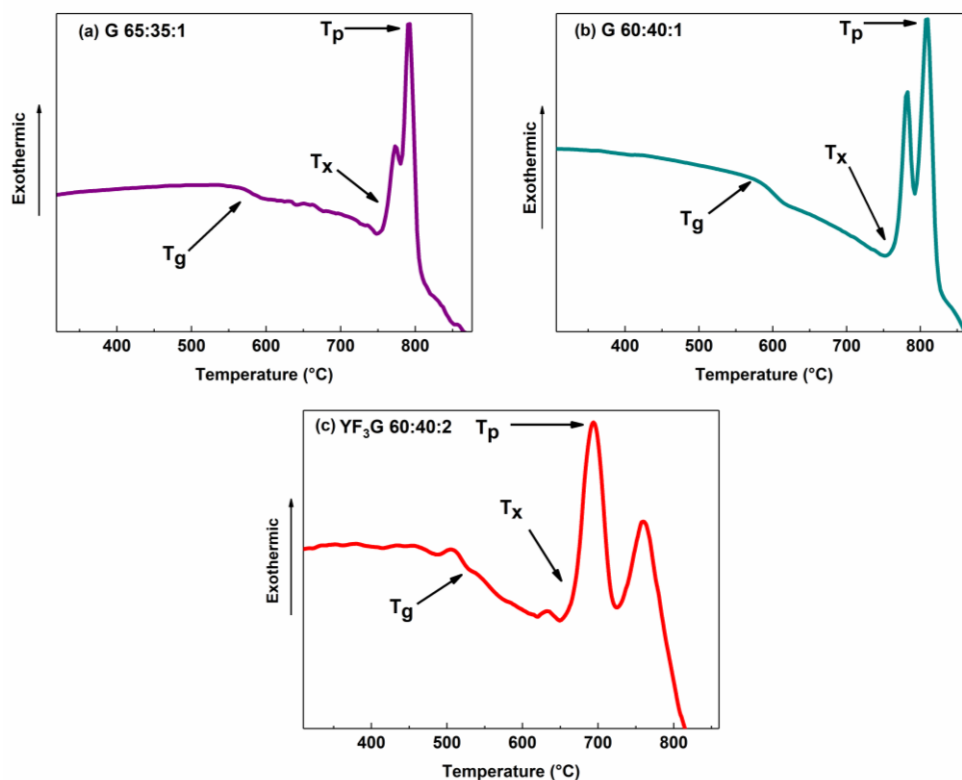


Figure 5.2: DSC curve of the (a) G 65:35:1, (b) G 60:40:1 and (c) YF_3 G 60:40:2.

5.3.2 Optical transmission and refractive index properties

Optical transparency is one of the most important properties of GCs used for optical cooling. The near IR transmission spectra of the prepared Gs and GCs are shown in Figure 5.3(a-d). As observed in Figure 5.3(a), for GC 65:35:2, the transparency was ~75 % and 85 % in the visible and NIR region respectively. But the corresponding glass (G 65:35:2) presented a higher transparency of ~82 % and ~92 % in the visible and NIR region respectively. For GC 60:40:2, the transparency was ~78 % and ~84 % in the visible and NIR region respectively. But the parent glass (G 60:40:2) had a higher transparency of ~84 % and ~95 % in the visible and NIR region respectively (Figure 5.3(b)). Owing to Rayleigh scattering caused by density changes in the glass by the presence of nanocrystals, atomic absorption and reflection the transparency reduces in glass ceramics compared to [195].

The transparency around 980 nm of glass samples decreases by increasing of ytterbium content, due to absorption from the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb^{3+} ions. The transmittance was more than ~82 % in the visible region and as high as ~90 % in the NIR region for GC 60: 40: 1 which is higher than that of GC 60:40:2 (Figure 5.3(c)).

The transmittance of GCs containing YLiF_4 crystals has been compared with that of the YF_3 GCs. YF_3 GCs present a much higher crystalline fraction compared to YLiF_4 GCs [192]. Note that a high crystallinity could mean that a higher amount of Yb^{3+} ions could be encapsulated inside the nanocrystals. Also, the smaller crystal diameters allow a higher transparency as shown in Figure 5.3(d). The higher transparency in these glasses is obtained by controlling the crystal size to the nanometer scale. The XRD of the GCs with YLiF_4 and YF_3 are provided in appendix (Figure 5). After 7h of heat treatment at $T_g + 60$ °C, YLiF_4 containing GCs present crystals with mean diameters of 45 to 60 nm, estimated from Scherrer equation, but for YF_3 GCs it was 26 to 31 nm. Also, to control the nucleation and growth processes of nanocrystals inside the glass matrix a detailed investigation on the crystallization mechanism was done through Ref [192]. It was mentioned that the crystallization behavior difference between the two glasses is caused by a mixed effect of the viscosity and the ionic mobility during ceramization treatment.

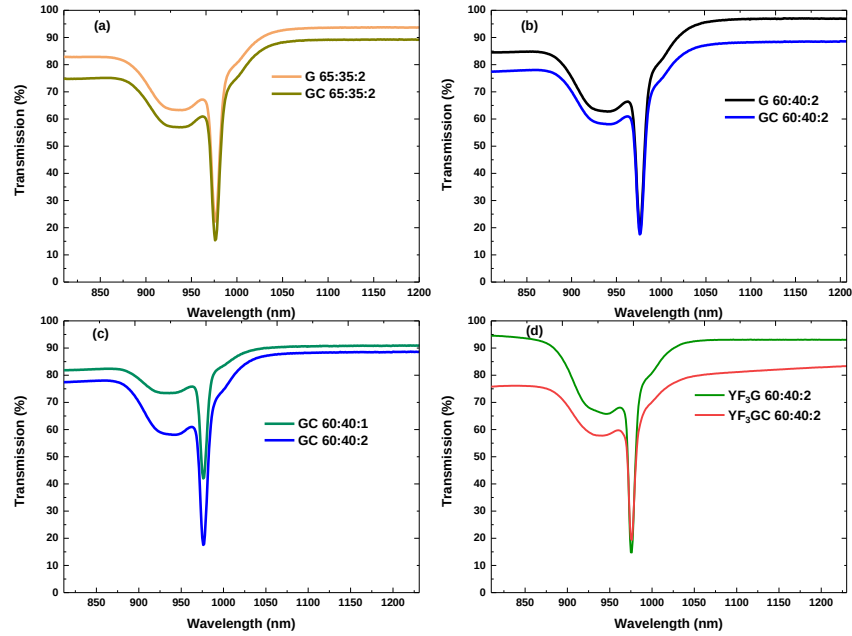


Figure 5.3: The transmission spectra of (a) G 65:35:2 & GC 65:35:2, (b) G 60:40:2 & GC 60:40:2, (c) GC 60:40:1 & GC 60:40:2 and (d) YF₃G 60:40:2 & YF₃GC 60:40:2.

One of the important parameters to take into consideration while designing glass based optical devices is the refractive index (RI). To understand the effect of oxide: fluoride ratio and ytterbium concentration on the refractive index (RI), we have investigated the RI through m-lines spectroscopy. The RI of the glasses and glass-ceramics at different wavelengths are shown in Figure 5.4(a) and 5.4(b). As we decrease the oxide: fluoride (O/F) ratio, the refractive index increases, as expected. The introduction of polarizable fluorides enhances the refractive index and molar refractivity of the material [194]. Within the experimental uncertainty, the measured RI in transverse electric (TE) and transverse magnetic (TM) polarisation modes are equal. As a result, birefringence is negligible for GCs.

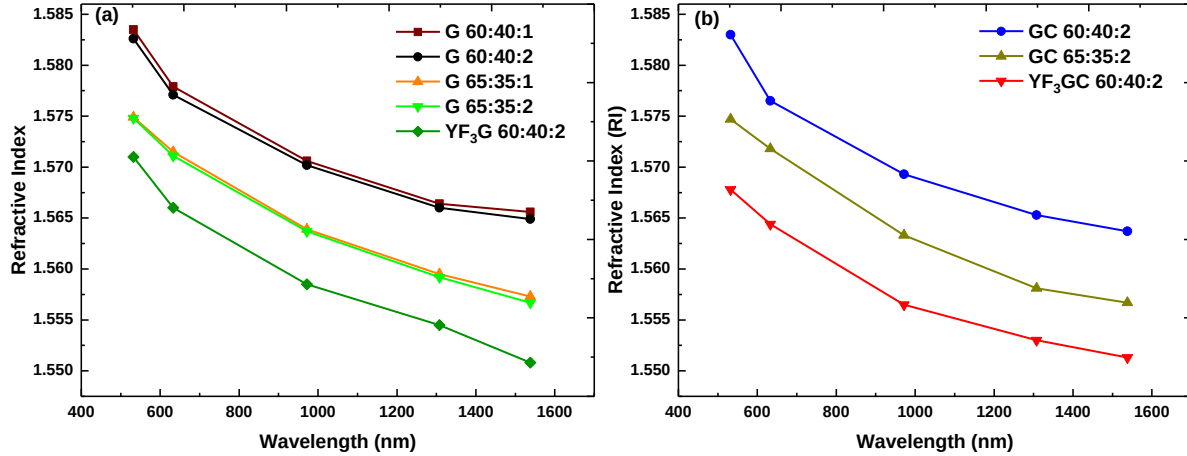


Figure 5.4: The Refractive index values at 532.0, 632.8, 972.0, 1308.0 and 1538.0 nm for (a) all glass samples and (b) for GC 60:40:2, GC 65:35:2 and YF₃GC 60:40:2.

The refractive index decreases with increasing wavelength as expected [141]. Previous studies on YLiF₄ embedded transparent oxyfluoride glass–ceramics showed that the refractive index of the parent glasses at 632 nm were slightly lower compared with the GCs heat-treated at 550° C [46] and our results are in good agreement with that. The refractive index of YF₃GC 60:40:2 reduced due to the increasing content of fluorine. Fluorine has lower polarizability than that of oxygen ($F = 0.557 \text{ \AA}^3$, $O = 0.802 \text{ \AA}^3$). This property is used to reduce the refractive index of silica in the glass chemical vapor deposition process [196, 197]. A similar trend can be observed here, both from base composition when comparing samples 65:35 and 60:40, and from final composition, with GC 60:40:2 and YF₃GC 60:40:2; the later having higher fluorine content.

According to R. I Epstein and M. Sheik Bahae the refractive index affects the optical cooling material in two different counteracting ways [64]. Firstly, it controls the escape of fluorescence light and secondly the rate for excited state spontaneous relaxation scales linearly with the local field correction factor which is given by the equation (5.1).

$$\chi = \frac{n(n^2+2)^2}{9} \quad (5.1)$$

Where n is the refractive index at the emission wavelength. They mentioned that the local field correction varies by a factor of three for typical laser cooled materials. In principle, higher radiative rates in higher RI materials can improve quantum yield and therefore the cooling efficiency. The local field correction factors are ~ 3.42 , ~ 3.47 , ~ 3.42 and 3.46 for GC 65:35:1, GC 60:40:1, GC

65:35:2 and GC 60:40:2 respectively. For YF₃GC 60:40:2 and the corresponding parent glass it was ~3.37 and ~3.39 respectively. Even though the total internal reflection is high at higher RI, the advantage of high local field correction factors can counter the inconvenience caused by enhanced reabsorption. Therefore, tailoring the local field correction factor of the laser cooling material is of great importance. Our findings in Figure 5.4 (a & b) highlight the fact that, using oxyfluoride glass ceramics, the RI and the local field correction factor can be adjusted by simply changing the volume fractions of the glass constituents, for example by adding or reducing the content of fluorides.

5.3.3 Photoluminescence (PL) properties

Consider the ground and excited electronic states in the oxyfluoride glass doped with Yb ions, both of which are split into several sub-levels by the crystal field. We excite the system with energy $E_p = hc/\lambda_p$. In a picosecond time scale, electron-phonon interaction will establish a Boltzmann equilibrium population in the excited state manifold. The mean fluorescence energy, $E_f = hc/\lambda_f$ depends on the temperature and the crystal-field splitting of the glass. When we excite the system at $E_p < E_f$, an energy difference of $\Delta E = E_f - E_p$ is required to establish thermal equilibrium and that will be provided by the phonons in the solid. The excited electrons decay by radiative relaxation which leads to cooling of the system. The PL characteristics of RE ions in inorganic glasses are determined by host material composition, the concentration of RE ions, and the pump power [198]. Along with these factors, the total phonon energy of the material mainly influences the PL emission efficiency of excited states of Yb³⁺ ions in the investigated glasses. We studied the spectroscopic properties of all the investigated glasses and GCs in detail to assess the cooling potentiality of these materials.

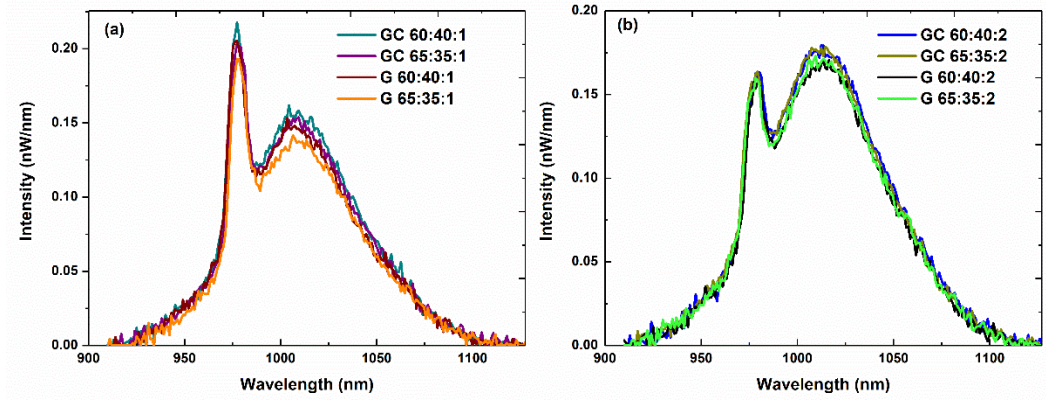


Figure 5.5: (a) The PL emission spectra of GCs & corresponding parent glasses doped with 1 mol % Yb using a pump wavelength of 980 nm and (b) The PL emission spectra of glass ceramics & corresponding parent glasses doped with 2 mol % Yb at a pump wavelength of 980 nm.

In Yb-doped glasses, the PL emission spectra possess the same shape despite the excitation wavelength, as a result of the thermal re-equilibrium processes ($\sim$ ns) is significantly faster than the radiative lifetime ($\sim$ ms) [198]. Figure 5.5(a) and 5.5(b) shows the obtained room temperature PL spectra of glasses and glass ceramic doped with 1 mol % and 2 mol %, respectively at an excitation wavelength of 980 nm. In GC 65:35:1 and GC 60:40:1, the PL emission observed around 1010 nm indicates that Yb^{3+} ions were incorporated into the fluoride phase. As we increased the Yb content from 1 to 2 mol % the mean fluorescence wavelength (MFW) changed from 1010 nm to 1013 nm. The PL intensity in GCs is higher compared to the parent glasses. This indicates that the formation of crystallites altered the environment of the Yb^{3+} ions, resulting from ion migration either into the YLiF_4 crystals or toward the nanocrystal/glass boundary. The probability of multi-phonon relaxations reduces in GCs with low phonon energies and therefore the intensity of the PL emission increases. According to the Miyakawa and Dexter theory [199], the multi-phonon decay rate relies exponentially on the energy gap difference between the energy levels and the phonon energy of the material. Silicate oxide glass possesses a maximum phonon energy of 1100 cm^{-1} , but it reduces to 250 cm^{-1} for a YLiF_4 crystal. Moreover, it should be mentioned the PL intensity scales with fluoride content ($\sim 40\%$). Since Yb^{3+} ions possess large absorption cross section at 980 nm, the emission intensity is approximately 7 times larger than that recorded under 1020 nm excitation. To further investigate and assess the role of crystallinity in the PL emission enhancement of glass ceramic, we compared GCs containing YF_3 crystals ($\text{YF}_3\text{GC } 60:40:2$) and YLiF_4 crystals (GC

60:40:2) while exciting with 980 and 1020 nm. Due to the higher crystalline fraction, YF₃GC 60:40:2 has a higher PL intensity centred at 1016 nm (Figure 5.6(a) & (b)) at a pump wavelength of 980 or 1020 nm than that of GC 60:40:2.

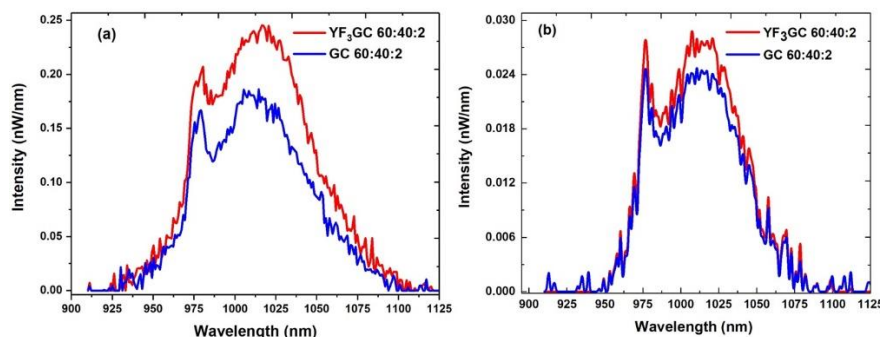


Figure 5.6: (a) The PL emission spectra of YF₃GC 60:40:2 & GC 60:40:2 with the corresponding parent glasses with a pump wavelength of (a) 980 nm, (b) Comparison of the PL emission spectra of YF₃GC 60:40:2 & GC 60:40:2 with a pump wavelength of 1020 nm.

Table 5.2: The measured internal quantum yield (iQY) of all the glasses and glass ceramics using different pump wavelengths.

	Internal quantum yield (iQY) (in %)		
Glass Composition	920 nm	980 nm	1000 nm
G 65:35:1	67	58	55
G 60:40:1	57	66	49
G 65:35:2	52	77	67
G 60:40:2	65	79	70
YF ₃ G 60:40:2	67	83	74

	Internal Quantum yield (iQY) (in %)			
Glass-ceramic Composition	920 nm	980 nm	1000 nm	1020 nm
GC 65:35:1	70	98	75	64
GC 60:40:1	77	99	75	65

GC 65:35:2	72	94	76	68
GC 60:40:2	80	95	79	71
YF ₃ GC 60:40:2	84	96	80	76

To probe the effect of compositional variations on the internal quantum yield (iQY) of all the samples at several excitation wavelengths, we used an integrating sphere method [11, 46, 140] which is shown in Table 5.2. The iQY values of GCs were larger than that of Gs as expected. For the GC 65:35:2, the iQY varies between 68 % and 94 % for different excitation wavelengths. For GC 60:40:2 the iQY values at different excitation wavelengths varies between 71 % and 95 %. Samples with 2 mol % of Yb possess higher iQY values at pump wavelengths of 1000 and 1020 nm. The PL intensity as well as iQY in GCs were larger than that of parent glasses and provided the advantage of low phonon energy crystals. The external quantum yield (eQY) of all samples was less than 15 % due to radiation trapping effects [11].

The quantum efficiency of the GC 60:40:2 sample at an excitation of 1020 nm was obtained as 71 % and it was elevated to 76 % with the increase in the crystallinity in YF₃GC 60:40:2 samples. Along with the results obtained in this study for Yb doped GC 60:40:2 and YF₃GC 60:40:2, it should be noted that through a suitable compositional modification and purification process an enhancement in quantum yield could be expected as mentioned in Section 5.5.

It has been observed in all the investigated glass and glass ceramic samples that the PL emission decay from the 4F_{5/2} level follow a single exponential time dependence. Table 5.3 provides the PL emission decay time values of Yb³⁺: 2F_{5/2} level at a pump wavelength of 920 nm obtained by fitting the decay curves using a single exponential function.

Gs and GCs containing larger amounts of fluoride content with 2 mol % of Yb demonstrate a longer lifetime. Compared with the parent glasses, the GC samples exhibited longer lifetimes. The majority of Yb³⁺ ions are placed inside the YLiF₄ nanocrystals that are precipitated in the glass during the thermal treatment. Consequently, the multi-phonon decay rate in the Yb³⁺ ions inside the YLiF₄ crystals is reduced and therefore, the lifetime of the ions inside the nanocrystals is longer. In GC 65:35:1 and GC 65:35:2 the fluorine content was reduced and as a result the lifetime of the Yb³⁺ ions are reduced compared to the GC 60:40:1 and GC 60:40:2 due to the higher phonon energy of the glass. The addition of fluoride promotes the experimental lifetime increase, as previously reported in Yb³⁺ doped tellurite glasses [200].

Table 5.3: PL emission decay time values of $\text{Yb}^{3+}: {}^2F_{5/2}$ level in all glasses and glass-ceramics

Sample	Lifetime (ms)	Sample	Lifetime (ms)
G 65:35:1	1.37	GC 65:35:1	1.37
G 60:40:1	1.37	GC 60:40:1	1.41
G 65:35:2	1.38	GC 65:35:2	1.38
G 60:40:2	1.41	GC 60:40:2	1.44
YF ₃ G 60:40:2	1.51	YF ₃ GC 60:40:2	1.55

The luminescence lifetime (τ) values ascribed to the $\text{Yb}^{3+}: {}^2F_{5/2}$ level for YF₃GC 60:40:2 under excitation at 920 nm is also provided in Table 5.3. The decay curves are given in appendix (Figure 6). We observe that the YF₃GC 60:40:2 has a slightly longer lifetime than the GC 60:40:2 as it contains more fluoride and has more ytterbium inside the nanocrystals. Also, as previously stated, YF₃ GCs are more crystalline than YLiF₄ GCs, so the averaged lifetime of Yb^{3+} in YF₃GC 60:40:2 is much longer than that in GC 60:40:2.

Radiation trapping can occur in the glass due to total internal reflection and can lead to reduction in cooling efficiency due to re-absorption. This relies on the RI difference of the cooling medium from the surrounding media.

The fluorescence extraction efficiency is given by the equation (5.2) [201]

$$\eta_e = 3(1 - (1 - (\frac{1}{n})^2)^{1/2}) \exp(-\alpha_r(\lambda)l) \quad (5.2)$$

Where n is the RI of the cooling medium, α_r is the resonant absorption coefficient, and l is the length of the medium. The fluorescence reabsorption along the length l of a sample is considered using the exponential factor. The extraction efficiency of all glass ceramics at a wavelength of 1030 nm is given in Table 5.4. The YF₃GC 60:40:2 has a higher extraction efficiency of 69.0 % compared to other samples under investigation.

Table 5.4: The extraction efficiency of all glass ceramics at a wavelength of 1030 nm

GC composition	GC 65:35:1	GC 60:40:1	GC 65:35:2	GC 60:40:2	YF ₃ GC 60:40:2

Extraction efficiency (η_e)	67.6 %	67.4 %	65.7 %	63.4 %	69.0 %
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5.3.4 Calorimetry

The presence of anti-Stokes emission along with higher quantum efficiency in all glass ceramics motivated us to perform additional investigations on the potentiality of this material as a cooling media.

The steady state glass-ceramic temperature (ΔT) was extracted using the FBG direct contact method [80] and P_{abs} is calculated from the input and transmitted laser powers along with the known absorption spectra of the glasses. To elucidate the temperature change at different pump wavelengths ranging from 980- 1040 nm, we plotted the temperature changes (ΔT in Kelvin) normalized by the absorbed laser pump power (in Watt) supplied to the samples (Figure 5.7(a) and (b)). Beginning at 980 nm, significant heating ($\Delta T / P_{\text{Abs}} \sim 15\text{-}22 \text{ K/W}$) is observed in all samples. But the temperature was significantly reduced near a pump wavelength of $\sim 1030 \text{ nm}$ ($0.6\text{ - }3.0 \text{ K/W}$). Beyond 1030 nm the samples heat due to the background absorption. The GC sample with higher fluoride content and lower oxide content having 2 mol % of ytterbium demonstrates the lowest heating compared to the other samples.

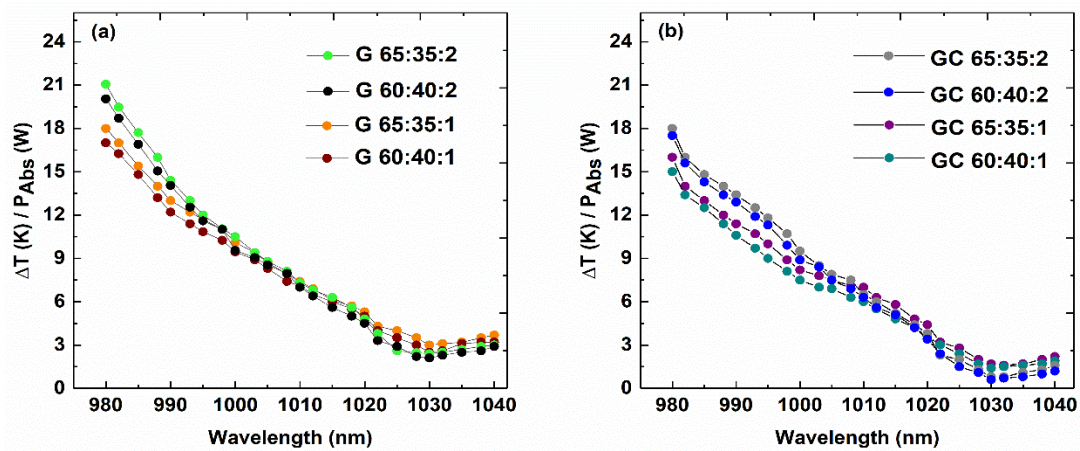


Figure 5.7: (a) The temperature variations of all Gs normalized by absorbed power ($\Delta T / P_{\text{Abs}}$) for different pump wavelengths varying from 980 nm to 1040 nm, (b) The temperature variations of

all GCs normalized by absorbed power ($\Delta T / P_{\text{Abs}}$) for different pump wavelengths varying from 980 nm to 1040 nm.

We then compared the cooling potentiality of GCs containing YF_3 nano crystals and glass ceramics containing YLiF_4 crystals. The temperature dynamics of YF_3GC 60:40:2 at various pump wavelengths varying from 1000- 1032 nm is shown in Figure 5.8. For YF_3GC 60:40:2, the maximum $\Delta T / P_{\text{Abs}}$ was of ~ 0.4 K/W at a pump wavelength of 1032 nm. This is the most striking finding of this study, namely, that the highly crystalline YF_3 GCs exhibit higher quantum efficiency and greater temperature reduction than that of lower crystallinity YLiF_4 glass ceramic obtained from the same initial composition. The change in optimum pump wavelength for both types of glasses can be ascribed to the change in MFW as well as the change in the resonant absorption coefficient.

However, the higher background absorption in these glasses preclude the possibility of observation of laser induced cooling. More insight would be extracted from the background absorption coefficient since it is one of the generally used procedures to know the impurity level in laser cooling materials. The background absorption coefficient (α_b) determined using calorimetric technique [7] is provided in Table 5.5. The α_b lies in the range of 0.14-0.15 m^{-1} in all the GCs we investigated, which is not low enough to cool.

Table 5.5: The background absorption coefficient of all the investigated glass ceramics

Sample	background absorption coefficient (α_b)
GC 65:35:1	0.154 m^{-1}
GC 60:40:1	0.148 m^{-1}
GC 65:35:2	0.159 m^{-1}
GC 60:40:2	0.157 m^{-1}
YF_3GC 60:40:2	0.152 m^{-1}

To examine the cause of background absorption, we conducted elemental analysis using ICP measurements. It was determined that the main impurity that needed to be reduced in order to improve cooling performance was Fe^{3+} . The amount of Fe was estimated to be ~ 21 ppm. For achieving cooling, the highest value of quantum yield and the lowest one for background absorption is required. For improving the performance of these glass ceramics, minimization of impurities in the glass host is necessary which can be achieved by sample preparation in controlled environments and by the use of high purity precursors. Once this problem is entirely resolved, we will be able to control the optical behaviour of these glass ceramics and therefore tackle the practical optical cooling issues.

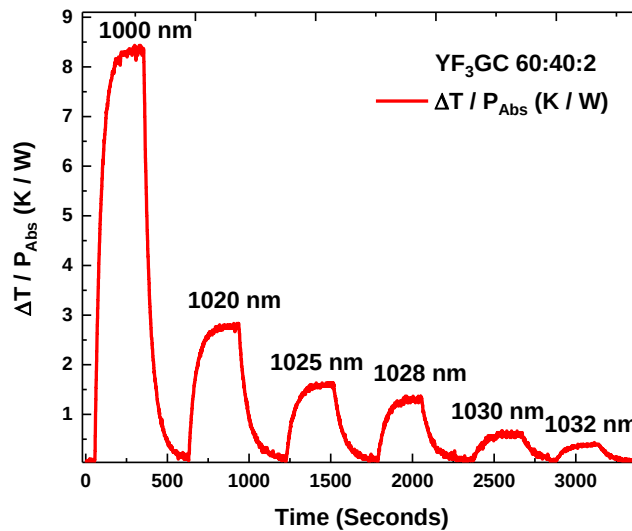


Figure 5.8: The temperature change as a function of time for the $\text{YF}_3\text{GC 60:40:2}$ at different pump wavelengths varying from 1000- 1032 nm.

5.3.5 Effect of purification on the optical properties of glasses

Although the role of impurities is not clear in the present study, the PL quantum yield is expected to be significantly enhanced after purification, which is a crucial subject for a future study. It is worthwhile to highlight that our first step of the purification of precursor materials used to synthesize GCs containing YLiF_4 crystals via chelated assisted extraction (CASE) purification method [72] improved the PL emission intensity and quantum yield. The precursor materials were purified using APDC-MIBK chelate cleaning process followed by re-fluorination using high purity

HF [202]. The chelate agent was employed to bind to impurities/metal ions in an aqueous phase before transferring the metal-chelate complexes to a second organic phase [72] [202]. We noticed a reduction in the α_b to 0.095 m^{-1} from 0.157 m^{-1} after the purification.

Figure 5.9 shows the PL emission spectra of purified GC and normal GC (GC 60:40:2) at a pump wavelength of 980 nm. The quantum efficiency of the GC 60:40:2 sample at an excitation of 980 nm was obtained as 95 % and it was elevated to 98 % after purification. Also, in contrast to prior experiments, the CASE purification helped in obtaining the best quantum yield of 78 %, with a pump wavelength of 1020 nm. The higher iQY value of purified GC indicates that through purification the non-radiative contribution of the glass was reduced and therefore the luminescent efficiency was increased. This purification non-optimized process only led to a reduction of iron concentration to 8 ppm which is good but not enough to cool the material.

The lifetime (τ) of GC 60:40:2 was evaluated before and after purification to investigate the effect of purification in influencing the PL characteristics. The τ value for the G and GC increased to 1.60 and 1.62 ms from 1.41 and 1.44 ms, respectively after purification. This is compelling evidence of reduction in the non-radiative contributions of impurities and we'd like to exploit this in a future study to obtain maximum temperature reduction. Further study of background absorption and elemental analysis is desired in each step of purification because the small amount of impurities even with few a ppm can preclude the observation of real cooling [203]. Improved sample quality and precursor purification can help to tackle these while also providing more direct proof of optical cooling.

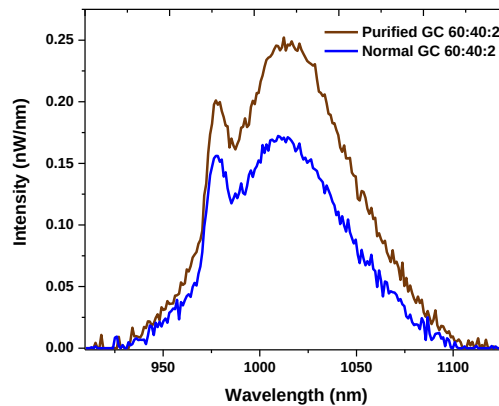


Figure 5.9: The PL emission spectra of purified GC 60:40:2 and normal GC 60:40:2 (without purification) with a pump wavelength of 980 nm.

The effect of CASE purification on the structural and spectroscopic properties of these GCs are the subject of another article in preparation. However, the present result opens the possibility of optical cooling in glass ceramics, which are significant roadblocks for important applications, such as sensors, heat balanced laser systems and satellite instrumentations. Our findings also give a starting point for further research into the compositional diversity in these glass ceramics for optical cooling applications.

5.4. Conclusions

In conclusion, the optical properties of ytterbium doped highly transparent glass–ceramics containing YLiF_4 or YF_3 nanocrystals were studied exploring the effect of compositional variations (O/F ratio and crystallinity) and ytterbium content for laser cooling applications. The glass–ceramics and corresponding parent glasses were systematically analyzed for thermal and optical properties through DSC, absorption and fluorescence spectral measurements. Our work evidence that the optimization of oxide: fluoride ratio and rare earth ion concentration in these glass ceramics are necessary to obtain high photoluminescent quantum yield. Samples having higher fluoride content with 2 mol % of Yb possess higher iQY value of 71 % at 1020 nm, which is beneficial for laser cooling. This was elevated to 76 % with the increase in crystallinity as well as fluorine concentration in YF_3GC samples. The enhanced lifetime and quantum yield performance is expected to facilitate the application of oxyfluoride glass ceramics in laser cooling applications. Calorimetric measurements performed on these glasses showed that the GC sample containing YLiF_4 nano crystals with higher fluoride content and lower oxide content having 2 mol % of ytterbium presented fewer heating effects compared to the others. Highly crystalline YF_3GCs exhibit higher quantum efficiency and larger temperature reduction than that of lower crystalline YLiF_4 glass ceramic obtained from the same initial composition.

The main obstacle to simultaneously achieving high quantum efficiency and low background absorption for glass ceramics must be overcome before they could possibly be a viable material for laser cooling applications. The enhanced PL emission, lifetime and higher internal quantum yield value of 78 % achieved using purified GC at 1020 nm indicates that the purification helps to decrease the non-radiative contribution in the glass and consequently enhances the luminescent

efficiency. Our findings offer a unique insight into exploring the compositional variations in the ytterbium doped oxyfluoride glass ceramics as a promising candidate for laser cooling.

Acknowledgements

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC), Canadian Excellence Research Chair program (CERC) on Photonic Innovations, Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT), Merit scholarship program for foreign students (PBEEE Quebec-India) and Canada Foundation for Innovation (CFI).

CHAPTER 6 ARTICLE 3: DEMONSTRATION OF LASER COOLING IN A NOVEL ALL OXIDE GAYY SILICA GLASS

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Published in: Scientific Reports, March 17, 2023

We demonstrate laser induced cooling in ytterbium doped silica (SiO_2) glass with alumina, yttria co-doping (GAYY- Aluminum: Yttrium: Ytterbium Glass) fabricated using the modified chemical vapour deposition (MCVD) technique. A maximum temperature reduction by -0.9 K from room temperature (296 K) at atmospheric pressure was achieved using only 6.5 W of 1029 nm laser radiation. The developed fabrication process allows us to incorporate ytterbium at concentration of 4×10^{26} ions/m³ which is the highest value reported for laser cooling without clustering or lifetime shortening, as well as to reach a very low background absorptive loss of 10 dB/km. The numerical simulation of temperature change versus pump power well agrees with the observation and predicts, for the same conditions, a temperature reduction of 4 K from room temperature (RT) in a vacuum. This novel silica glass has a high potential for a vast number of applications in laser cooling such as radiation-balanced amplifiers and high-power lasers including fiber lasers.

6.1 Introduction

Optical cooling of solids was first postulated by Pringsheim in 1929 [2] via anti-Stokes emission of radiation. It took 65 years for the stringent requirements of material properties to be met before it could be demonstrated successfully as a -0.3 K drop from room temperature in low phonon energy ZBLANP glass doped with Ytterbium ions[1]. The requirement for using low phonon energy materials is linked to the ease with which phonon assisted non-radiative relaxation can counter cooling, unless the bandgap is sufficiently large compared to the phonon energy, making the probability for this detrimental channel to be low [180]. Additionally, any background absorption in the material becomes a parasitic heat load reducing the cooling efficiency significantly [90]. Thus, even high-gain laser-grade materials are not typically of sufficiently high

quality for laser cooling applications and care needs to be exercised in purifying materials to reduce impurity-assisted relaxation and background absorption. Until recently, much of the cooling activity was restricted to highly purified crystals with low phonon energies with the preferred dopant Yb. The 4f electrons responsible for cooling are deeply buried within the electron shell, and thus shielded from the lattice vibrations of the surrounding medium [204]. The ground state to the first excited state energy gap is also the largest of all rare-earth elements, making phonon assisted non-radiative transition less likely and thus a material of choice for laser cooling experiments [205]. While fluoride host materials have been used for the demonstration of cryogenic operation and cooling of thermal loads [101] many applications motivate the need to broaden the selection of host materials, particularly to include oxide glasses due to their excellent mechanical and optical properties, compatibility with optical fibers and the ease with which they retain their properties through heat treatment, moulding, cutting and polishing. The solubility of rare earths in silica must be increased via the addition of network modifiers [206-208]. The MCVD process has seen an improvement in REE solubility due to the addition of network modifiers in SiO_2 . Al_2O_3 and P_2O_5 have both been successful individually [207, 209], as well as when they are combined in specific ratios, forming [210, 211] AlPO_4 entities. This has resulted in an increase in the silica concentration quenching limit from 10^{25} ions/ m^3 to 10^{26-27} ions/ m^3 [69, 212]. Although this increases the concentration of rare earths, the high phonon energy environment of the oxide glass also limits the concentration at which quenching occurs [213]. This leads to reduced quantum efficiency through non-radiative interactions and lifetime shortening of the radiative emission from the excited manifold [214]. Thus, high phonon energy and detrimental aggregation of Yb ions encountered at high doping in oxide glasses remain challenging, making it necessary to improve material purification and increase the concentration of the rare earth, principally Yb ions, to improve cooling efficiency.

To counter these limitations, our previous work concentrated on artificially creating a low phonon environment for the rare earth in high phonon energy oxide glasses, by the use of fluoride [11, 12, 46, 67, 132, 140, 144, 192]. While this technique showed enhanced quantum efficiency of emission and increased lifetimes, the fabrication route was limited by the purity of starting materials and the process by which the glasses were made [138], requiring a radical change in the glass making process.

The modified chemical vapour deposition (MCVD) technique using a silica host offers a promising route to intrinsically high purity materials. Alternative routes to enhance the luminescent properties of silica, such as the sol-gel process & integration of nanoparticles, could potentially lead to higher quantum yields and concentrations, as well as greater control over the environment of the rare earth elements [215-217]. Despite showing promise, the results obtained from these methods have not exceeded those produced by standard vapor deposition technique. Recently, laser cooling has been achieved in silica-based glasses by a number of groups [205, 218-220], with the largest temperature drop reported from room temperature of -18K in an alumina rich silica fiber under vacuum using an optimum pump wavelength power of 20W at 1035nm [220]. The temperature drop at atmospheric pressure for another fiber was reported to be -6 K with 185 W of pump power at 1035nm. These results were obtained by increasing Yb solubility by the addition of alumina and showing the potential for laser cooling in silica glass. The potential for increased dopant concentration for better cooling may be limited due to the phase separation of the rare earth in the silica-rich glass.

In this work, we modify the MCVD approach to achieve the production of silica glass preform with high Yb concentration. We increase the rare earth's solubility by the addition of alumina but promote increased phase separation of the rare earth in the oxide glass [220, 221]. The fully oxidized active rare-earth ions are immersed in another non-active rare earth to create a local phase separated low phonon energy oxide environment, shielding the rare earth from the detrimental effects of the high phonon energy silica. With this technique, we report a concentration of Yb in the silica host of 2.5x the highest value reported in the literature [218] for laser cooling, without significant lifetime shortening or reduction in cooling efficiency. We also target to highlight the effect of ytterbium ion density on the optical properties of GAYY glasses. In addition, all the glasses are doped with 0.15% atomic percent of germanium (Ge) to make it photosensitive for fabricating a self-cooled laser in future. Si is replaced by the Ge (IV) atoms in the glass matrix, and the environment for Yb ions essentially stays the same [221].

While our preliminary results are with a non-optimized pump wavelength and limited pump power, we show cooling by -0.9 K using 6.5 W pump power at 1029 nm, which is better than has been reported in the literature to date, to the best of our knowledge. This approach opens the potential for many new applications for rare earth doped oxide glass, not only for cooling but for high-power amplifiers and lasers as well as new wavelength windows for amplification.

6.2 Experimental results and discussion

The investigation of the effect of the network modifier (Al and Y) on the material properties started from the structural characterizations of the rare-earth doped preforms. A series of glasses were prepared in order to study the effect of ytterbium ion concentration on achieving maximum cooling. In addition, a normal silica glass without network modifiers was prepared to study the effect of glass composition on optical properties as well as cooling characteristics. The resulting samples had an 1.5 mm diameter core in the centre and undoped (no Yb doping) silica glass cladding region of 0.3 mm. These were cut and polished into 10 mm long, 2.1 mm square cross-section samples. The fiber preforms along with the ytterbium ion, Al and Y concentrations (in atomic percent), the mean fluorescence wavelength (MFW) and quantum yield at RT while exciting with 1029 nm laser with 5 W pump power are listed in Table 6.1. The propagation losses of glasses were measured to be 10 ± 3 dB/km.

Table 6.1: The Yb ion concentration of investigated glasses along with the terminology used in the text, Al & Y concentration (in atomic percent), the mean fluorescence wavelength (MFW) & quantum yield at RT while exciting with 1029 nm laser with 5 W pump power.

Yb concentration (ions/m ³)	Terminology	Al concentration (atomic percent)	Y concentration (atomic percent)	MFW (λ_f) (nm) (± 0.5 nm)	Quantum yield (η_{ext}) at 1029 nm ($\pm 0.5\%$)
1.3×10^{26}	GAYY-1	8.5 (± 0.5)%	4.9% (± 0.2)%	1004.60	98.7
2.4×10^{26}	GAYY-2	8.2 (± 0.4)%	4.5% (± 0.3)%	1006.06	99.1
4.0×10^{26}	GAYY-3	7.6 (± 0.3)%	4.6% (± 0.2)%	1008.10	99.4
2.4×10^{26}	MCVD SiO ₂ glass	0	0	1008.60	87.0

Electron probe microanalyses (EPMA) were used to assess the average dopant levels within the core region. An example of EPMA is given in Figure 6.1(a) for the GAYY-2 sample. The highest Yb concentration obtained was of 4×10^{26} ions/m³ at the center of the preform core (GAYY-3) which is the largest value reported in the literature for laser cooling. Figure 6.1(b) & (c) depict the SEM images showing the phase separated Yb-Y-rich regions with an average size of 29 nm. If no external variation (change of tube diameter, precursors with different hydration levels etc.) is applied to process parameters influencing the soot porosity, the final concentration of elements remain stable. We control these parameters using elemental analysis via electron probe microscopy, on slices of preform and refractive index profile. The elemental profiles of the GAYY-2 glass at the bottom and top of the silica tube along with the SEM images are provided in the appendix (Figure 7). We observed longitudinal in-homogeneities in every preform, caused by our vertical method of solution doping. The bottom of the tube, where the solution enters usually present 10 to 15 % higher concentration of elements, local concentration also present disturbance. On the other side, the top two-third of the tube (from 250 to 600 mm) present higher quality material, with well-dispersed concentrations. For this reason, the samples we use for fiber drawing and bulk preparation are extracted from the top part of the preform, where the homogeneity is better.

A very interesting feature of this particular glass is the phase separation. The majority of commercially available Yb fibres are co-doped with Al because it is an extremely important RE ion solubilizer in While phase [207, 220, 221] separation is usually considered as a detrimental to luminescence, the GAYY glasses exhibit the opposite effect. The excess addition of yttrium creates the phase separation, dissolving ytterbium ions in well-defined regions. The incorporation of alumina plays a promoting role in decreasing the magnitude of the phase separated droplets to tens of nanometers, greatly reducing Rayleigh scattering effects. Transmission electron microscopy (TEM) was used to detect phase separation in fibre preforms at the nanometer scale. Droplet particles enriched in Yb³⁺, Y³⁺, and Al³⁺ were found in the investigated samples in a main silicate phase background. In GAYY glasses, the formation of Yb³⁺-enriched droplets of 29 nm diameter in size was evidenced. As the distance between Yb ions grows, Y and Yb ions can be easily substituted in yttria-alumina silica glass because of their similar ionic radii (104 pm for Y³⁺ and 100.8 pm for Yb³⁺). Similar to the formation of Er-O-Y-O-Er as reported previously [222], Yb-O-Y-O-Yb forms in such glasses which avoids the daunting challenges associated with the Yb

clustering. As a result, the development of oxygen defect centres related to Yb ceases. By mixing fully oxidised active rare-earth ions with another non-active rare earth, low phonon solvation shell around the Yb^{3+} ions are formed which shield rare-earth from the detrimental impact of the high phonon energy silica and increases the luminescence efficiency.

All of the preforms were highly transparent ($> 90\%$ in the near infrared region). The Yb^{3+} ion possesses a broad absorption band (Figure 6.1(d)) varying from 850 to 1050 nm, related to the ground ($2F_{7/2}$) and excited ($2F_{5/2}$) Stark sublevel electronic transitions. As the Yb ion concentration in the GAYY glasses increases, the absorption coefficient at 976 nm also increases. The transmittance data of the glasses from VUV to IR region is provided in the appendix (Figure 8).

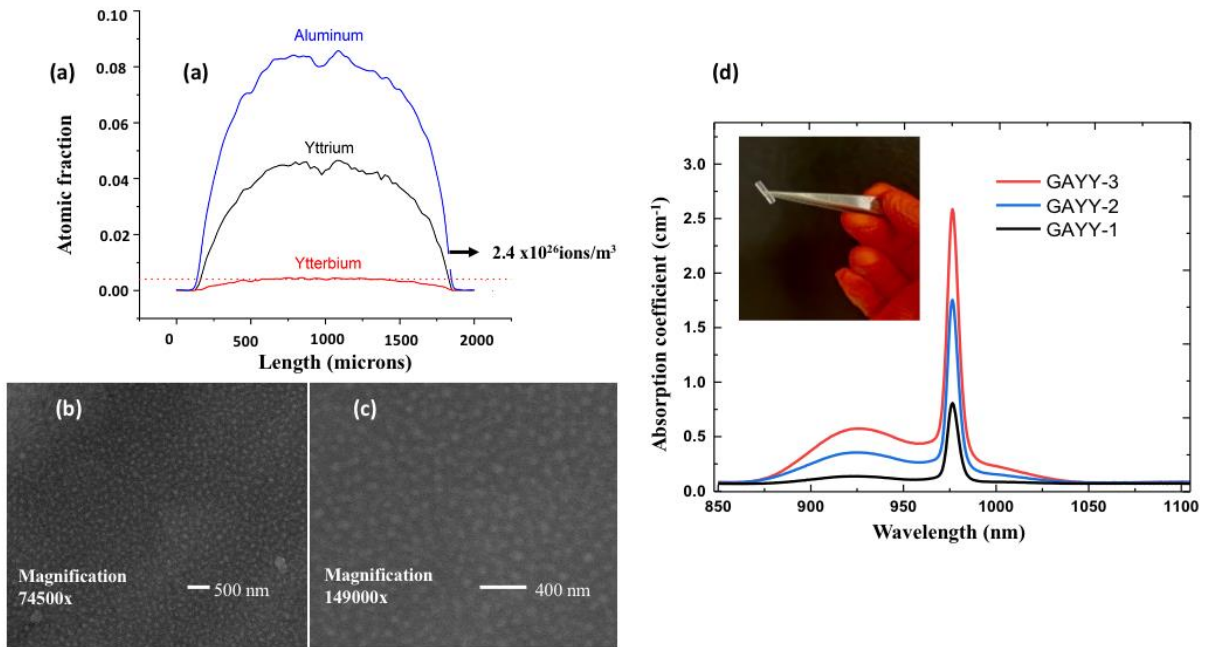


Figure 6.1: (a) EPMA analysis of GAYY-2, (b, c) SEM Image of phase separated preform (GAYY-2) at different magnifications, using backscattering electron mode (d) The absorption spectra of all GAYY glasses. The inset shows the highly transparent GAYY-2 preform.

6.2.1 Spectral properties of GAYY glasses

Excellent optical quality of the GAYY glasses were attested by photoluminescence measurements. The characteristic emission spectra between 900 and 1100 nm for the transition from the $2F_{5/2}$ manifold to the $2F_{7/2}$ ground state can be observed in all of the Yb-doped glasses. while pumping with 1029 nm [198] (Figure 6.2(a)). The PL intensity in GAYY glasses is higher compared to the MCVD SiO₂ glass under the same illumination and detection conditions. Even if the Yb ion concentration in MCVD SiO₂ glass and GAYY-2 were almost the same, PL intensity is lower in MCVD SiO₂ glass due to the concentration quenching effect. This is due to the Yb-O-Yb interaction at high doping levels. In GAYY glasses this interaction is lowered due to the advantage of network modifiers such as Y and Al. Due to the lower phonon energies in GAYY glasses, the rate of multi-phonon relaxations is reduced, resulting in a higher PL emission intensity. The presence of high concentrations of yttrium (III) heavy ions in phase separated droplets leads to a decrease in the maximum phonon energy of silicate oxide glass, which is normally 1100 cm⁻¹. As per the Miyakawa and Dexter theory [199], the rate of multi-phonon decay is exponentially dependent on the difference in energy gap between the energy levels and the maximum phonon energy of the material [62]. The mean fluorescence wavelength (MFW) of the glass system is determined mostly from the composition and temperature of the host materials. The MFW, λ_f is found by the following equation using the measured fluorescence spectrum while exciting at 1029 nm [49, 205, 223].

$$\lambda_f = \frac{\int \lambda I_f(\lambda) d\lambda}{\int I_f(\lambda) d\lambda} \quad (6.1)$$

where $I_f(\lambda)$ is the spectral density, measured for our samples by exciting them at 1029 nm. The MFW in GAYY glasses changes from 1004.6 nm to 1008.1 nm depending on the Yb concentration (Table 6.1). The optical cooling can occur only when λ_p is greater than λ_f . The laser cooling efficiency η_c can be briefly expressed as

$$\eta_c = \frac{\lambda_p}{\lambda_f} p - 1 \quad (6.2)$$

where $p(\lambda) \lesssim 1$ denotes the probability of converting the absorbed pump photon to an emitting fluorescence photon. According to Eq. (6.2), the larger the energy difference between the pump

and mean fluorescence photons, the higher will be the cooling efficiency. However, due to the reduction in the resonant absorption coefficient at longer wavelengths, increasing the pump wavelength gradually creates a practical limit on pump detuning. Moreover, at higher detuning where resonant absorption is decreased, the effect of the background absorption (contained in the definition of $p(\lambda)$) begins to dominate, even negating cooling for sufficiently large detuning.

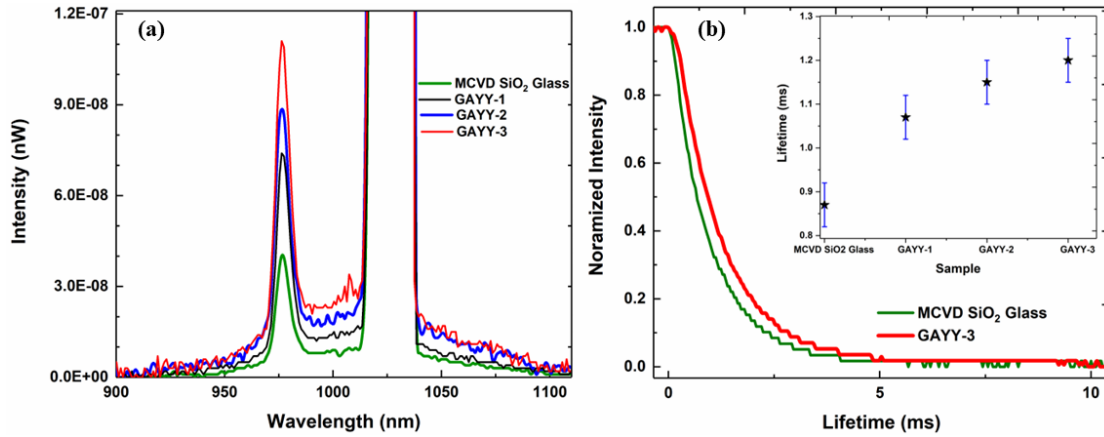


Figure 6.2 (a): The anti-Stokes emission in all the GAYY glasses as well as MCVD SiO₂ glass while exciting with 1029 nm laser with 5 W pump power, (b) The lifetime decay curves of MCVD SiO₂ glass and GAYY-3 at an excitation wavelength of 920 nm. The inset shows the lifetime values of all glasses.

Furthermore, concentration quenching was evident in the quantum yield as well as lifetime measurements in the case of MCVD SiO₂ glass. The quantum yield of all glasses obtained through integrating sphere method [46, 140, 192] while exciting with 1029 nm laser are provided in Table 6.1. A maximum quantum yield of ~99.4% was achieved for GAYY-3 glass. The quantum yield values of the GAYY glasses were higher than that of the MCVD SiO₂ glass as expected provided by the advantage of low phonon energy environment and high solubility of RE ions which eliminates the concentration quenching effect.

Taking this into consideration, further investigation of the optical properties was achieved for the MCVD SiO₂ glass and GAYY glasses by examining the lifetime decay curves at an excitation wavelength of 920 nm. Figure 6.2(b) shows the lifetime decay curves of MCVD SiO₂ glass and GAYY-3. The inset in Figure 6.2(b) shows the lifetime of Yb³⁺: 5/2 level in all glasses. The presented curves demonstrate a single exponential decay for Yb³⁺ ions. During the measurement

of the intrinsic decay time of the $2F_{5/2}$ level, care was taken to minimise the impact of various reabsorption processes. In contrast to the GAYY glasses the MCVD SiO_2 glass without phase separation showed a shortened luminescence decay time of 0.87 ms due to concentration quenching [224]. Since the Yb^{3+} are in a low phonon energy pool of yttrium rich domains the lifetimes of all GAYY glasses are higher than that of the MCVD SiO_2 glass. Also, the lifetime was observed to be increase from 1.04 ms to 1.20 ms with the increment in ytterbium ion concentration provided by the prominent advantage of networking modifiers (Al and Y) [225]. This enhancement in lifetime would also highlight the lower probability of non-radiative energy transfer and therefore higher quantum efficiency. The lifetime is expected to be decreased in the quenching regime [226].

Another finding that further supports the above description is the presence of higher cooperative emission intensity in the MCVD SiO_2 glass compared to the GAYY glasses. Cooperative luminescence at a wavelength of 500 nm was used to probe Yb^{3+} clustering in the MCVD SiO_2 glass. It is a viable technique to indicate the formation of Yb^{3+} pairs and clusters in glasses. When two Yb^{3+} ions are simultaneously de-excited, cooperative luminescence occurs, which causes the emission of one photon with a shorter wavelength in the visible spectrum. Figure 9 in appendix shows the emission spectra of the MCVD SiO_2 glass and GAYY-3 with 400 mW of absorbed pump power at 980 nm wavelength. The cooperative emission intensity decreases in GAYY-3 due to the higher RE ion solubility ascribed to the presence of Al and Y.

The enhanced lifetime and quantum yield in GAYY glasses is expected to enable their use in a wide range of optical devices and to provide significant insights in the design of glassy materials for radiation balanced lasers and fibre amplifiers. Apart from that, the GAYY glasses possessed higher purity which make it highly promising for laser cooling applications. The use of MCVD process allows us to achieve higher purity glasses which is essential to observe cooling. Since one of the primary sources of loss that contributes to heating is background absorption, worldwide efforts have been concentrated on different purification techniques to be used to fabricate laser cooling materials [71, 72]. Hopefully, the characteristics of MCVD make it possible to reduce the absorption of impurities in our GAYY glasses. The background absorption coefficient of 10 dB/km determined using calorimetric technique [7, 80] shows that the investigated glasses are highly promising for cooling. We deepened the insights into background absorption using elemental analysis done through by inductively coupled plasma (ICP) measurements. The amount of

impurities such as iron or rare earths measured by ICP mass spectrometry showed less than 200 ppb of both Fe/Cu (major impurities which are detrimental for cooling) [227].

6.2.2 Laser induced cooling in GAYY glasses

To investigate the potential of fabricated glasses for laser cooling we performed the temperature measurements on all glasses at an excitation wavelength of 1029 nm with different pump power varying from 0.5 W to 6.5 W. A 1029 nm laser was the only high-power pump source (6.5 W) that was accessible in our lab. Since this pump wavelength is higher than that of the mean fluorescence wavelengths ($\lesssim 1008.6$ nm), a net heat extraction was obtained in all GAYY glasses. The temperature dynamics of all the GAYY glasses while exciting with a 6.5 W 1029 nm laser is shown in Figure 6.3. The pump laser is kept off for ~ 1 minute, and then it is turned on for ~ 10 minutes. The GAYY glass with ytterbium ion concentration of 4.0×10^{26} ions/m³ showed a -0.1 K cooling using 0.5 W of pump power and reached to a maximum of -0.9 K from RT using 6.5 W at atmospheric pressure. A maximum temperature reduction of -0.5 and -0.8 K from RT was achieved in the case of GAYY-1 and GAYY-2 glasses respectively. Since only the core of the preform is doped with ytterbium the heat extraction only tends to happen there, however the entire glass cools evenly in 1 minute (Figure 6.3).

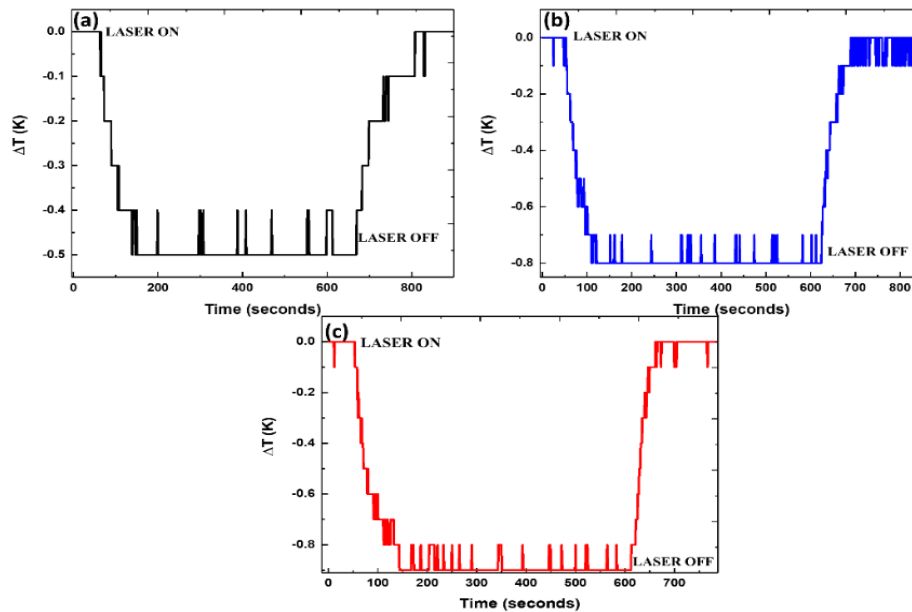


Figure 6.3: The temperature dynamics of (a) GAYY-1, (b) GAYY-2, and (c) GAYY-3 and while pumping with 6.5 W 1029 nm laser.

The thermal coupling time constant of the GAYY-3 was estimated to be $\tau_t = 31$ s. The overall heat transfer coefficient h_{eff} was approximated as $h_{eff} = h_{cv} + 4\sigma_B\epsilon T_r^3$ in which h_{cv} is the convective heat transfer coefficient, ϵ is the hemispherical emissivity of the sample, σ_B is the Stefan–Boltzmann constant and T_r is the ambient room temperature. According to lumped-capacitance model [7, 62] the $h_{eff} = C/(\tau_t A_{surf}) = 23.39 \text{ Wm}^{-2}\text{K}^{-1}$, where C is the heat capacity of the preform. Using the model described in Ref [7] and [62] the heat load $P_{load} = -A_{surf}h_{eff}\Delta T$ was found to be 1.4 mW where A_{surf} is the surface area of the preform and $\Delta T = T_r - T_s$. The thermal parameters of the GAYY-3 glass is summarized in Table 6.2.

The steady state temperature measured using FBG contact technique was further supported by the FLIR thermal camera images. The resolution of the temperature change measured using the FBG method as well as using the FLIR is 0.1 K. The thermal camera images of the GAYY-3 while exposed to 1029 nm laser is shown in appendix (Figure 10). The thermal camera image darkens after being exposed to the 1029 nm wavelength laser which can be easily observed by the unaided human eye (see around the crosshair in each picture). There is a 0.2 K discrepancy between the measurements using FBG and thermal camera due to the poor resolution as well as lesser emissivity options available in the thermal camera [49]. However, they are widely utilized in optical cooling experiments due to the ease of handling [1, 205].

We performed a comparative study between the glasses having different cladding diameter in order to evaluate the effect of heat load using GAYY-2 glass. During the initial laser cooling experiments, we used samples that were surrounded by an undoped silica glass cladding region of 0.5 mm, which was a significant thermal load. Despite this substantial thermal loading, a cooling of -0.5 K from RT was achieved with a pump power of 6.5W. Later, in order to lower the thermal load and enhance cooling, we removed the majority of its undoped cladding region, and it showed a -0.8 K temperature difference from RT using the same pump conditions. On the contrary, the MCVD SiO₂ glass sample heated to ~5 K using a pump power of only 1 W. This is the most remarkable outcome of our study, namely, that the GAYY glass demonstrated such a dramatic difference compared to the normal preform while pumping with 1029 nm laser. The heating is associated with the concentration quenching effect. The thermal camera images of the MCVD

SiO₂ glass while exposed to 1029 nm laser is shown in Figure 6.4(a). The temperature rises to 301 K from 296 K. The temperature dynamics is depicted in Figure 6.4(b). Here the amount of absorbed pump power before the Yb absorption reaches saturation is greatly limited. In this case, the additional pump power is absorbed mainly by the background impurities and efficiently converts pump power to heat [61]. Therefore, even if the purity of the MCVD SiO₂ glass without phase separation is high, cooling would be hindered due to quenching.

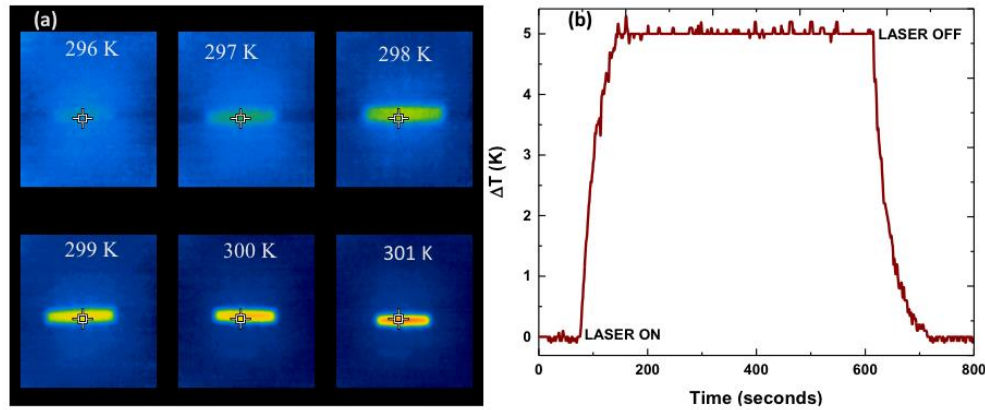


Figure 6.4: (a) The temperature evolution of MCVD SiO₂ glass while it is exposed to 1029 nm 1 W laser obtained through FLIR thermal camera, (b) ΔT vs. time curve of MCVD SiO₂ glass while pumping with 1 W at 1029 nm measured using FBG direct contact technique.

Table 6.2: The thermal parameters of GAYY-3 glass.

Parameter	Value	Units
Mass density ρ	2750	kg.m ⁻³
Specific heat c_h	680	J.kg ⁻¹ .K ⁻¹
Heat capacity C	0.049	J.K ⁻¹
Surface area A_{surf}	7.3×10^{-5}	m ²
Thermal coupling time constant τ_h	31	s

6.2.4 Theoretical model and numerical results

The full potential of these findings was determined by a simulation, since we were unable to increase the pump power being limited by our available laser. The cooling efficiency, defined in equation (2) can be expanded as follows

$$\eta_c = P_{cool}/P_{abs} = \frac{\lambda_p}{\lambda_f} \eta_{abs} \eta_{ext} - 1, \quad (6.3)$$

where the absorption efficiency can be expressed as

$$\eta_{abs} = \frac{\alpha_r}{\alpha_r + \alpha_b}. \quad (6.4)$$

Also α_r is the resonant absorption coefficient and α_b is the background absorption coefficient. The quantum efficiency can be approximated as [69, 118, 121, 228].

$$\eta_{ext} \cong \frac{\gamma_{rad}}{\gamma_{rad} + \gamma_q} = \left[1 + \frac{9}{2\pi} \left(\frac{N}{N_c} \right)^2 \right]^{-1}, \quad (6.5)$$

where γ_{rad} and γ_q are radiative and quenching rate respectively. N is the density of ions and N_c is the critical density of ions due to the quenching. Rewriting Eq. (6.5), the critical concentration, N_c is as follows

$$N_c = N \sqrt{\frac{\frac{9}{2\pi} \eta_{ext}}{(1 - \eta_{ext})}}. \quad (6.6)$$

We calculated the critical concentration corresponding to the concentration of 4.0×10^{26} ions/m³ for GAAY-3 and found it to be 6.16×10^{27} ions/m³ which is ~5 times larger than the highest value reported in literature (i.e., 1.2×10^{27} ions/m³) [218].

Next, we determine the temperature drop for each pump power at 1029 nm excitation using a numerical calculation. Refs. [118, 229] and introduced and established a two-level model for absorption and emission processes between the $\text{Yb}^{3+} 2F_{7/2}$ ground-state manifold and the $2F_{5/2}$

excited-state manifold. The cooling power of the preform can be calculated using the following equation [229].

$$P_{cool} = \frac{a_{eff} \sigma_a(T_s) N I_s(T_s) (\lambda/\lambda_{f*}(T_s)-1)}{1+\sigma_e(T_s)/\sigma_a(T_s)+a_{eff} I_s(T_s)/P} \quad (6.7)$$

where $I_s(T_s) = hc\gamma_{rad}/\lambda_p\sigma_a(T_s)$ is the saturation intensity, $\lambda_{f*}(T_s)$ is the effective mean fluorescence wavelength, and $\sigma_a(T_s)$ and $\sigma_e(T_s)$ are the absorption and the emission cross sections, respectively. P is the pump power and a_{eff} is the effective pump mode area. The sum of radiative and convective heat load on the sample is given by

$$P_{load} = A_{surf}\epsilon\sigma_B(T_r^4 - T_s^4) + A_{surf}h_{cv}(T_r - T_s) \quad (6.8)$$

At thermal equilibrium, $P_{cool} = P_{load}$ allows the determination of temperature drop for each pump power for a given pump wavelength using a numerical calculation. Figure 6.5(a) shows temperature change curves as a function of the pump power in GAYY glasses in air considering $h_{cv} = 18.4 \text{ W/m}^2\text{K}$ and the background absorption coefficient of 10 dB/km. Maximum temperature drops of -0.75, -1.40 and -1.58 K are expected at 26.6, 35.1 and 36.1 W for GAYY-1, GAYY-2 and GAYY-3, respectively. Further increase in the pump power leads to heating in the sample due the pump absorption by background impurities. The experimentally obtained values illustrated by markers on each curves, are in excellent agreement with the simulation.

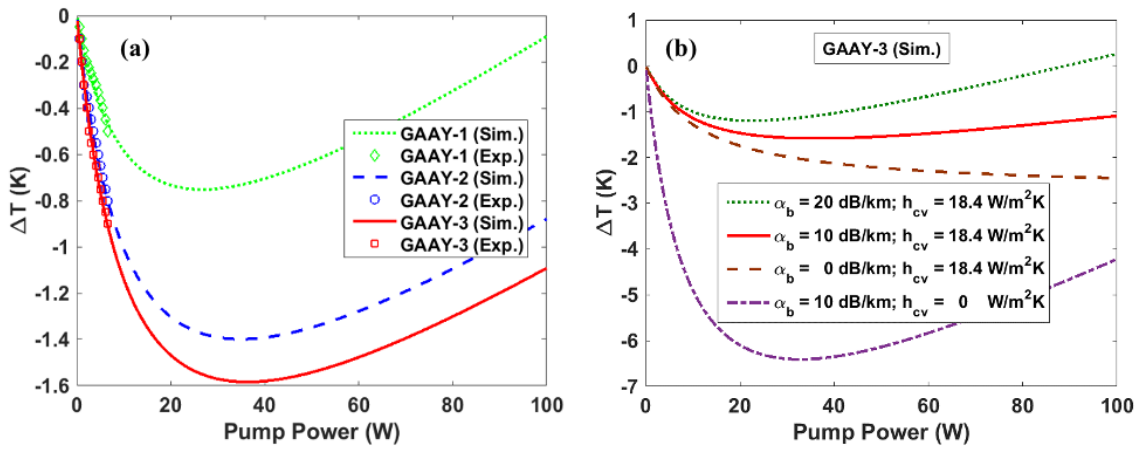


Figure 6.5: (a) The temperature change as a function of the pump power in GAYY glasses in air. The markers show the experimental results for the pump powers up to 6.5 W, (b) The effect of background absorption and convective heat load in obtaining temperature reduction with a change in pump power in GAYY-3 glass.

For practical applications it is essential to demonstrate ASF cooling in atmospheric pressure since it can be useful to make self-cooled lasers and amplifiers. For our sample having a convective heat transfer coefficient of $18.4 \text{ W/m}^2\text{K}$, the maximum obtainable temperature reduction is also limited by the background absorption. For a given pump power, higher purity results in more temperature reduction as depicted in Figure 6.5(b). Due to the convective heat load while performing optical cooling experiments at atmospheric pressure, most of the experiments are performed in vacuum [90, 180, 205, 220]. Figure 6.5(b) shows that a maximum temperature reduction of -6.4 K for a 32.6 W pump power is predicted for GAYY-3 if we conduct the experiments in vacuum, i.e., $h_{cv}=0$. A -3.95 K drop in temperature in vacuum for a 6.5 W pump power is also predicted. However, at atmospheric pressure, i.e., $h_{cv} = 18.4 \text{ W/m}^2\text{K}$, for the GAYY-3 having $\alpha_b = 10 \text{ dB/km}$, the expected temperature drop is $\sim 1.58 \text{ K}$ for a pump power of 32.6 W . The temperature drop is even smaller i.e., 1.13 K , if α_b is 20 dB/km . It is clear that the background absorption plays a critical role in achieving maximum temperature reduction.

We have thus realized optical cooling in highly Yb doped silica glasses that will find broad applications in solid-state laser cooling, radiation balanced lasers, amplifiers etc. GAYY glass is unique from other Yb doped silica glasses explored in the past for laser cooling applications due to its higher quantum efficiency and longer lifetime due to its controlled phase separation effect which hold Yb^{3+} ions in yttrium-rich domains, compared to regular silica glass. Because of the increased Y_2O_3 concentration, these areas showed not only significantly higher rare-earth solubility but also much smaller phonon energy in comparison with a pure silica matrix. We have demonstrated the ability to regulate the local environment of Yb^{3+} ions by dissolving them in domains containing a high concentration of yttrium, which benefit from the immiscibility between rare earth elements and silica. By adding Al_2O_3 , the scale of this phase separation was reduced to nanometer-sized particles, resulting in significantly diminishing Rayleigh diffusion effects in the Near Infra-Red region. This approach is distinctly different to the more traditional approach, in which phase separation is considered a nuisance and is avoided.

Further optimization efforts will focus on the use of several excitation wavelengths longer than that of 1029 nm, increasing the pump power, optimizing the sample geometry etc. We have fabricated optical fibers out of the GAYY glasses and temperature measurements are in progress. Longer term research may additionally involve the exploration of optical fibres made out of GAYY glasses for radiation balanced fiber lasers. Since the cooling GAYY glass preform is doped with Ge, the glass is photosensitive enough to make reflective gratings in order to fabricate RBLs. Also, the proposed approach for achieving high emission efficiency will be extended to other rare earth materials with different network modifiers to achieve cooling.

6.3 Conclusions

In this work, we show laser cooling in Yb-doped 100% oxide glasses with different ytterbium concentration. A maximum temperature reduction of -0.9 K from room temperature at atmospheric pressure was obtained experimentally using only 6.5 W of 1029 nm pump radiation. A maximum temperature reduction of -6.4 K for a 32.6 W pump power is predicted in vacuum. The temperature change versus pump power was also presented using a numerical simulation that well agrees with the experimental ones. The results also demonstrated that, despite its high phonon energy, silica can tolerate unexpectedly high Yb concentrations without compromising its optical properties as demonstrated by cooling a glass with 4×10^{26} ions/m³. We have reported cooling in the highest concentration of Yb ions (a ~2.5x improvement) with little or no degradation in lifetime or quantum efficiency, compared to the best results previously reported in the literature. This incredible achievement was made possible by tailoring the material to substantially lower non-radiative relaxation sources, such as concentration quenching and background absorptive loss. Co-doping the glass with Al and Y, resulted in a record-breaking critical concentration, N_c that is ~5 times higher than the previous reports. Combining the optical absorption, photoluminescence, and fluorescence decay data, the effect of ytterbium ion concentration on the spectroscopic properties and cooling properties of glasses were studied systematically. The cooperative emission intensity decreases in GAYY glass compared to MCVD SiO₂ glass which indicates a reduction of Yb³⁺ pairs due to the presence of network modifiers. Our findings indicate that this novel glass is a highly suitable candidate for radiation-balanced lasers and amplifiers. It also opens up some intriguing possibilities for further research into more glass compositions with various RE ions and network modifiers suitable for laser cooling applications.

Materials and characterization methods

The glasses used in this work were fabricated using modified chemical vapour deposition (MCVD) technique [230, 231]. The detailed procedure is provided in appendix (appendix 2).

The microstructural analysis of the preform was performed using scanning electron microscopy (SEM) with an FEI Quanta 3D FEG, using 10 kV voltage excitation, backscattering electrons. To prevent charge accumulation on the sample, an 8 nm thick Pt/Rh layer was applied to the polished preform cores. The elemental analysis was carried out using electron probe microscopy on a Castaing CAMECA-SX100. Absorption coefficient spectra were obtained from transmission measurements on slices of preforms. Parallel slices of preform ranging from 1.5 to 2 mm in thickness are taken and optically polished. Samples are then processed using a Carry 5000 UV-Vis spectrometer for the 200 – 1500 nm range, and on a Perkin Elmer FTIR spectrometer from 1500 to 5000 nm. Also, the photoluminescence (PL) emission spectra as well as the quantum yield of the samples were measured using a 1029 nm laser (Pharos). A Thorlabs IS200-4 integrating sphere was connected to an Ando AQ6317B optical spectrum analyzer (OSA) via a multimode optical fiber in order to gather the emitted light [122, 140].

Fluorescence excitation and time-decay characteristics associated to the $\text{Yb}^{3+}: 2\text{F}_{5/2}$ level were measured using a 920 nm pump from a Ti: Sapphire laser. The luminescence lifetime (τ) values were acquired using a fast oscilloscope (Tektronix). The signal was recorded using a photodiode (Thorlabs SM05PD1B) and then amplified by a benchtop trans-impedance amplifier. The elimination of the pump wavelength was achieved by using an edge filter, while the modulation of the external signal was done by applying a Thorlabs MC100A chopper with two slot blades operating at a frequency of 20.0 Hz. The background absorptive loss measurements were made using fiber Bragg grating (FBG) direct contact technique with an IPG ELR-70-1550-LP 1550 nm ytterbium-erbium fiber laser at 5 W, as a source of optical power [80].

Laser cooling measurements were done by evaluating the steady-state temperature change of the glasses while exciting with a 1029 nm laser (Pharos) with varying pump powers ranging from 0.5 to 6.5 W. The maximum peak power density of $1.708\text{e}+8 \text{ W/cm}^2$ used in our measurements showed no optical damage. The samples were supported by a pair of silica optical fibers, which were adhered to a stainless-steel holder located inside an aluminum chamber to minimize the heat

load on the samples. A schematic of the experiment is depicted in Figure 6.6. To monitor the temperature, the fiber Bragg grating (FBG) direct contact method [7, 12, 80] was employed. The shift in central wavelength of the FBG is directly proportional to the temperature change of the sample. A thermal camera (FLIR) was also employed to measure the temperature change upon laser irradiation at 1029 nm.

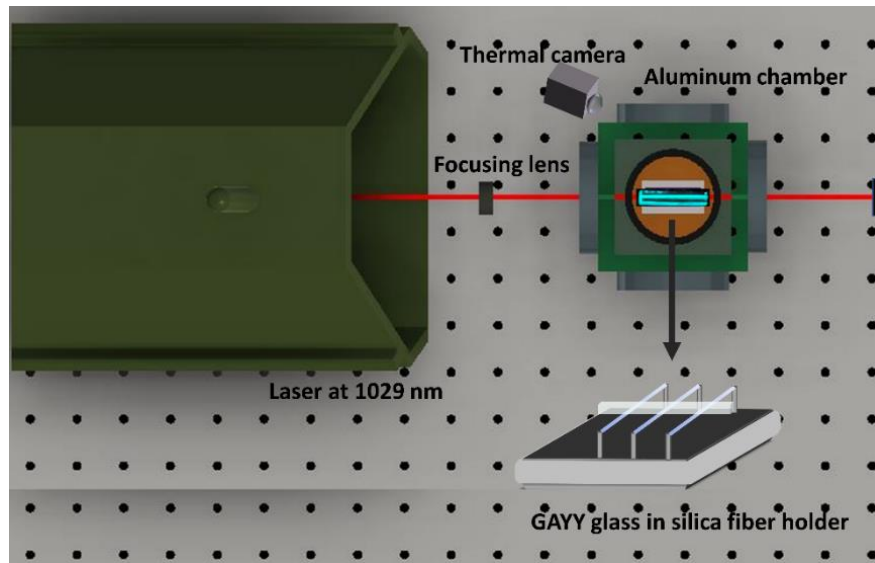


Figure 6.6: The experimental setup used for temperature measurements in laser cooling experiment. The zoomed-in circle shows GAYY glass placed on the silica optical fibres.

Acknowledgements

The authors thank Wagner Correr for the SEM imaging, Steeve Morency and Steve Lizotte for cutting and polishing of silica preforms.

CHAPTER 7 ARTICLE 4: ANTI-STOKES COOLING IN HIGHLY YTTERBIUM DOPED PHASE SEPARATED ALUMINIUM-YTTRIUM OXIDE GLASS BY 4 K

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Published in: Optical Materials, September 17, 2023

Silica glass is a strong candidate in the development of radiation balanced fiber lasers and amplifiers due to its properties such as high stability, high mechanical robustness and chemical durability, thermal resistance, high purity and so on. However, low rare-earth ion solubility lead to inter-ionic energy transfers processes which cause multi-phonon relaxation through a non-radiative decay process and hinder it from being used for aforementioned applications as well as for optical cooling. In the present work, we report cooling to a record low temperature of -4 K from room temperature at atmospheric pressure in a novel silica based highly Yb doped phase separated oxide glass (named as PS: GAYY glass - aluminium: yttrium: ytterbium) using 20 W of 1037 nm pump wavelength. We further theoretically show a global minimum achievable temperature of ~165 K in our glass. Here, the basic limitation for laser induced cooling in silica glass associated with the existence of clustering of rare earth ions is significantly mitigated. This was achieved by the addition of suitable co-dopants such as aluminum and yttrium which modified the local rare-earth ion environment to avoid clustering as well as reducing the phonon energy. The fabricated glass using modified chemical vapor deposition process in combination with a solution doping technique achieved a maximum doping concentration of 5.57×10^{26} ions/m³ and exhibits better performance than other silica-based host glasses in terms of both optical properties and laser cooling characteristics. We believe PS-GAYY glasses may open new avenues in the field of solid-state laser cooling, promising exciting and broad applications in radiation balanced lasers and amplifiers.

7.1 Introduction

Laser induced cooling relying on the principle of anti-Stokes fluorescence was firstly proposed by Pringsheim in 1929 [2]. In this process, a lower pump energy laser is used to excite the material and it emits higher energy photons by extracting thermal energy through phonon annihilation [204]. Epstein *et al.* first demonstrated this process in Yb-doped ZBLAN in 1995 [1]. Later the pioneering studies on solid state materials such as crystals, semiconductors, and glasses have stimulated a surge of interests to use these materials for optical cryocoolers, radiation balanced lasers, amplifiers, in satellite instrumentation, sensors etc. [7, 27, 28, 69, 90, 102, 104, 114, 118, 180, 232-235]. The optical refrigeration field is currently dominated by fluoride single-crystals since their crystalline environment coupled with fluoride low-phonon energy host allow efficient anti-Stokes fluorescence [7, 27, 28, 90]. The utilization of low phonon energy materials is essential in order to prevent phonon-assisted non-radiative relaxation from interfering with the cooling process. However, this only becomes a concern when the bandgap is not large enough in comparison to the phonon energy, as a larger bandgap decreases the probability of non-radiative transition. Previously, cooling was predominantly limited to highly purified crystals with low phonon energies that were doped with Yb. Yb, in particular, was favored for its ability to shield the cooling-related 4f electrons from lattice vibrations, as well as its substantial energy gap between the ground state and first excited state. This gap decreases the probability of phonon-assisted non-radiative transition, making Yb an ideal candidate for laser cooling experiments.

Although fluoride host materials have been mainly utilized for cooling of thermal loads, numerous applications necessitate a wider variety of host materials, including oxide glasses. The high cost and limited geometry of crystals create a demand for more flexible materials to diversify designs around their applications. In this manner, rare-earth (RE) doped silica glass are of tremendous interest for radiation balanced lasers and amplifiers, given their singular structural and optical characteristics spanning high stability, high mechanical and chemical durability, thermal resistance, mouldability, high purity etc [235].

The demonstration of laser cooling in silica optical fiber in 2020 [69] triggered intensive investigations into the advancement of radiation balanced lasers (RBLs), particularly in fiber-based RBLs [235] which are optically cooled by anti-Stokes fluorescence (ASF). This was driven by the potential for RBLs to facilitate the advancement of fiber lasers with high coherence and stability, with the potential of reduced thermal management and higher power extraction. In addition, silica glass has enabled many applications utilizing the optical fiber geometry in the

optical telecommunication field, photomasks and lenses for microlithography with ultraviolet light etc [236]. Despite its widespread implementation, their practical utilization for laser cooling applications have been hindered by low solubility of RE ions in silica and the high phonon energy of the material. To circumvent such limitations, attempts have been made to engineer the material, for instance, by adding network modifiers such as Al, Y, Ce, F etc. [69, 180, 218, 232, 233].

The modified chemical vapor deposition (MCVD) fabrication in combination with solution doping was chosen as the best method for producing exceptionally pure glasses with higher Yb density, which have background absorptive losses of less than 10 dB/km [230, 231]. Capitalizing on this facile fabrication method, we have recently shown that ytterbium doped GAYY glasses (aluminum : yttrium : ytterbium system) possess enhanced lifetime values than that of the alumino-silicate glass phase, and near unity quantum efficiency making them a suitable host for laser cooling applications [14, 234]. In the present work, we report laser cooling of ytterbium doped silica glass by 4 K starting at room temperature (RT). This is more than a four-fold improvement of our previous work which demonstrated cooling by a 0.9 K from RT in an Yb doped silica GAYY glass with 6.5 W of 1029 nm laser [14]. Fine tuning in the incorporation of aluminum (Al) led to a controlled phase separation effect, providing confinement of Yb^{3+} ions in yttrium-rich domains [220]. These regions not only showed much higher RE solubility, but also presented lower phonon energy compared to a pure silica matrix, brought by the high concentration of Y_2O_3 . This helps in improved quantum efficiency and enhanced lifetime compared with the conventional silica glass and thus makes the GAYY glass to stand out from other Yb doped silica glasses investigated before for laser cooling applications.

So far, the largest reported temperature reduction from RT is -40 K in an Yb doped silica glass in vacuum utilising 50 W of 1030 nm laser [233]. In previous reports, the maximum obtained temperature drop of the laser-cooled Yb-doped silica sample at atmospheric pressure using a 20 W pump was less than ~3.6 K [218]. This was achieved with an Yb ion density of 6.5×10^{25} ions/ m^3 . Here, we focus on a highly Yb doped sample (5.57×10^{26} ions/ m^3 at the center of the core), which is the highest value of Yb ion concentration reported in the literature, which exhibited high external quantum efficiency ($\eta_{\text{ext}} = 0.99$) and better cooling performance (-4.0 K temperature difference from RT at atmospheric pressure) compared to others. To enhance cooling, it is vital to optimize the excitation wavelength and pump power. In our study we give special emphasis on the aforementioned concerns, both theoretically and experimentally.

The wide tunability of our fiber laser helped to demonstrate cooling in Yb doped silica glass using several excitation wavelengths ranging from 1030-1080 nm and it is for the first time that cooling is experimentally demonstrated for excitation wavelengths larger than that of 1070 nm in Yb doped silica glass. We also predict the temperature changes with different excitation wavelengths in atmospheric pressure as well as in vacuum, by the numerical solution of the governing equations. A global MAT of ~ 165 K is estimated in PS-GAYY glass which is the lowest value predicted for the phase separated non-crystalline glass. A detailed study based on how the compositional variations can affect the cooling properties are also presented. In addition to PS-GAYY glasses we fabricated and investigated another type of Yb-doped silica glass based on lanthano-alumino-silicate composition (PS-GALY glass) to follow-up the research. The incorporation network modifiers such as La in the core of silica-based fibers for laser cooling application is in an early stage and there is a need of further studies, both from material science point of view, as well as their optical properties. Since the photoluminescence properties of Yb ions are known to be strongly dependent on the phonon energy of the host matrix, a low phonon energy of La_2O_3 (around 400 cm^{-1}) is expected to be a good choice for the fabrication of glass for laser cooling applications. In short, this article provides an overview of the wavelength dependent temperature change in PS-GAYY and PS-GALY glasses along with the estimation of the global MAT for optical refrigeration applications.

7.2 Experimental

7.2.1 Materials

The glasses were fabricated using the MCVD process [230, 231]. An Heraeus F300 grade silica tube was placed within an MCVD system. Initial preparation of drying, welding and alignment of the tube were realized beforehand. On the inner walls of the tube, SiO_2 soots deposited by flowing a mixture of SiCl_4 / He / O_2 , heated at 1350°C with a moving H_2/O_2 flame burner. The aforementioned process was then repeated for deposition of three layers. A solution containing high-purity chloride salts of the doping elements was prepared ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ / $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ / $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ – 6N purity Pure Analytical). Once full dilution is obtained, the solution is passed through the porous SiO_2 soot. The drying steps were as follows: After the solution is removed from the soot, the tube is left under dry nitrogen overnight. The next day, the tube is reinstalled on the

MCVD bench and welded onto to connective tubes. 21 steps of thermal drying are applied, with a 0.5 H₂/O₂ ratio going from 10 sccm to 40 sccm, gradually increasing the tube temperature from 300°C to 1150°C. A flow of 100 sccm of Cl₂ is applied to provide additional drying. The next step constitutes the pre-vitrification of the soot at 1600°C. The rest of the process (ie., vitrification and collapse) does not contain Cl₂. Finally, the tube was heated above 2100°C to collapse and close the tube to obtain a compact preform.

A positive refractive index variation of 2.8×10^{-2} was observed in the core's central zone, measured by laser deflection technique, on a PK2660. The increased polarizability and high concentration of Al, Y, and Yb in comparison to Si enables the refractive index contrast to achieve those values. The Yb concentration is said to be ~2.8 times higher than earlier reports in reference [212].

The preforms were drawn into large core diameter glasses with minimal cladding, to minimize the thermal load in laser cooling experiments. The glasses were of 10 mm long with a 1.5 mm core diameter and 0.3 mm cladding thickness.

7.2.2 Structural characterization

To examine the glass microstructure, a high-angle annular dark field (HAADF) detector was employed to capture images of the droplets within the lamella. The imaging process utilized a dwell time of 10 μ s. Additionally, to improve the resolution of the phase-separated regions, a thermal treatment was conducted by subjecting the sample to a temperature of 1400 °C for a duration of 10 minutes. At the center of the core, the concentration of elements Al, Y/La and Yb in PS-GAYY and PS-GALY glass was measured by using the EPMA analysis which is provided in the supplementary information (SI Table 1).

7.2.3 Experimental setup for temperature measurements

The experimental design that we employed for temperature measurement is shown in Figure 7.1. It is similar to what we have used in the past [14]. But instead of a single frequency laser, a tunable fiber laser with a wavelength range of 1030–1080 (MPB communications Inc.) with a maximum output power of 20 W was used to pump the glasses. The glasses are placed on a couple of silica fibers inside of an aluminum chamber in order to reduce the conductive heat load (See Figure 7.1).

The measurements were performed under atmospheric pressure. The pump beam passes through the glass sample and is then beam dumped. Temperature monitoring was carried out using the direct contact method of fiber Bragg grating (FBG) [7, 80]. During laser cooling of silica glass, the temperature was measured by monitoring the Bragg wavelength shift of the FBG in contact at the beginning of the sample. Since the glasses were only 1 cm long, the temperature was almost uniform along the length of the glass while pumping with 20 W of pump power. With 20 W input power, the absorbed power per unit length in the glass is 8W/cm. Additionally, a FLIR thermal camera was utilized to measure the temperature variation resulting from laser irradiation.

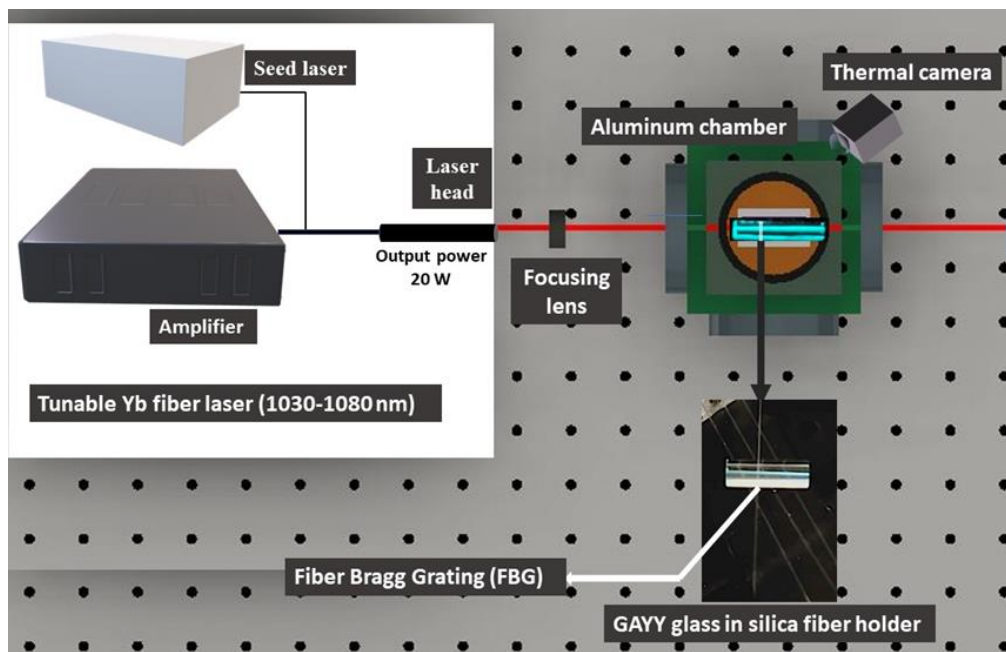


Figure 7.1: The temperature measurement setup employed during laser cooling experiments, with an inset image demonstrating the placement of the FBG in contact with the glass for temperature measurement.

7.3. Results and discussion

The Yb-doped silica glass sample that is explored in this study was made at COPL, University of Laval. This present high degree of purity (less than 200 ppb transition metal, 10 ppm hydroxyls groups). To modify SiO_2 network, aluminum (Al) and yttrium (Y) were added. Clustering of Yb^{3+}

ions in pure vitreous silica prevents its the utilization as a laser cooling material [234]. When the concentration of RE ions surpasses a certain level, the photoluminescence lifetime is reduced due to concentration quenching. This occurs as energy is transferred between RE ions, leading to non-radiative relaxation to the ground state [206, 214, 224, 228]. Due to the low solubility of RE oxides in silica, it is challenging to incorporate elevated amounts of RE ions into silica glasses without phase separation [228]. Recent studies demonstrated that the inclusion of Al_2O_3 into a pure SiO_2 matrix facilitates the homogeneous dissolution of RE oxides, consequently diminishing concentration quenching [206, 209]. Yb clusters in high-concentration Yb-doped silica glass are typically joined by Yb-O-Yb bonds, however, co-doping with Y can replace these bonds with Yb-O-Y linkages, thereby decreasing the number of Yb^{3+} pairs [207]. Figure 7.2 displays a high-resolution image of the phase separation captured in TEM high angle annular dark field (HAADF) mode. The higher average atomic mass is revealed by the brighter particles in the grey scale. There is clear boundary between the particle/matrix interface. Figure 7.2 confirms the amorphous structure of the glass. According to the Energy-dispersive X-ray (EDX) analysis conducted on a single droplet, the phase separated region contains a higher concentration of lanthanides Y and Yb ions as well as Al, compared to the surrounding matrix which is primarily composed of Si. Due to the significant concentration of rare-earth (RE) elements (Y+Yb), the phase separation effect was observed only at the nanometer scale. This unique characteristic helped to mitigate concentration quenching effects, even at a higher density of Yb (5.57×10^{26} ions/ m^3), by maintaining a low-phonon environment. More details on the microstructure of the glass and phase separation dynamics will be published elsewhere.

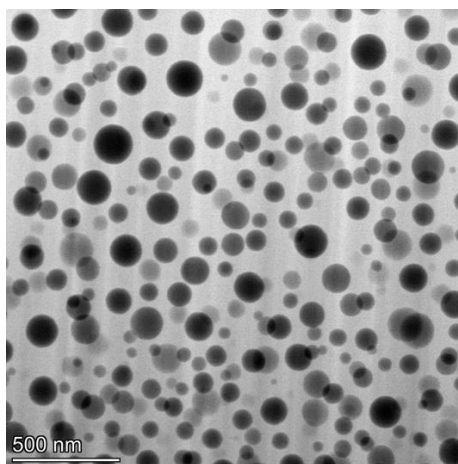


Figure 7.2: The HAADF TEM image of the PS-GAYY glass

The low phonon energy environment of yttrium (650 cm^{-1}) makes it especially attractive for laser cooling where multi-phonon relaxation is a major concern [204]. The phonon energy (E_p) of the material has a great impact on the quantum efficiency of the glass. This describes the capacity of a system to relax to the ground state through radiative decay in opposition to non-radiative decay that accumulates heat in the material system. The E_p of silica glass is approximately 1100 cm^{-1} , and the quantum efficiency when illuminated at an excitation wavelength of 1030 nm is less than 80% [14]. Yttrium is added in order to reduce the phonon energy in the RE ion environment and thus enhance the quantum efficiency.

7.3.1 Laser induced cooling in PS-GAYY glass

The real time temperature change in the glass upon laser irradiation is measured using a fiber Bragg grating (FBG) direct contact technique [7, 212]. The use of FBG enables more accurate temperature monitoring because of their key benefits of high sensitivity and resolution, low thermal mass, and wide dynamic range. The Bragg wavelength changes with the temperature can be expressed by $\Delta\lambda_B = \lambda_B \xi \Delta T$ where λ_B is the Bragg wavelength, ξ is the thermo-optic coefficient and ΔT is the temperature difference [83]. The usage of FBGs for laser cooling measurements was first proposed and demonstrated by our group in 2014 and is used as a standard method for temperature monitoring in optical cooling experiments of crystals and glasses.

[7, 11, 12, 14, 140, 234]. The silica fiber based FBG is transparent in the range of $300\text{-}2000 \text{ nm}$ and can be used for temperature monitoring in laser cooling experiment under bright fluorescent light. In addition, due to its tiny diameter of $125 \mu\text{m}$, it represents a relatively low heat load. FBGs are thus good candidates for long-term study as a reliable, quantitative technique that is applicable to almost all sample.

The temperature change in glass was studied experimentally as a function of the laser wavelength ($1030\text{-}1080 \text{ nm}$) with the fixed absorbed power of 8 W which is shown by red circles in Figure 7.3(a). Starting at an excitation wavelength of 1030 nm a net temperature change of -3.5 K from RT was observed at atmospheric pressure. The wavelength range for cooling was larger in this glass since it possesses a longer absorption tail. Increasing the pump wavelength to 1080 nm led

to a ΔT of -0.4 K from RT. The observed increment in ΔT from -4.0 to -0.4 K from RT while exciting using 1037 to 1080 nm is due to the decrease in the resonant absorption coefficient as well as the increase in background absorptive loss from impurities. The temperature change of -4.0 K from RT at the optimum wavelength of 1037 nm (20 W pump) is shown in Figure 7.3(b). The thermal camera captured images of the glass during exposure to 1037 nm laser radiation, and these images are included in the inset of Figure 7.3(b). Upon exposure to the 1037 nm laser, the image undergoes darkening, which is indicative of cooling. The temperature change curve that we measured continuously for 20 minutes while exciting the sample with the laser is provided in the supplementary information as SI Figure 12. This temperature change curve would show that the cooling effect remains stable and consistent over time, as long as the laser is providing a constant pump power to the sample.

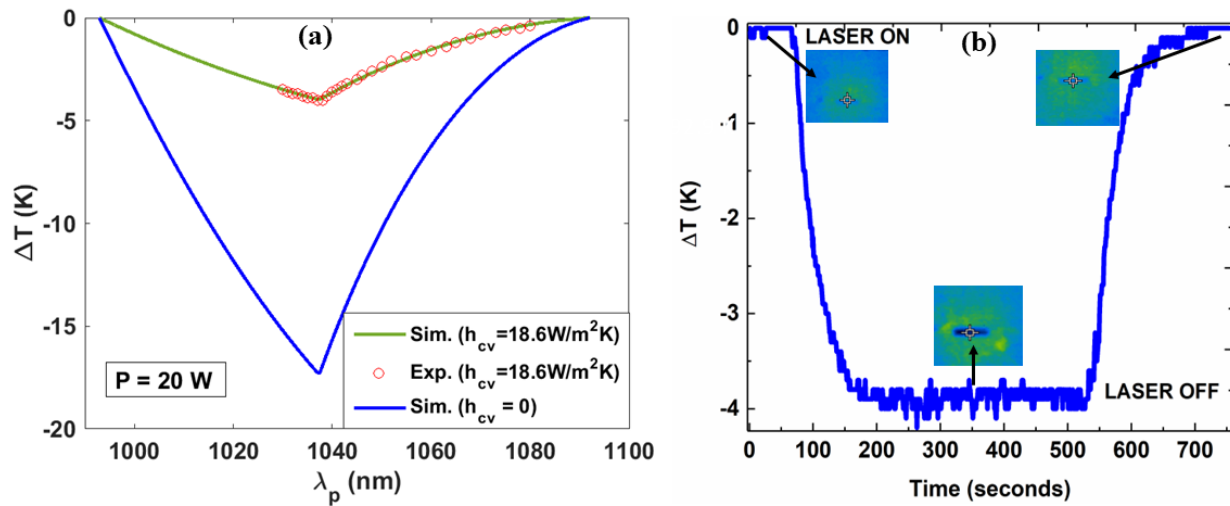


Figure 7.3 : (a) The experimental (red circles) and simulated temperature change of the glass while exciting with different excitation wavelengths with 20 W of pump power at atmospheric pressure (green line) and in vacuum (blue line), (b) Temperature dynamics of the glass when irradiating with 1037 nm laser radiation obtained using the FBG direct contact technique. The FLIR thermal camera images corresponding to each region is also shown.

7.3.2 Theoretical model and simulation results

Since the cooling measurement was performed at atmospheric pressure while pumping the glass with 1030-1080 nm tunable laser, the studies were augmented by numerical calculations using the model described in ref. [118] and [229]. This refers to the absorption and emission processes taking place between the ground-state manifold $2F_{7/2}$ and the excited-state manifold $2F_{5/2}$ of Yb^{3+} , creating a two-level system.

Those describe the absorption and emission processes occurring between the Yb^{3+} $2F_{7/2}$ ground-state manifold and the $2F_{5/2}$ excited-state manifold, forming a two-level system. In order to precisely determine the wavelength dependent temperature change, in particular the equation described in Ref. [229] has been modified and expanded by considering the effect of quenching and convective heat load at atmospheric pressure, respectively. The amplified spontaneous emission and reabsorption are neglected in the model. When the pump intensity is sufficiently high, the absorption saturation of Yb^{3+} ions can occur, leading to a reduced effective absorption cross-section. This effect can lower the probability of reabsorption of AS light. The following equation can be used to numerically calculate the temperature drop resulting from a specific pump wavelength at thermal equilibrium, for each pump power:

$$\frac{La_{eff}\sigma_a(T_s,\lambda)NI_s(T_s,\lambda)[(\lambda/\lambda_F^*(T_s))-1]}{1+\sigma_e(T_s,\lambda)/\sigma_a(T_s,\lambda)+a_{eff}I_s(T_s,\lambda)/P} = A_{surf}\epsilon\sigma_B(T_r^4 - T_s^4) + A_{surf}h_{cv}(T_r - T_s). \quad (7.1)$$

The left-hand and right-hand side of Eq. (7.1) are cooling power, P_{cool} and heat load, P_{load} , respectively, where $I_s(T_s, \lambda) \cong hc\gamma_{rad}/\lambda\sigma_a(T_s, \lambda)$ is the saturation intensity of the sample with the length L and γ_{rad} is the radiative decay rate. $\lambda_F^*(T_s)$ is the effective mean fluorescence emission wavelength, and $\sigma_a(T_s, \lambda)$ and $\sigma_e(T_s, \lambda)$ are the absorption and the emission cross sections, respectively. Also, P is the pump power, a_{eff} is the effective pump mode area, N is the doping concentration, h_{cv} is the convective heat-transfer coefficient and A_{surf} is the surface area of the glass, $\epsilon = 0.85$ is the hemispherical emissivity of the sample, $\sigma_B = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is the Stefan–Boltzmann constant.

Since our experiments are conducted at atmospheric pressure, ΔT is influenced by the convective heat load using the second term in the right-hand side of Eq. 7.1 including $h_{cv} = 18.65 \text{ Wm}^{-2}\text{K}^{-1}$.

Consequently, as shown in Figure 7.3(a) a good agreement between the experimental values and simulation curve in air is found where the maximum obtained temperature reduction was limited to ~ 4 K from RT. If the experiments are conducted in a vacuum, where $h_{cv} = 0$, a maximum temperature decrease of 17 K from room temperature is expected for the glass. In Figure 7.4, we consider the power dependence for the temperature change in glass at a wavelength of 1037 nm. At this wavelength, initially the glass cooled down to 0.1 K from RT using a 300-mW of 1037 nm laser radiation. Then, while increasing the pump power $|\Delta T|$ was also increased and reached 4 K at 20 W. Our simulation using the above-mentioned model shows that an optimum temperature reduction of 18.9 K and 56.1 K can be achieved for 460 W and 334 W of pump power using 1037 nm at atmospheric pressure and in vacuum, respectively. Increasing the pump power above the optimum value, the PS-GAYY glass gets less cool due the background absorption from impurities in our present sample used in the simulations.

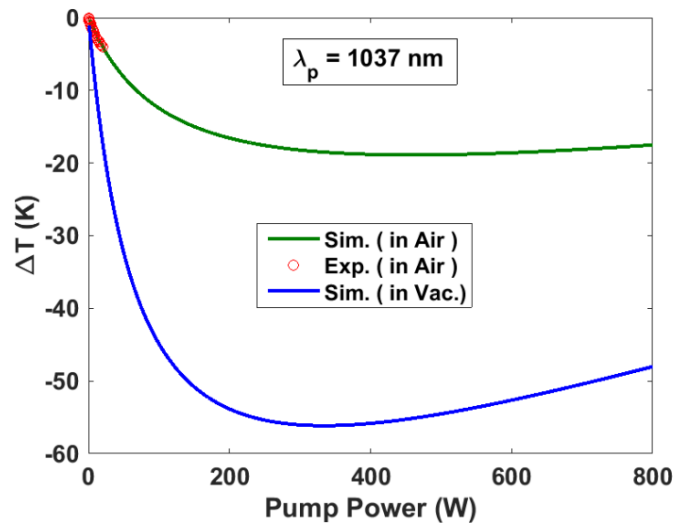


Figure 7.4: Temperature change of glass while exciting with 1037 nm laser with different pump powers varying from 300 mw to 20 W in experiment (red circles) along with the predicted temperature change in atmospheric pressure (green line) and in vacuum (blue line) for pump powers up to 800 W in simulations.

The cooling efficiency, η_c is a key factor when it comes to implementing an optical cooling device. It is expressed as the ratio of cooling power to absorbed power, or the number of photons emitted for each absorbed photon.

$$\eta_c = \frac{\lambda_p}{\lambda_F^*} - 1, \quad (7.2)$$

where $\lambda_F^* = \frac{\lambda_F}{\eta_{abs}\eta_{ext}}$ and $\eta_{abs} = \frac{\alpha_r}{\alpha_r + \alpha_b}$ is the absorption efficiency where α_b is the background absorption coefficient which is assumed to be independent of temperature, α_r is the resonant absorption coefficient defined as

$$\alpha_r = N \left[\sigma_a - (\sigma_a + \sigma_e) \left(1 + \frac{\sigma_e}{\sigma_a} + \frac{I_s}{I_p} \right)^{-1} \right], \quad (7.3)$$

where I_p is the pump intensity. $\eta_{ext} \cong \frac{\gamma_{rad}}{\gamma_{rad} + \gamma_q}$ is the quantum efficiency where γ_q is the quenching decay rate. Equations (7.1) and (7.2) were employed to conduct an in-depth exploration into the wavelength-dependent changes in temperature and the cooling efficiency of the glass. Since our tunable laser is limited to 1030-1080 nm it is impossible to experimentally evaluate the zero-crossing wavelengths (ZCW). However, the crossover wavelengths from heating to cooling are found by fitting to the curve from the experiment as depicted in Figure 7.3(a). Using the fitted curve from the simulation the ZCWs are placed to be at 1003 nm and 1085 nm and an external quantum efficiency of ~ 0.99 is obtained for the glass. The MFW of the GAYY glass was determined to be 993 nm. Both the MFW and ZCW values were obtained through numerical calculations using Eq. 1. To determine these values, an appropriate curve fitting method was utilized to align well with the experimental data of temperature change versus wavelength, as shown in Figure 7.3(a). The impurity concentration can be assessed by utilizing the quantum efficiency of the material as a measurement method, providing a numerical standard to assess the quality of the sample. Using the integrating sphere method [7], the QE of the glass was estimated to be $\sim 99 \pm 0.5$ %. The short ZCW occurs for λ_f being close to λ_p when α_r is large and α_b is negligible allowing for the estimation of η_{ext} . At the heat-balanced point, $\eta_c = 0$, the quantum efficiency is the ratio of the mean fluorescence wavelength (MFW) to the short ZCW [90, 204]. The quantum yield of ~ 0.99 is ascribed to the collaborative contributions of the network modifiers in increasing the RE ion solubility and lowering phonon energy. The lifetime of Yb^{3+} emission from the $2F_{7/2}$ level in the glass was around 1.26 ms. The PL emission decay curves for PS-GAYY glass corresponding to Yb^{3+} : $2F_{5/2} \rightarrow 2F_{7/2}$ transition with an excitation wavelength of 920 nm is provided in the supplementary information (SI Figure 11). The long ZCW helps solve the background absorption loss α_b on the basis of Eq. (2) considering η_{ext} and α_r calculated using Eq. 7. (3). All absorption processes that interfere with the Yb^{3+} ions' resonant absorption at the

pump wavelength are addressed by background absorption loss. The major source of background absorptive loss arises from 3d transition metals such as Fe²⁺, Cu²⁺ etc. which have prominent and spectrally broad absorption bands around 1 μm that coincide with Yb³⁺ pump wavelength [71, 72]. Therefore, the measurement of impurity concentration is of paramount importance. ICP mass spectrometry analysis revealed that the glass contained less than 200 ppb of both Fe and Cu. Through calculations using the Rayleigh scattering equation [237] we have determined that the scattering loss in our study is indeed low, measuring less than 0.5 dB/km. Therefore, scatter does not substantially affect the overall cooling as the samples cool better than other glasses reported in the literature. When laser light is used to cool a glass material, the cooling power is generated by the absorption and re-emission of photons by the glass. However, when the laser light scatters, some of the photons are redirected which reduces the amount of cooling power available to the system. This can lead to a decrease in the cooling efficiency and cooling rate of the glass material. In addition, when scattered photons are absorbed by other materials, such as water and impurities in the glass, they generate heat and lead to localized heating of the glass material. This can also reduce the efficiency of the cooling process and potentially cause thermal damage to the glass.

To mitigate the impact of scattering on laser cooling, various strategies were employed. One approach was to use materials with low scattering coefficients, such as high-purity glasses. Additionally, the geometry of the cooling system was optimized to minimize the path length of the light through the material and reduce the amount of scattering.

The cooling efficiency, η_c as a function of wavelength and temperature is calculated using Eq. 7.(2) and 7.(3) and illustrated by the contour maps in Figure 7.5. The cooling efficiency reduces at longer wavelengths due to the reduction in the resonant absorption which results in being increasingly dependent on the background absorption. The global minimum achievable temperature (MAT_G) is given by the lowest temperature at which $\eta_c = 0$. By considering $\eta_{\text{ext}} = 0.99$ and $\alpha_b = 0.5$ dB/km, the estimated MAT_G is 164.8 K at a pump wavelength of 1014 nm, which represents the lowest temperature predicted so far for the Yb-doped phase-separated oxide-only silica glass. However, the calculated MAT_G is 180.5 K for a background absorptive loss of 5 dB/km, which is considered to be a more realistic value. In Figure 7.5, the cooling efficiency is represented as a function of wavelength and temperature [90, 205, 233, 238]. The cooling contour curves show how cooling efficiency changes with pump wavelength and temperature, with the Minimum Achievable Temperature (MAT) representing the lowest achievable temperature when

cooling efficiency becomes zero. The cooling efficiency reduces to zero at the MAT because there are hardly any phonons left at this low temperature to cause any cooling because of the background heat load that is present in the sample. At negative cooling efficiencies (e.g., -0.02), the system may be heated instead of cooled at certain pump wavelengths. The MATG is a critical parameter, indicating the best cooling performance achievable. The cooling efficiency decreases with decreasing temperature due to mean fluorescence wavelength red-shift and reduced resonant absorption. Multiple points of zero cooling efficiency in the contour plot correspond to different optimal cooling conditions. The convergence of curves to one line on the plot is due to the MATG, representing the lowest achievable temperature. This demonstrate high potential of the PS-GAYY glass to be used for radiation balanced lasers and amplifiers.

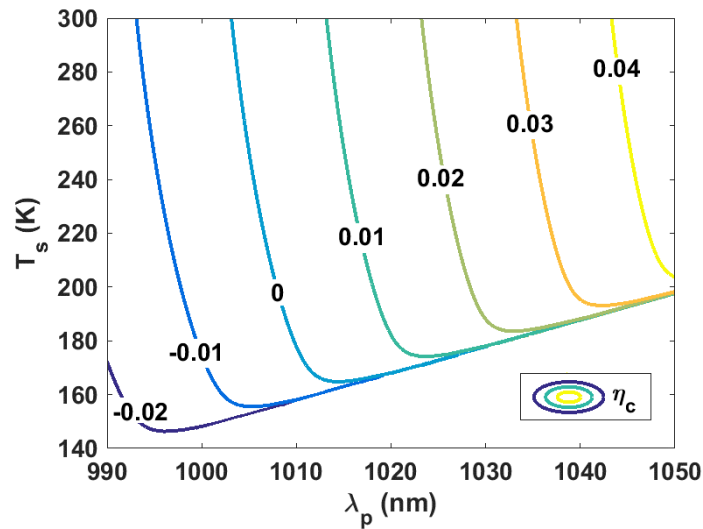


Figure 7.5: Contour map of cooling efficiency as a function of temperature and pump wavelength.

7.3.3 Optical cooling in GAYY glasses with different Yb ion concentration

Glasses with lower Yb concentrations were also investigated and the results are shown in Figure 7.6. We found that as the maximum Yb ion density increased from 1.3×10^{26} to 5.57×10^{26} ions/m³ the temperature change from RT also increased from -2.1 K to -4.0 K. But the optimum pump wavelength for each glass was different as depicted in Figure 7.6(a). For the lowest Yb concentration (1.3×10^{26} ions/m³), the optimum pump wavelength was at 1030 nm. And then while increasing the maximum concentration up to 5.57×10^{26} ions/m³, the optimum pump wavelength

shifted to 1037 nm. It is due to the difference in MFW as well as the α_r value. Another interesting fact is that except for the glass which has lowest concentration of Yb ions all the glasses cooled down even at 1080 nm pump wavelength. It is for the first time that laser induced cooling in silica glass is experimentally demonstrated for excitation wavelengths that are longer than that of 1070 nm.

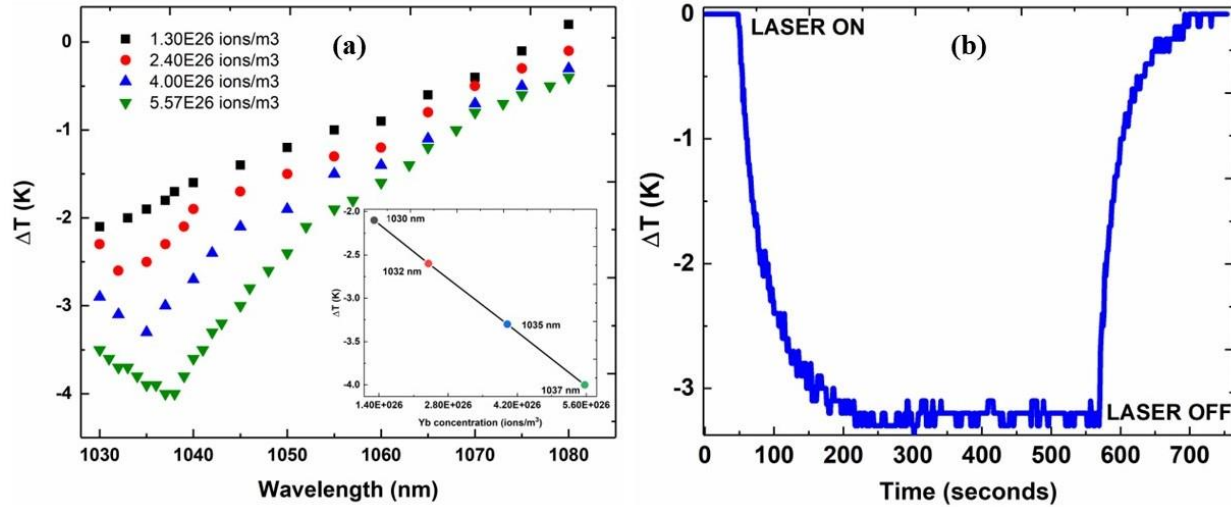


Figure 7.6: (a) The temperature change of the glasses with different Yb concentrations while exciting with different excitation wavelengths ranging from 1030 to 1080 nm with a 20 W pump power. The optimum pump wavelength to obtain maximum temperature change for each Yb ion concentration is shown in the inset, (b) The temperature dynamics of the GAYY glass with 4×10^{26} ions/m³ of Yb concentration while exciting with ~ 20 W of 1035 nm laser measured using FBG direct contact technique.

7.3.4 Optical cooling in PS-GALY glass

To push the range of maximum obtainable temperature reduction, one could engineer the material in such a way that it possesses low phonon energy. This would also diminish the impact of non-radiative transition probabilities, which is detrimental for cooling [204]. As a continuation of the research, we fabricated and studied one more type of Yb doped silica glass based on lanthano-alumino-silicate composition (named as PS-GALY glass: aluminum : lanthanum : ytterbium). The incorporation of La in the core of silica-based fibers for laser cooling application is in an early

stage and there is a need of further studies, both from material science point of view, as well as optical properties [225]. Due to the fact that Yb ions' photoluminescence properties are highly dependent on the phonon energy of the host matrix, La_2O_3 , which has a low phonon energy (approx. 400 cm^{-1}), was chosen as an ideal material to use for the fabrication of glass for laser cooling applications.

The fabricated PS-GALY glass has an Yb ion concentration of $2.4 \times 10^{26}\text{ ions/m}^3$ and the lifetime of Yb: $2F_{5/2}$ level was of 1.2 ms. Similar to the GAYY glass, the PS-GALY glass was also studied with the tunable fiber laser from 1030-1080 nm in order to evaluate the temperature change upon laser irradiation. The wavelength dependent temperature change with 20 W pump power is provided in Figure 7.7(a).

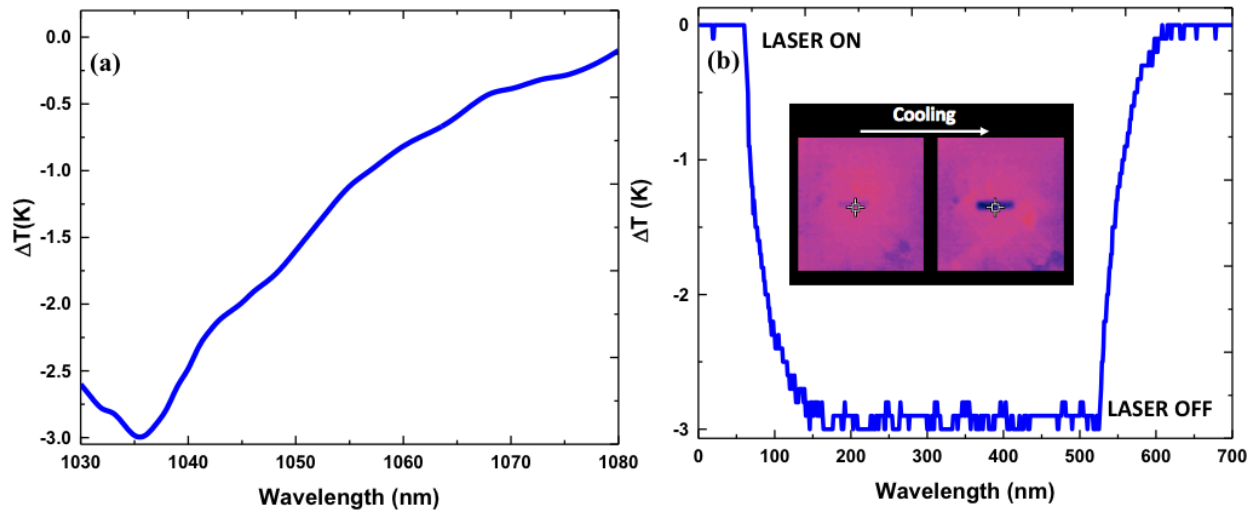


Figure 7.7: (a) Temperature change of the PS-GALY glass while exciting with different excitation wavelengths ranging from 1030 to 1080 nm with 20 W of pump power, (b) Temperature dynamics of the PS-GALY glass when irradiating with ~ 20 W of 1030 nm laser obtained using FBG direct contact technique. The inset shows the thermal image of the glass taken while exciting with laser.

At an initial excitation wavelength of 1030 nm and a maximum pump power of 20 W, a net temperature decrease of -2.6 K from room temperature was observed. When the pump wavelength was increased to 1035 nm (20 W), the maximum temperature decrease from room temperature was -3.0 K. However, tuning the pump wavelength to 1080 nm resulted in a ΔT value of -0.1 K from

room temperature, due to the decrease in the resonant absorption coefficient and the increase in background absorptive loss.

Figure 7.7(b) shows the temperature changes in the glass when excited with a 20 W 1035 nm laser, as measured using the FBG contact technique. In addition, the inset of Figure 7.7(b) displays thermal camera images of the glass captured during the laser excitation. The image darkens after being excited the samples with 1035 nm laser which indicate cooling. Results revealed that co-doping silica glass with La^{3+} ions raise Yb solubility and reduces clustering, as evidenced by a temperature change of -3.0 K. When we compare the PS-GALY glass and PS-GAYY glass having the same Yb ion concentration, the PS-GALY performs better, we believe due to the added advantage of lower phonon energy environment provided by La. The maximum cooling in PS-GAYY glass of the same glass dimension and Yb concentration was of -2.6 K from RT.

The future optimization efforts on PS-GALY glass will focus on the fabrication of glasses with higher Yb concentration. Furthermore, we plan to investigate the potential use of PS-GAYY and PS-GALY glasses for optical fibers in radiation balanced lasers in the future. This design is very feasible, and our team is currently working to fabricate the fibers.

7.4. Conclusions

In this work, we report to the best of our knowledge, the lowest temperature achieved to date in optical cooling of Yb-doped phase separated 100 % oxide glass at atmospheric pressure using 20 W of 1037 nm pump radiation by more than 4 K. Wavelength dependent temperature change is studied both experimentally and theoretically while using a tunable fiber laser from 1030 to 1080 nm. Our numerical calculations predict a global MAT of ~165 K in the glass which is the lowest value reported in the literature for amorphous Yb doped phase separated oxide glass. We explored a series of oxide glasses for which the Yb ion density increased from 1.3×10^{26} to 5.57×10^{26} ions/m³ and the optimum pump wavelength shifted from 1030 to 1037 nm resulting in a temperature change from -2.1 K to -4.0 K. The PS-GALY glass cooled down (-3.0 K), better than that of PS-GAYY glass (-2.6 K) with the same Yb concentration under identical experimental conditions. This will be beneficial in bringing future opportunities to incorporate different rare earths with silica to be used for radiation-balanced lasers and amplifiers. We anticipate this ground-breaking research would open another dimension for highly rare earth doped silica glasses for laser cooling

applications and accelerate the material discovery of new glass compositions with different network modifiers.

Funding

Authors acknowledge Fredric Monet for the fabrication of FBG used for temperature measurements. Authors acknowledge Dr. Jesus Angel Valdez Aguilar, Dr. Stephen Kelly Sears and Mr. Weawkamol Leelapornpisit for the TEM image. Authors acknowledge Natural Sciences and Engineering Research Council (NSERC) of Canada's Strategic grants program, NSERC's Discovery Grants program, the Canadian Excellence Research Chair (CERC) in Photonic Innovations and the Government of Canada's Canada Research Chairs program for the financial support.

Author contributions

J. T.- Data curation, Formal Analysis, Investigation, Methodology, Writing – original draft; T. M.- Investigation, Methodology, Review & editing; A.T.- Modeling using MATLAB, Visualization, Review & editing; N. G- Methodology, V. K.- Resources, Review & editing D. S - Review & editing; Y. M.- Supervision, Resources, Review & editing; R. K.- Conceptualization, Resources, Supervision, Review & editing.

CHAPTER 8 GENERAL DISCUSSION

This chapter is devoted to the discussion of the thesis's overall findings, which are divided into two main sections. The first part will focus on the use of oxyfluoride glass ceramics made by melt quenching technique for laser cooling applications along with the challenges identified. The discussion on the proposed solutions and the idea of using Yb doped silica glass made by solution doping and MCVD are given in the second part.

8.1 Oxyfluoride glass-ceramics for laser cooling

The scientific community is increasingly interested in RE-doped oxyfluoride glass ceramics as cooling materials due to several key advantages. These materials involve RE ions situated within a fluoride nanocrystalline environment, characterized by lower phonon energy in contrast to the higher phonon energy of oxide vitreous hosts. Furthermore, glass ceramics are highly adaptable, cost-effective, and easily manufactured from glassy materials, rendering them suitable for practical implementation in solid-state laser cooling. Throughout this thesis, our focus has been on synthesizing various oxyfluoride glass ceramics with the aim of utilizing their potential for laser cooling applications.

To effectively mitigate heat, it is essential to discover the right combination of RE ions and host matrix that enhances quantum yield while reducing background absorption. To address this goal, the initial objective was to examine two types of glasses: germanate and aluminosilicate. The glasses featured nanocrystals with diverse compositions, each hosting varying Yb ion concentrations ranging from 0.5 to 3 mol%. These variations were explored for their potential suitability as hosts for laser cooling applications. [12]. The measurements of photoluminescence showed an IR emission attributed to Yb^{3+} with the intensity and peak shape were observed to be contingent on both the host material and the concentration of Yb ions within it. As the concentration reaches 2 mol%, the emission decreases due to reabsorption and trapping. Quantum yield of the PL varies between 70-99% depending on concentration and excitation wavelength. Calorimetric measurements on GCs with 1.50-2.00 mol% of Yb^{3+} showed their potential for optical refrigeration with near zero net heating.

As a continuation of the research with the first objective, in order to achieve a near unity quantum yield for laser cooling applications, the oxide : fluoride ratio, crystallinity, and ytterbium ion concentration in aluminosilicate oxyfluoride GCs was optimized [13]. The iQY in glass ceramics varied from 70 to 99 % at different excitation wavelengths, depending on the ratio of oxides to fluorides (O/F) and the ytterbium content. A reduced fluorine content resulted in the predominant formation of YLiF_4 as the major phase during ceramization, whereas a higher fluorine content promoted the formation of YF_3 . The radiative lifetime of YF_3 GCs was found to be higher than YLiF_4 GCs, which increased the quantum yield, which is advantageous for laser cooling applications. The analysis of emission properties (quantum yield and lifetime) of oxyfluoride glass ceramics in article 1 (chapter 3) and article 2 (chapter 4) implies that the amount of Yb^{3+} ions that are incorporated in the nanocrystals increases after undergoing heat treatment and crystallization processes. This consequently causes a decrease in the multi-phonon decay of the GC sample. Interestingly, similar to prior research by our team, the GCs displayed a much greater temperature reduction when exposed to a wavelength of 1030 nm in comparison to glass [13].

Given that impurities in these glasses inevitably cause background absorption, it is crucial to find and get rid of them to improve cooling performance. As was previously mentioned, common impurities like Cu^{2+} , Fe^{2+} , and Co^{2+} that are found in the raw materials used to make glass competes with the Yb^{3+} when it is excited near $\sim 1 \mu\text{m}$ pump wavelength [71, 72]. Moreover, other lanthanide ions may also act as acceptors in nonradiative energy transfer from the excited Yb^{3+} ion to the other lanthanide ions. Therefore, the development of high purity materials is a crucial prerequisite for the realisation of laser induced cooling. The chelated assisted extraction method is one of the approaches employed to produce glass ceramics. Patterson *et al.* have successfully employed this method to attain quantum efficiencies of over 99% in both crystals and fluoride glasses for cooling purposes [72]. This process has produced promising results but has yet to be further explored.

A comparison was conducted between oxyfluoride GCs incorporating YF_3 nanocrystals to assess their purity and identify the influence of impurities such as iron on the properties of the glass [202]. The process known as APDC-MIBK chelate cleaning (AMCC) was employed to obtain the precursors for the glasses. The precursors were subjected to re-fluorination using high-quality HF, resulting in a great improvement in the precursors purity. The iron content was significantly decreased in various materials: from 11 ppm to below 0.02 ppm for YF_3 , from 9 ppm to 2.85 ppm for LiF, from 34 ppm to below 0.02 ppm for Al_2O_3 , and from 5 ppm to 0.36 ppm for YbF_3 [202].

The purification significantly improved transparency, reaching about 90% in the near-infrared range. This process also enhanced PL emission intensity and quantum efficiency by reducing non-radiative transitions, as seen in Figure 8.1(a). The quantum efficiency at 920 nm excitation increased from 84% to 89% post-purification. Furthermore, background absorption coefficient decreased from 0.152 m^{-1} to 0.084 m^{-1} , resulting in longer lifetimes: from 1.51 to 1.85 ms for the parent glass and from 1.55 to 1.87 ms for the glass-ceramic, as illustrated in Figure 8.1(b). This improvement was also observed in heat mitigation for laser cooling, with a maximum temperature change (ΔT) per absorbed power (PAbs) of approximately 0.5 K/W while pumping with 1030 nm following the purification process, in contrast to the previous maximum $\Delta T/\text{PAbs}$ of approximately 1 K/W, as shown in Figure 8.1(c).

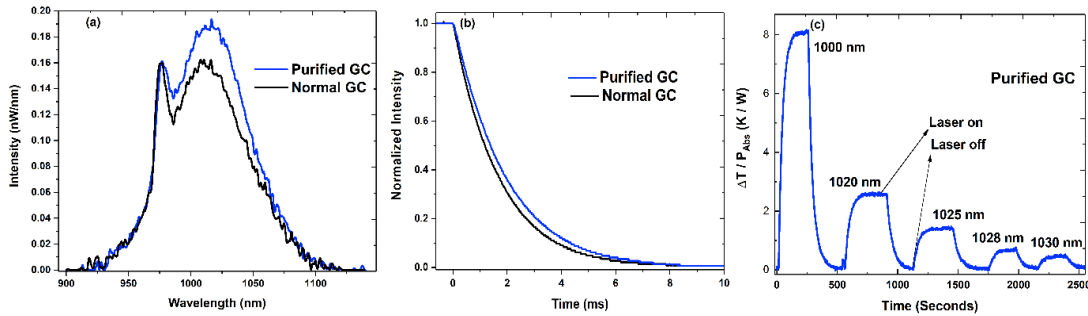


Figure 8.1: (a) PL emission spectra and (b) PL emission decay curves for $\text{Yb}^{3+}:\text{2F}_{5/2}$ level, obtained through single exponential fitting, in purified GC and non-purified GC (excitation wavelength: 920 nm). (c) $\Delta T/\text{PAbs}$ behavior over time for purified GC at pump wavelengths ranging from 1000 nm to 1030 nm. (adapted from [202]).

However, the fabrication process of conventional melt quenching technique was limited due to the purity of the starting materials, although it showed potential in terms of enhanced quantum yield and lifetime. To resolve these issues, a change in the glass manufacturing procedure was proposed, i.e., the use of MCVD with solution doping.

8.2 Laser cooling in a novel all oxide GAYY silica glass

The use of a silica host in the modified chemical vapour deposition (MCVD) technique has the potential to produce high intrinsic purity materials. In the third objective, modifications to the

MCVD technique were used to obtain the fabrication of a high Yb concentration silica glass preform. By adding alumina, the rare earth's solubility was increased but also promoted phase separation of the RE in the oxide glass. To shield the RE ions from the high phonon energy of silica, fully oxidized active RE ions were surrounded by non-active RE ions. This arrangement resulted in the creation of a local, phase-separated oxide environment with lower phonon energy [234]. Introducing germanium (Ge) as a dopant at an atomic percentage of 0.15% in all glasses to impart photosensitivity allows for the creation of a laser with self-cooling capabilities in forthcoming endeavors. Through this fabrication technique, a concentration of ytterbium at 4×10^{26} ions/m³, which represents the highest reported value for optical refrigeration without encountering issues like clustering or reduction in lifetime was achieved. Furthermore, an exceptionally minimal background absorptive loss of ~ 10 dB/km was also demonstrated.

The third article [14] featured a successful demonstration of optical refrigeration in ytterbium-doped silica glass (SiO₂) with alumina Yttria codoping, denoted as GAYY glass. This particular glass was manufactured using the MCVD method. Through the use of a 6.5 W 1029 nm laser, a highest temperature drop of -0.9 K was achieved, starting from the standard room temperature of 296 K under atmospheric pressure. Additionally, numerical simulations comparing temperature changes to pump power aligned with observed results and anticipated a 4 K drop in temperature from room temperature within identical conditions in a vacuum.

It was shown that the local surroundings of Yb³⁺ ions can be controlled by dissolving them within regions rich in yttrium. With the addition of Al₂O₃, the size of these domains was reduced to nanometer sized particles. As a result, Rayleigh diffusion effects in the NIR spectrum have significantly decreased. As anticipated, the GAYY glasses had greater quantum yields ($\sim 99.4\%$) than the MCVD SiO₂ glass (87%) due to their low phonon energy environment and high RE ion solubility, that reduces concentration quenching. The most remarkable result of the research was that the MCVD SiO₂ glass heated to ~ 5 K with a pump power of only 1 W, which is an immense difference compared to the GAYY glass under 1029 nm laser pumping.

The wide-tunable fiber laser allowed us to achieve cooling in Yb-doped silica glass across pumping wavelengths from 1030 to 1080 nm [15]. Notably, this marked the first experimental demonstration of cooling with excitation wavelengths beyond 1070 nm in Yb-doped silica glass. With the fourth objective, ytterbium-doped silica glass was cooled by 4 K from RT using a 20 W 1037 nm laser. This signifies a notable advancement beyond our earlier research, where a 0.9 K

reduction in temperature from ambient was attained in Yb-doped silica GAYY glass, employing a 6.5 W laser with a wavelength of 1029 nm. With the consideration of $\eta_{\text{ext}} = 0.99$ and $\alpha_b = 0.5$ dB/km, the projected MATG stands at 164.8 K when utilizing a 1014 nm pump wavelength. This temperature achieved is the lowest reported for Yb-doped phase-separated oxide-only silica glass, showcasing GAYY glass's strong potential for radiation-balanced lasers and amplifiers. For the lowest Yb concentration of 1.3×10^{26} ions/m³, the temperature change from room temperature (RT) was -2.1 K, whereas for the highest Yb concentration of 5.57×10^{26} ions/m³, the change was -4 K. During this increase in Yb concentration, the optimal pump wavelength shifted from 1030 nm to 1037 nm, which might be attributed to variances in MFW and α_r values. Notably, all glasses, except the one with the lowest Yb ion concentration, exhibited cooling even at a pump wavelength of 1080 nm. To enhance the maximum attainable temperature reduction, a potential strategy involves engineering the material to possess a lower phonon energy. This adjustment can also help mitigate the adverse effect of non-radiative transition probabilities, which can hinder the cooling process. In our ongoing research, we produced and examined a novel Yb-doped silica glass known as GALY glass (comprising aluminum, lanthanum, and ytterbium) [15]. GALY glass featured a Yb ion content of 2.4×10^{26} ions/m³ and an optical lifetime of 1.2 ms. The introduction of La³⁺ ions through co-doping in silica glass enhanced Yb solubility while reducing clustering, resulting in a temperature reduction of -3.0 K. In comparison to GAYY glass with an equivalent Yb ion concentration, GALY glass displayed superior performance, likely attributed to the additional advantage of a reduced phonon energy environment offered by lanthanum. On the other hand, in GAYY glass with the same glass dimensions and Yb concentration, the temperature change was -2.6 K from room temperature.

Future efforts in optimizing GALY glass for laser cooling applications will be directed towards fabricating glasses with higher Yb ion concentrations. Moreover, it is recommended to explore the feasibility of employing GAYY and GALY glasses in radiation-balanced laser systems by developing optical fibers made from these materials. Our team is actively working towards fabricating such fibers, and we believe that this design is highly feasible.

CHAPTER 9 CONCLUSION AND FUTURE PERSPECTIVES

In the preceding chapters, the findings of this doctoral study on solid-state laser cooling in ytterbium doped oxide glass, including both experimental and theoretical findings were discussed. Finally, the distinguishing features of this completed project will now be highlighted by providing a brief summary of the findings. In addition, potential avenues for additional research and advancements in this field are suggested.

To address the four objectives, all aspects and parameters influencing the laser cooling properties of Yb doped glasses, such as the host composition, phonon energy of the material, purity of the material, structural and optical properties, were thoroughly examined during this research. The first two goals involved investigating the compositional variations, ytterbium concentration, and purity of oxyfluoride Gs and GCs for laser cooling uses. The first article [12] focused on using fluoride nanocrystals to artificially create a low phonon environment for RE ions embedded in oxide glasses characterized by high phonon energy. This objective was achieved through an investigation of ytterbium-doped germanate and aluminosilicate oxyfluoride glass ceramics featuring a range of RE ion concentrations (varying from 0.5 to 3.0 mol%). These materials were prepared using the conventional melt quenching method. Significantly, glass-ceramics featuring Yb^{3+} ion concentrations in the range of 1.50–2.00 mol% exhibited negligible net heating when subjected to 1030 nm excitation, as determined through calorimetric assessments performed with fiber Bragg gratings. This strongly suggests their potential suitability for applications in optical refrigeration.

The second paper [13] examined how varying the initial composition over time and at various fusion temperatures affected the optical characteristics of GCs with YF_3 and YLiF_4 crystals. When we compare highly crystalline YF_3 glass ceramics (YF_3GCs) with the less crystalline YLiF_4 glass ceramic, both having the identical initial composition, we observe that YF_3GCs demonstrate improved quantum efficiency and a more substantial temperature reduction. The optical characteristics of purified and unpurified GCs were also compared, and it was found that purifying the GCs led to enhancements in the PL emission intensity and iQY, while concurrently reducing background absorption. Ytterbium-doped oxyfluoride glass ceramics are an ideal choice for laser cooling because of the composition-dependent optical properties that are revealed by the research in articles 1 and 2. The main issue that must be addressed before oxyfluoride GCs can be considered a viable option for optical refrigeration applications is the difficulty in achieving both

high quantum efficiency and minimizing background absorption. The purity of the raw materials and the glass fabrication process (melt quenching technique) hampered the fabrication path, necessitating an essential modification in the glass manufacturing process, despite the fact that this method demonstrated higher quantum efficiency of PL emission and longer lifetimes.

In the third and fourth objectives of this thesis, modified chemical vapour deposition (MCVD) approach to produce inherently high purity ytterbium (Yb)-doped silica glass was discussed. Incorporating alumina into the silica host during MCVD improved rare earth solubility, resulting in a high Yb concentration in the silica glass preform and facilitating rare earth phase separation in the oxide glass. This technique, involving the encapsulation of active RE ions within non active RE, establishes a low phonon energy oxide environment, thereby protecting the RE ions from the high phonon energy of the silica host. Yb ions were successfully inserted into a low phonon environment, overcoming previous obstacles by encouraging phase separation, which is usually regarded as a nuisance.

As a result, GAYY (Aluminum: Yttrium: Ytterbium Glass) glasses with exceptionally high purity were developed and cooled down by 0.9 K from RT using a 6.5 W pump power at 1029 nm [14]. The meticulous design of the material, which minimised factors contributing to non-radiative relaxation, including concentration quenching and background absorptive losses, was critical to these results. According to theoretical calculations, employing a 32.6 W pump to power the GAYY glass, taking into account the background absorptive loss of 10 dB/km, would lead to a maximum temperature reduction of 6.4 K. The greatest temperature drop that could be achieved, however, was affected by background absorptive loss, convective heat load, non-optimized pump wavelength and power.

In the fourth objective, the pump wavelength and pump power were optimised for each value of Yb ion concentration to achieve the greatest possible temperature reduction in phase separated oxide glasses [15]. A maximum cooling of -4 K from RT under atmospheric pressure using a 20 W 1037 nm laser with a concentration of 5.57×10^{26} ions/m³ - to the best of our knowledge, the highest reported concentration in the literature - while maintaining high quantum efficiency and longer excited state lifetimes were reported for the first time. This is more than fourfold improvement over the third article's results. Previous research on Yb-doped silica glasses for optical refrigeration applications lacked the controlled phase separation effect, which effectively maintains Yb³⁺ ions within low phonon energy yttrium-rich domains, a feature distinct to GAYY

glass. The lowest expected MAT value for a phase-separated, non-crystalline GAYY glass was calculated to be 165 K.

Following up on the GAYY glass research, lanthano-alumino-silicate-based GALY glasses were examined. The use of network modifiers such as La in silica-based fibres for laser cooling is not completely understood, necessitating more investigation from the fields of material science and optical perspectives. La doped glasses are an appropriate choice for laser cooling applications due to their low phonon energy of about 400 cm^{-1} . La^{3+} ions were found to increase Yb solubility and decrease clustering in silica glass, as evidenced by a -3.0 K temperature decrease from RT. GALY performed better than GAYY glasses with the same Yb ion concentration, most likely due to the lower phonon energy provided by La. For the same dimension and Yb ion concentration (2.4×10^{26} ions/ m^3), the GAYY glass had a maximal cooling of -2.6 K from ambient temperature.

In conclusion, the experimental and theoretical research presented in this thesis have made significant contributions to the realization of optical cooling in Yb doped silica glasses, which has potential uses in solid-state optical refrigeration, radiation-balanced lasers, and amplifiers. This dissertation delves deeply into the spectroscopic study and characterization of rare earth doped silica-based oxide glasses and oxyfluoride glasses. In addition, several approaches were suggested for successfully implementing laser cooling in silica-based oxide glasses. Further optimization attempts should concentrate on reducing background absorptive loss, eliminating convective heat load, and so on. Improving pump power, incorporating a multi-pass scheme, and optimising material characteristics may pave the way for future advancements.

GAYY and GALY glasses can be used to make optical fibers. Further research is required to determine the feasibility of GAYY glasses to be used for making radiation-balanced fiber lasers. Reflective gratings for RBLs can be made using a Ge doped GAYY glass preform. Additionally, other RE doped glasses that include various network modifiers such as Lutetium (Lu) can be used.

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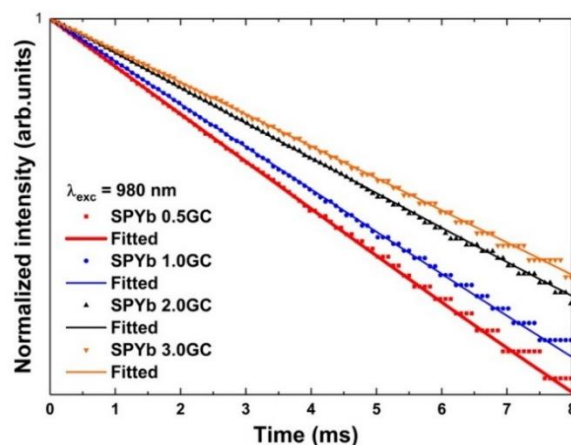
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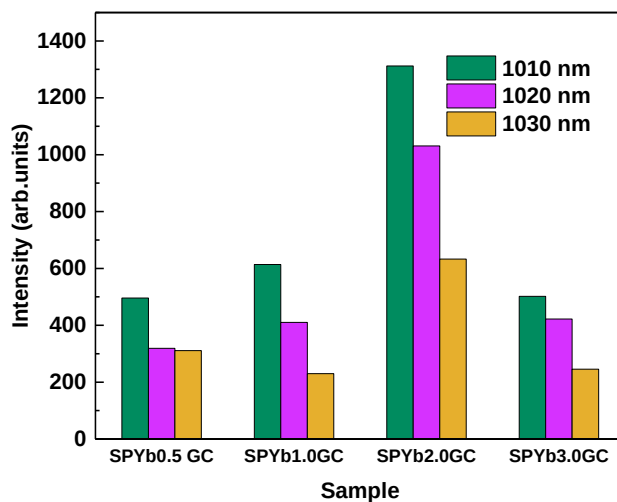
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APPENDIX A- SUPPLIMENTARY INFORMATION

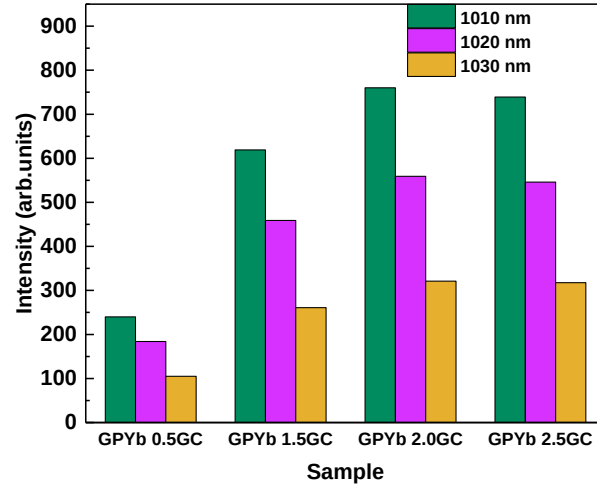


Appendix Figure 1: The room-temperature photoluminescence decay curves of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ level for all aluminosilicate glass ceramics at an excitation wavelength of 980 nm (at a pump power of 300 mW).

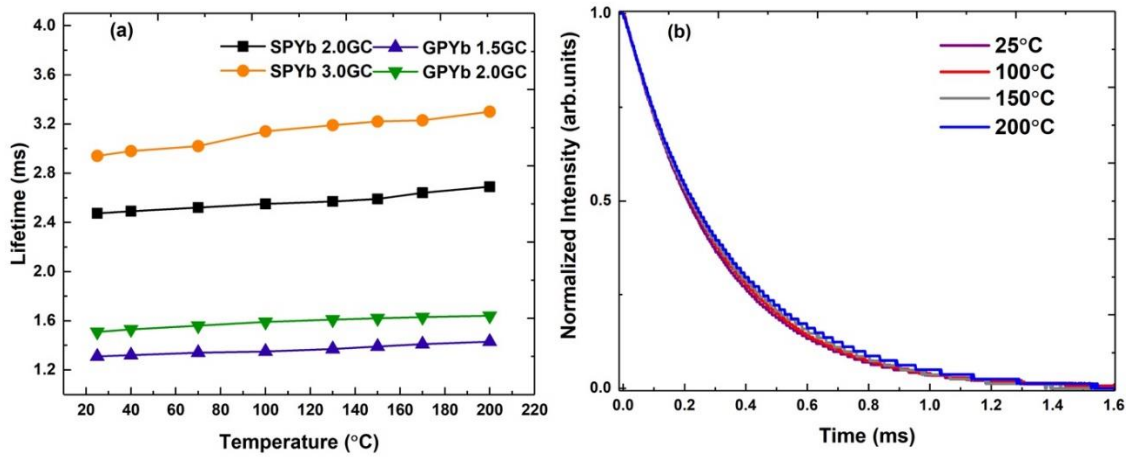
The emission wavelengths monitored were above 980 nm. The decay function is well described by a single exponential fit. It was observed that as the Yb^{3+} concentration increases from 0.50 mol % to 3.0 mol %, the fluorescence lifetime, τ , increases from 1.96 to 2.94 ms.



Appendix Figure 2: Comparison of anti-Stokes emission intensity between different compositions of SPYb GCs at 200°C with 1010, 1020 and 1030 nm excitations at a pump power of 300 mW.



Appendix Figure 3: Comparison of anti-Stokes emission intensity between different compositions of germanate glass ceramics at 200°C at 1010 nm, 1020 nm and 1030 nm with constant power of 300 mW.



Appendix Figure 4: The PL emission decay time values of $\text{Yb}^{3+} : ^2\text{F}_{5/2}$ level at different temperatures varying from 25°C to 200°C for SPYb 2.0GC, SPYb 3.0GC, GPYb 1.5GC and GPYb 2.0GC at an excitation wavelength of 1020 nm, (b) The PL emission decay curves for SPYb 3.0GC corresponding to $\text{Yb}^{3+} : ^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition with an excitation wavelength of 1020 nm at 25°C, 100°C, 150°C and 200°C.

Appendix Table 1: PL emission decay time values of $\text{Yb}^{3+} : ^2\text{F}_{5/2}$ level along with the adjusted R-square values obtained by fitting the curves of Figure 4.7(c) using single exponential function.

Sample code	$\lambda_{\text{exc}} = 920 \text{ nm}$	
	Lifetime ($\pm 0.05 \text{ ms}$)	Adj. R^2
GPYb 0.50GC	1.08	0.9998
GPYb 1.50GC	1.39	0.9998
GPYb 2.00GC	1.53	0.9999
GPYb 2.50GC	2.29	0.9995

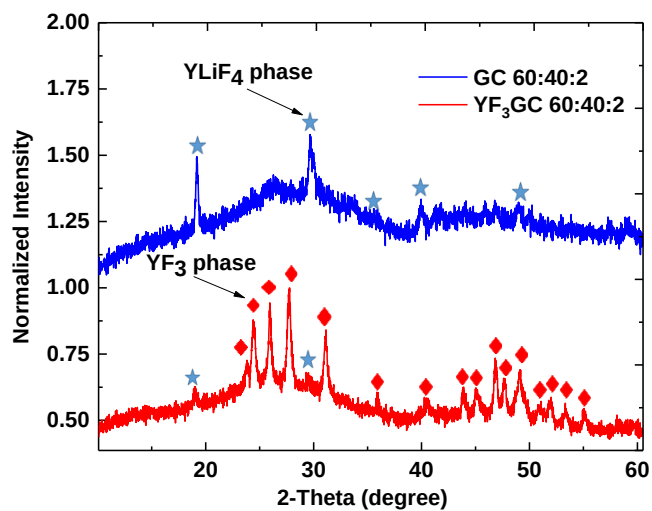
5 Calculation of photoluminescence quantum yield (PLQY)

The measurements were carried out by exciting the samples at different excitation wavelengths from a Ti: Sapphire laser.

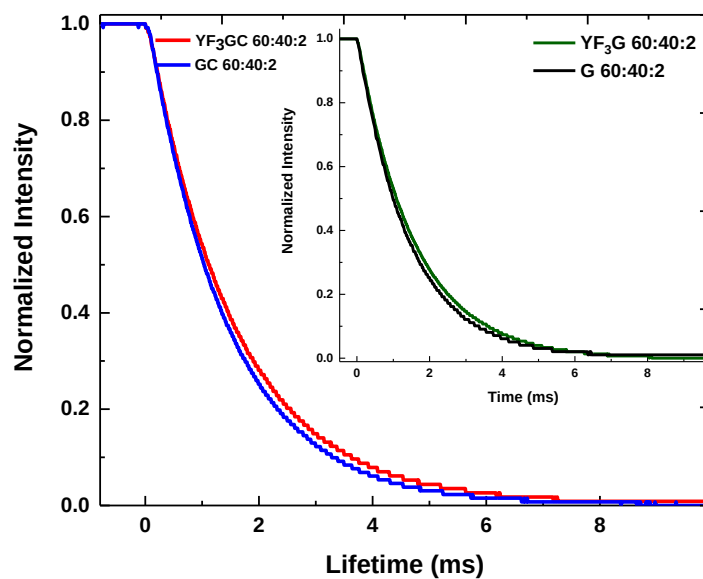
The internal PLQY is defined as the ratio of number of photons emitted to the number of photons absorbed.

$$iQY = \frac{N_{ep} - (1-A)N_{epd}}{N_{ip}A} \quad (1)$$

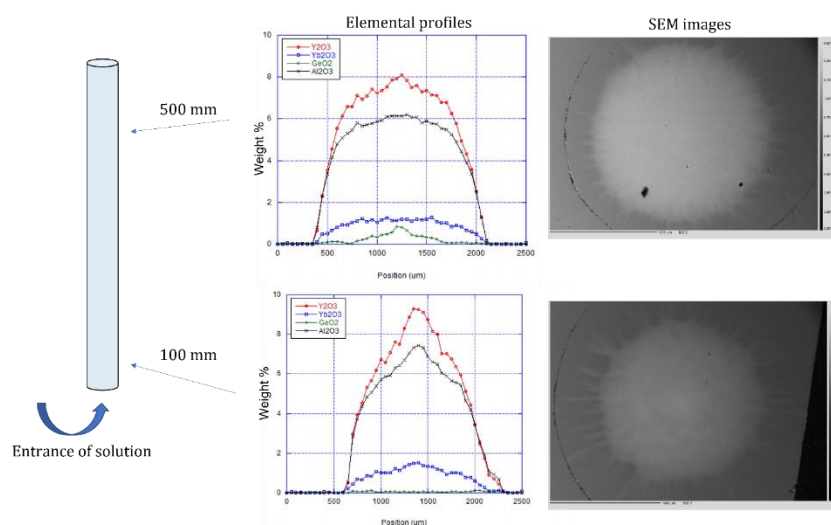
where N_{ep} is the number of emitted photons from the sample when the sample is inside the integrating sphere and the exciting laser beam is directed onto the sample, N_{ip} is the number of incident photons when the pump laser beam is directed towards empty integrating sphere (without sample), N_{epd} is the number of emitted photons by the sample when the sample is inside the integrating sphere and the exciting laser beam is directed onto the sphere wall (interaction of diffused light).



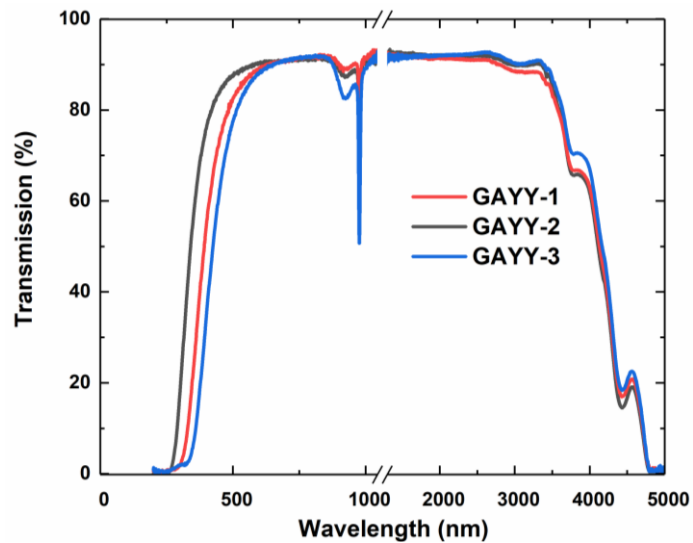
Appendix Figure 5: The X-ray diffraction (XRD) images of GC 60:40:2 and YF₃GC 60:40:2 showing the formation of YLiF₄ and YF₃ phase respectively.



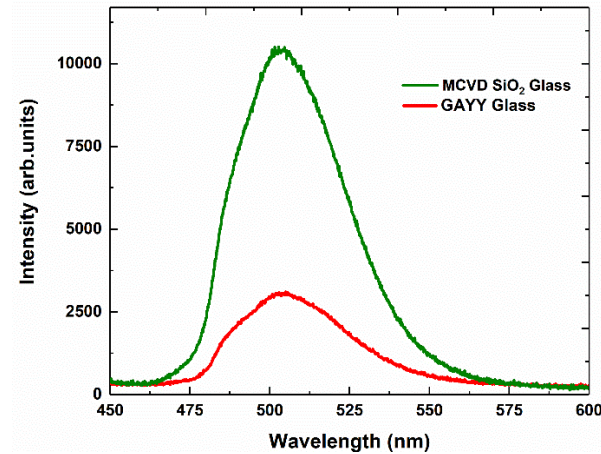
Appendix Figure 6: The lifetime decay curves of glass and glass ceramics containing YLiF₄ and YF₃ nanocrystals.



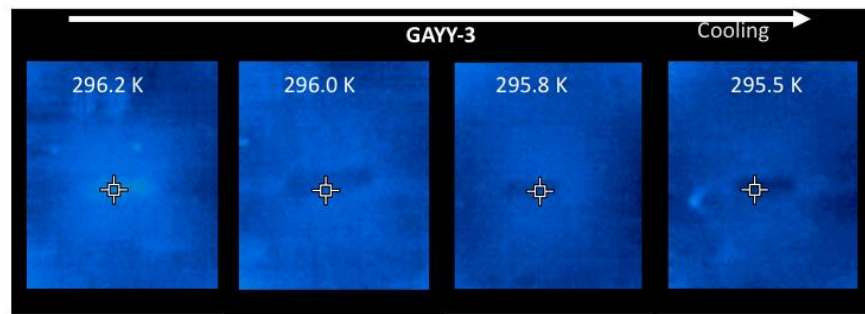
Appendix Figure 7: The elemental profiles of the GAYY-2 glass at the bottom and top of the silica tube along with the SEM images.



Appendix Figure 8: The transmission of the glasses from VUV to IR region



Appendix Figure 9: Cooperative luminescence spectra of MCVD SiO₂ glass and GAYY-3 with 400 mW of absorbed pump power while exciting with 980 nm laser.



Appendix Figure 10: The temperature evolution of GAYY 3 glass while it is exposed to 1029 nm 6.5 W laser obtained through FLIR thermal camera.

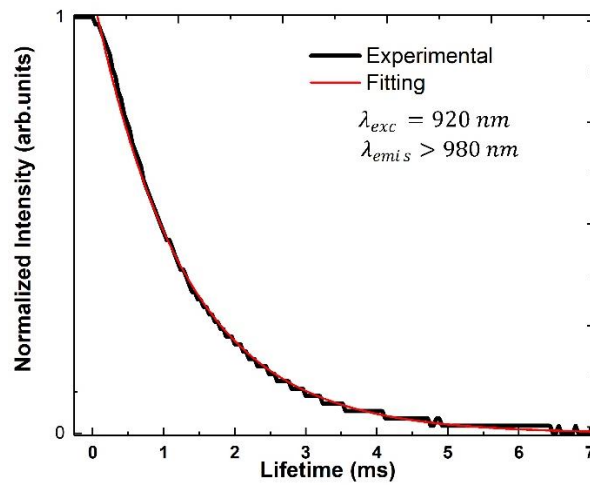
6. Glass fabrication using modified chemical vapor deposition (MCVD) process

A F300 grade Heraeus silica tube was placed inside of an MCVD system. After cleaning and drying steps, SiCl₄ and He/O₂ gas flowed through the tube. The tube was locally heated to 1325°C with a H₂/O₂ burner to oxidize the silicon tetrachloride into a SiO₂ soot. The flame is moved along the tube to create a first layer of SiO₂ on the inner walls of the tube. This step is then repeated two more times. The doping elements were added by an aqueous solution of 6N chloride salts of Al, Y and Yb (99.9999% Pure Analytical Laboratories). The solution flowed through the porous silica soot and left for 20 minutes. The solution is then removed and a 2L/min flow of dry N₂ passed for

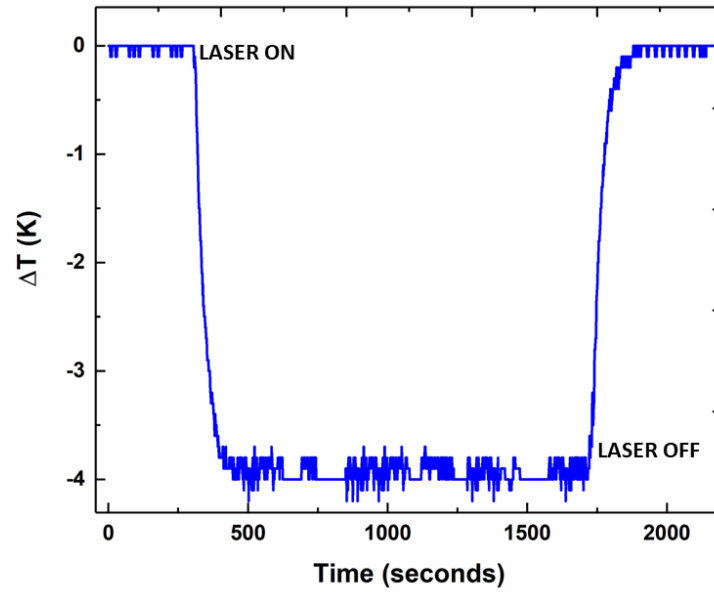
12h. The silica tube is then re-placed on the MCVD bench and dried at high temperature with multiple passes from 800 to 1500°C. Sintering and vitrification of the soot is realized at 1600°C, followed by a 2100°C pass. Collapse of the preform is performed from 2100 to 2200°C. The final preform is then fire polished at 2000°C.

Appendix Table 2: The concentration of elements Al, Y/La and Yb in PS-GAYY and PS-GALY glass

Sample	Al (atomic percent)	Y (atomic percent)	La (atomic percent)	Yb (atomic percent)
PS-GAYY	$7.98\% \pm 0.88$	$4.17\% \pm 0.65$	NA	$1.23\% \pm 0.12$
PS-GALY	$7.26\% \pm 0.70$	NA	$4.76\% \pm 0.71$	$0.45\% \pm 0.13$



Appendix Figure 11: The lifetime decay curve along with the single exponential decay fit of GAYY-4 at an excitation wavelength of 920 nm.



Appendix Figure 12: Temperature dynamics of the glass when irradiating with 1037 nm laser radiation obtained using the FBG direct contact technique.

APPENDIX B- LIST OF PUBLICATIONS AND AWARDS

Publications

Peer reviewed journal articles

1. **J. Thomas**, T. Meyneng, A. Tehranchi, N. Gregoire, F. Monet, D. Seletskiy, Y. Messaddeq, and R. Kashyap, ‘Anti-Stokes cooling in highly ytterbium doped phase separated aluminium-yttrium oxide glass by 4 K’, *Optical Materials*, 144 (2023).
2. A. Hlil J. S. boisvert, H. Titi, Y. Garcia-puente, W. Correr, S. Loranger, **J. Thomas**, A. Riaz, Y. Messaddeq and R. Kashyap, ‘Effect of photoinitiators in femtosecond-laser writing’, *ACS Omega*, 8 (2023): 32340–32351.
3. T. Meyneng, **J. Thomas**, N. Grégoire, R. Kashyap and Y. Messaddeq, ‘Controlled phase separation effect for enhanced optical refrigeration in yttrium-aluminosilicate glasses’, *Journal of Materials Chemistry C*, 11(2023): 7619-7628.
4. **J. Thomas**, T. Meyneng, A. Tehranchi, N. Gregoire, F. Monet, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘Demonstration of laser cooling in a novel all oxide GAYY silica glass’, *Scientific Reports*, 13(2023): 5436.
5. **J. Thomas**, T. Meyneng, Y. Ledemi, A. Roberge, F. Monet, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘Enhancing the optical performance of oxyfluoride glass ceramics by optimizing the oxide: fluoride ratio and crystallinity for optical refrigeration’, *Journal of Non-Crystalline Solids X*, 17 (2023): 2590-1591.
6. T. Meyneng, **J. Thomas**, Y. Ledemi, M. Allix, E. Veron, C. Genevois, R. Kashyap and Y. Messaddeq, ‘The role of fluorine in high quantum yield oxyfluoride glasses and glass-ceramics’, *Journal of Alloys and Compounds*, 900 (2022): 163512, 0925-8388.
7. **J. Thomas**, L. J. Q. Maia, K. V. Krishnaiah, Y. Ledemi, J -S Boisvert, A. Hlil, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘Optical properties of ytterbium doped oxyfluoride glassceramics-concentration and temperature dependence studies for optical refrigeration applications’, *Journal of Luminescence*, 238 (2021): 118278.
8. A R. Hlil, **J. Thomas**, Y. Garcia-Puente, J-S Boisvert, B. C. Lima, A. Rakotonandrasana, L. J. Q. Maia, A. Tehranchi, S. Loranger, A. S. L. Gomes, Y. Messaddeq and R. Kashyap,

‘Structural and optical properties of Nd:YAB- nanoparticle-doped PDMS elastomers for random lasers’, Scientific Reports, 11(2021): 16803.

9. A. Hlil, B. C. Lima, **J. Thomas**, J-S. Boisvert, H. Iden, Y. Garcia-Puente, L. J. Q. Maia, Y. Ledemi, Y. Messaddeq, A. S. L Gomes and R. Kashyap, ‘Rare earth doped PDMS elastomeric random lasers’, Optical Materials, 97 (2019): 109387.
10. J-S Boisvert, A. Hlil, I. Hassan, **J. Thomas**, P. Lorre, W. R. Correr, Y. Ledemi, Y. Messaddeq and R. Kashyap, ‘Photosensitised PDMS for femtosecond laser writing’, OSA Continuum, 3 (2020): 1334-1345.
11. P. Sankar, **J. Thomas** and R. Philip, ‘Enhanced bremsstrahlung X-ray emission from Ag nanoparticles irradiated by ultrashort laser pulses’, Optical materials, 92 (2019): 30-35.

Book Chapters

1. **J. Thomas**, L. Maia, Y. Ledemi, Y. Messaddeq and R. Kashyap, ‘Emerging Trends, Challenges, and Applications in Solid-State Laser Cooling’, Oxide Electronics (2021): 353-396.
2. L. J. Q. Maia, **J. Thomas**, Y. Ledemi, K. V. Krishnaiah, Y. Ledemi, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘Photonic properties of novel Yb³⁺ doped germanium-lead oxyfluoride glass-ceramics for laser cooling applications. Frontiers of Optoelectronics, 11 (2018): 189–198.

Conference Articles

1. **J. Thomas**, T. Meyneng, N. Gregoire, F. Monet, A. Tehranchi, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘Laser induced cooling of rare earth doped oxide only silica glass’, Photonic Heat Engines: Science and Applications V, SPIE-Photonics West, January 2023.
2. **J. Thomas**, T. Meyneng, A. Tehranchi, N. Gregoire, F. Monet, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘First demonstration of laser cooling in oxide only GAYY silica glass’, Montreal Photonics Networking Event, December 2022.

3. **J. Thomas**, T. Meyneng, N. Gregoire, F. Monet, A. Tehrani, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'Laser cooling of a novel GAYY glass at atmospheric pressure', in Optica Advanced Photonics Congress 2022, Technical Digest Series, Optica Publishing Group, paper JTh4A.5, July 2022.
4. **J. Thomas**, T. Meyneng, F. Monet, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'Enhanced optical properties of ytterbium doped oxyfluoride glass-ceramics for optical refrigeration', 9th International Conference on Optical, Optoelectronic and Photonic Materials and Applications & 14th Europhysical Conference on Defects in Insulating Materials, July 2022.
5. **J. Thomas**, T. Meyneng, A. Tehrani, P. Manarazan, F. Monet, J. S. Boisvert, S. Morency, N. Grégoire, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'Ytterbium doped nano-crystalline fibers for optical refrigeration', Photonics North, May 2022.
6. **J. Thomas**, T. Meyneng, A. Tehrani, P. Manarazan, F. Monet, J. S. Boisvert, S. Morency, N. Grégoire, D. Seletskiy, Y. Messaddeq, and R. Kashyap, 'Characteristics of Yb-doped silica fibers containing Y_2O_3 nanoparticles for optical refrigeration'. In Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series (Vol. 12018, p. 1201806), March 2022.
7. **J. Thomas**, T. Meyneng, Y. Ledemi, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'Impact of purification on the optical properties of oxyfluoride glass ceramics for laser cooling applications', (JM3A.47) Optica Congress 2021.
8. **J. Thomas**, T. Meyneng, Y. Ledemi, A. Roberge, J-S Boisvert, A. Hlil, D. Seletskiy, L. J. Q. Maia, Y. Messaddeq, and R. Kashyap 'Enhanced anti-Stokes emission in oxyfluoride glass ceramics for optical refrigeration', In Photonic Heat Engines: Science and Applications III, vol. 11702, p. 117020M, International Society for Optics and Photonics, March 2021.
9. J-S Boisvert, A. Hlil, **J. Thomas**, Y. Garcia-Puente, A. Riaz, Y. Ledemi, Y. Messaddeq, and R. Kashyap, 'Photosensitivity functionalization of PDMS for femtosecond laser writing', In Novel Optical Materials and Applications, pp. NoTh1C-4. Optical Society of America, 2020.
10. A. R. Hlil, **J. Thomas**, J-S Boisvert, B. C. Lima, Y. García-Puente, L. J. Q. Maia, Y. Ledemi, Y. Messaddeq, A. S. L. Gomes and R. Kashyap, 'Demonstration of a stable tunable random laser', In Novel Optical Materials and Applications, pp. NoTh1E.6., Optical Society of America, 2020.

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13. A. Hlil, L. J. Q. Maia, **J. Thomas**, J.S Boisvert, H. Iden, Y. Garcia-Puente., Y. Ledemi, Y. Messaddeq, and R. Kashyap, 'Random laser action in Nd:YAB doped polymer', Photonics North, Quebec City, Canada, May 2019.
14. A. Hlil, J. S Boisvert, **J. Thomas**, P. Lorre, I. Hassan, Y. Ledemi, Y. Messaddeq and R. Kashyap 'Novel functionalization of PDMS for photosensitivity', SPIE-Photonics East, San Francisco, California, United States, February 2019.
15. A. Hlil, J. S. Boisvert, **J. Thomas**, P. Lorre, I. Hassan, Y. Ledemi, Y. Messaddeq and R. Kashyap 'Novel functionalization of PDMS for photosensitivity', STARCOM, McGill University, February 2019.
16. **J. Thomas**, L. J. Q. Maia, W. Park, Y. Ledemi, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'Photonic properties of Yb^{3+} doped binary glasses and glass ceramics for optical refrigeration', International Conference on Optical, Optoelectronic and Photonic Materials and Applications, Maresias, Brazil, 26-31 August 2018.
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19. **J. Thomas**, L. J. Q. Maia, W. Park, Y. Ledemi, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'New insights into solid state laser cooling using nano- crystalline oxy-fluoride glass ceramics', Photonics North, Montreal, Canada, 5-7 June 2018.
20. L. J. Q. Maia, **J. Thomas**, K. V. Krishnaiah, Y. Ledemi, D. Seletskiy, Y. Messaddeq and R. Kashyap, 'Laser cooling with anti-Stokes emission in rare earth doped nano-crystalline oxy-

fluoride glass ceramics’, Autumn meeting- Brazilian physical society, Foz do Iguaçu Brazil, 6-11 May 2018.

21. L. J. Q. Maia, **J. Thomas**, K. V. Krishnaiah, Y. Ledemi, D. Seletskiy, Y. Messaddeq and R. Kashyap, ‘Structural and optical characterizations of Yb³⁺ doped GeO₂-PbF₂-PbO glass ceramics for optical refrigeration’, Proceedings of SPIE 10550, Optical and Electronic Cooling of Solids III, 105500O, February 2018.
22. P. Sankar, **J. Thomas and R. Philip** ‘Enhancement of bremsstrahlung X-ray emission from femtosecond laser irradiated metal nanoparticles’ (DAE –BNRS Theme meeting on ultrafast science, UFS 2017, Hyderabad, November 2017.

AWARDS

1. Won third prize in ‘My Thesis in 180 Seconds’ competition (3MT) competition organized by Training and Research Department as well as the Association of Graduate Students (AÉCSP) Polytechnique Montreal during April 2020.
2. Won Merit Scholarship for Foreign Students (PBEEE) during 2019-2021.