Synthesis and characterization of $(Al,Si)_3(Zr,Ti)$-$D0_{22}/D0_{23}$ intermetallics: Understanding the stability of silicon substitution

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Electronic Supplementary Material (ESM)

1. CRYSTAL SITES OF THE $D0_{22}$ AND $D0_{23}$ STRUCTURES

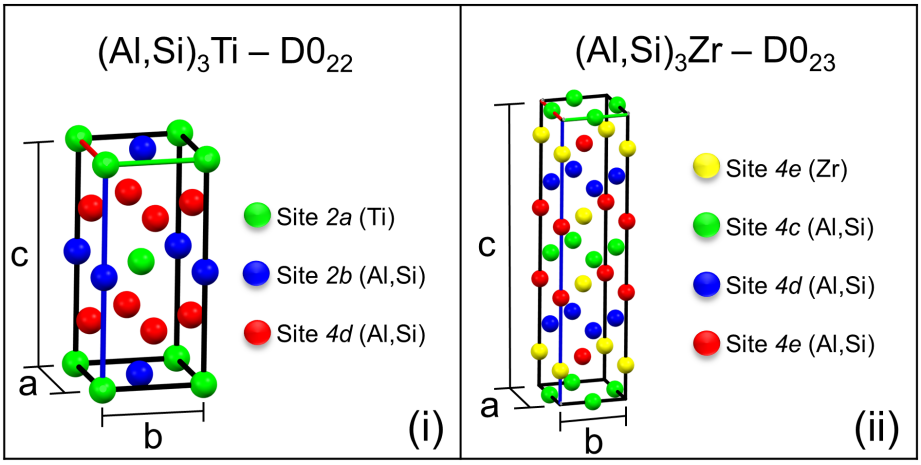


Figure E1. Schematic distribution of crystal sites in $(Al,Si)_3Ti$-$D0_{22}$ (i) and $(Al,Si)_3Zr$-$D0_{23}$ (ii) structures.

2. SIMULATED TEM DIFFRACTION PATTERNS

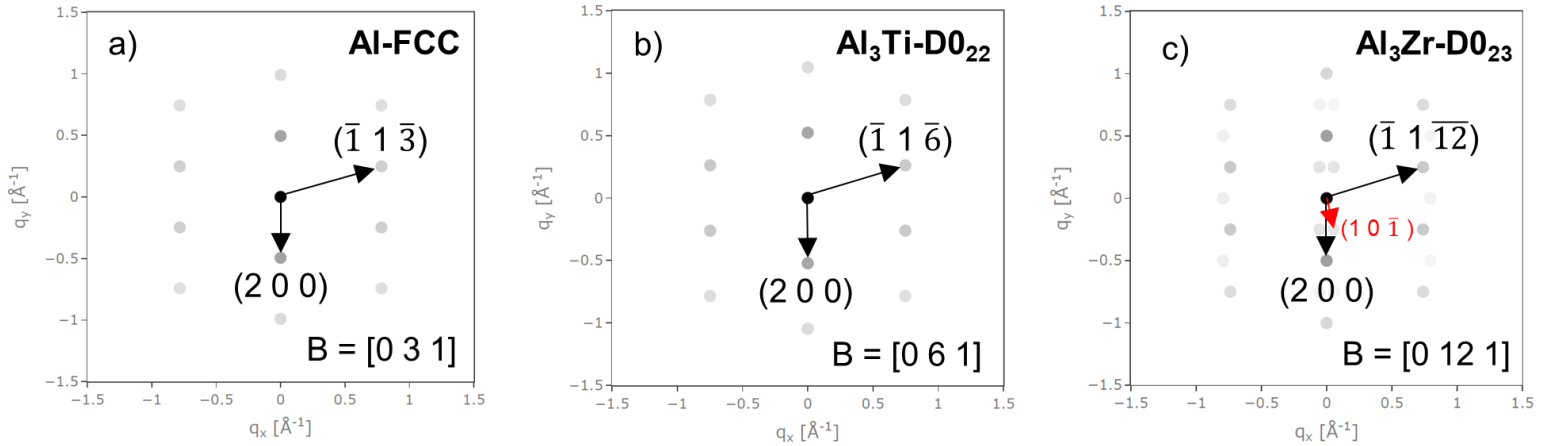
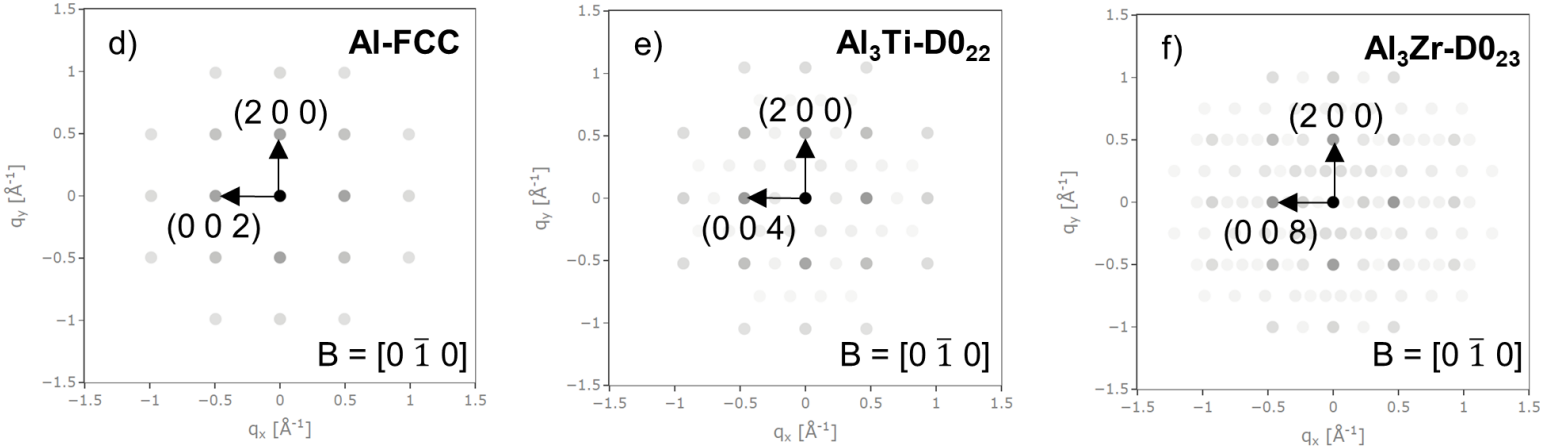
Sample	Simulated TEM diffraction patterns
S2	
S6	

Table E1. Simulated electron diffraction patterns (single crystal) of Al-FCC; Al_3Ti-$D0_{22}$ and Al_3Zr-$D0_{23}$ phases. Patterns were computed using the Diffraction module of the Materials Project (MP) database [1]. Beam directions are equivalent to the TEM experimental measurements of this work. A voltage of 200 kV and a maximum scattering angle of 1.25 Å were specified. (a), (b) and (c) patterns correspond to the conditions of sample S2. (d), (e), and (f) are comparable to experimental TEM measurements of sample S6.

3. FORMATION ENTHALPY OF *END-MEMBERS* IN $D0_{22}$ AND $D0_{23}$ SOLID SOLUTIONS

Table E2. Total energy (E_{tot}) and formation enthalpy (ΔH_f) of the $(Al,Si)_3Ti$-$D0_{22}$ and $(Al,Si)_3Zr$-$D0_{22}$ *end-member*. Reference states are Al ($A1$–fcc), Si ($A4$–*diamond*), Ti ($A3$–hcp) and Zr ($A3$–hcp) pure elements.

Crystal sites			E_{tot}	ΔH_f
			eV	kJ/mol-at
2*a*	**2*b***	**4*d***		
Ti	Al	Al	-41.322	-38.771
Ti	Si	Al	-44.619	-43.959
Ti	Al	Si	-46.715	-34.685
Ti	Si	Si	-49.095	-28.823
Zr	Al	Al	-43.196	-44.329
Zr	Si	Al	-46.456	-49.082
Zr	Al	Si	-48.487	-39.013
Zr	Si	Si	-51.026	-35.070

Table E3. Total energy (E_{tot}) and formation enthalpy (ΔH_f) of the $D0_{23}$ *end-member*. Reference states are Al ($A1$–fcc), Si ($A4$–*diamond*), Zr ($A3$–hcp) and Ti ($A3$–hcp) pure elements.

Crystal sites				E_{tot}	ΔH_f
				eV	kJ/mol-at
4c	**4d**	**4e**	**4e**		
Al	Al	Al	Zr	-86.841	-47.033
Al	Al	Si	Zr	-92.460	-46.353
Si	Al	Al	Zr	-92.239	-45.021
Al	Si	Al	Zr	-92.040	-43.822
Si	Al	Si	Zr	-96.984	-39.072
Al	Si	Si	Zr	-97.763	-43.773
Si	Si	Al	Zr	-96.777	-37.821
Si	Si	Si	Zr	-101.877	-34.013
Al	Al	Al	Ti	-82.721	-39.230
Al	Al	Si	Ti	-88.572	-39.949
Si	Al	Al	Ti	-88.245	-37.977
Al	Si	Al	Ti	-88.170	-37.525
Si	Al	Si	Ti	-93.080	-32.569
Al	Si	Si	Ti	-93.778	-36.778
Si	Si	Al	Ti	-93.104	-32.714
Si	Si	Si	Ti	-97.779	-26.341

4. SITE OCCUPANCY OF METASTABLE *END-MEMBERS*

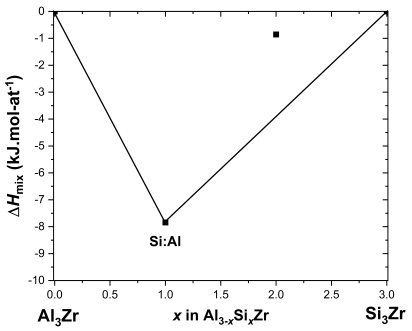


Figure E2. Mixing enthalpy of $(Al,Si)_3Zr$-$D0_{22}$ solid solution calculated by DFT at 0 K. The ground-state *end-member* is labeled with the first element occupying the site $2b$, the second element occupying the site $4d$. The ground-state is represented by the solid black line.

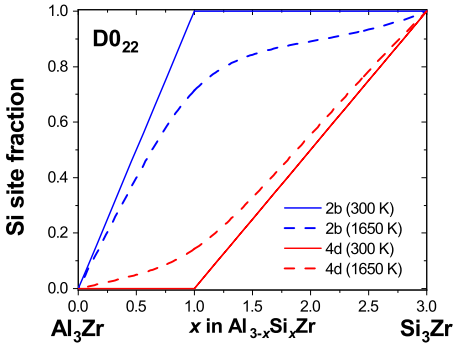


Figure E3. Site fraction of Si on sites $2b$ and $4d$ of the $D0_{22}$ structure calculated at 300 K (solid line) and 1650 K (dashed line).

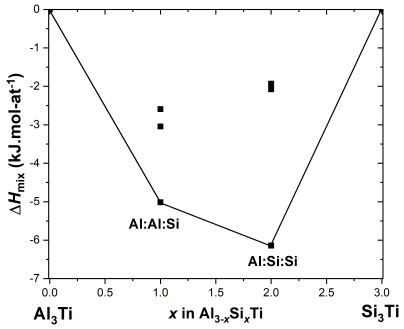


Figure E4. Mixing enthalpy of $(Al,Si)_3Ti$-$D0_{23}$ solid solution calculated by DFT at 0 K. The ground-state *end-member* is labeled with the first, second, and third elements occupying sites $4c$, $4d$ and $4e$, respectively. The solid black line represents the ground state.

REFERENCES

1. A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder *et al.*, "Commentary: The materials project: A materials genome approach to accelerating materials innovation," APL materials **1**, 011002 (2013).