

# Synthesis and characterization of (Al,Si)<sub>3</sub>(Zr,Ti)-D0<sub>22</sub>/D0<sub>23</sub> intermetallics: Understanding the stability of silicon substitution

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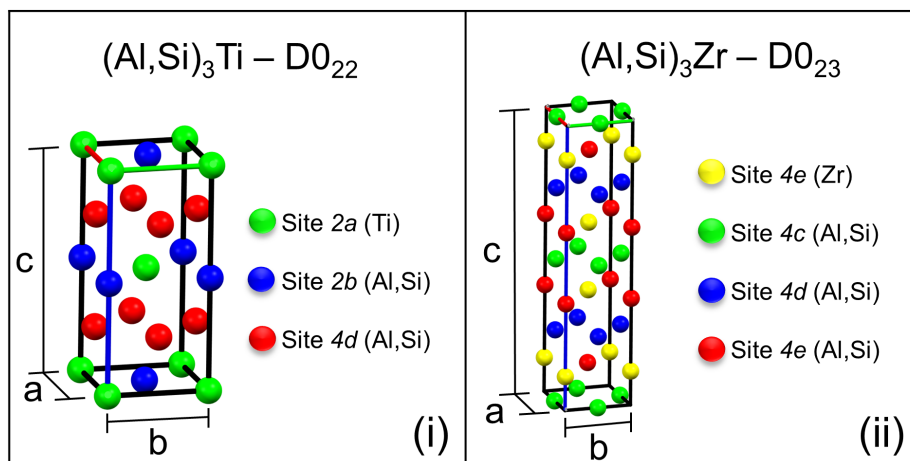
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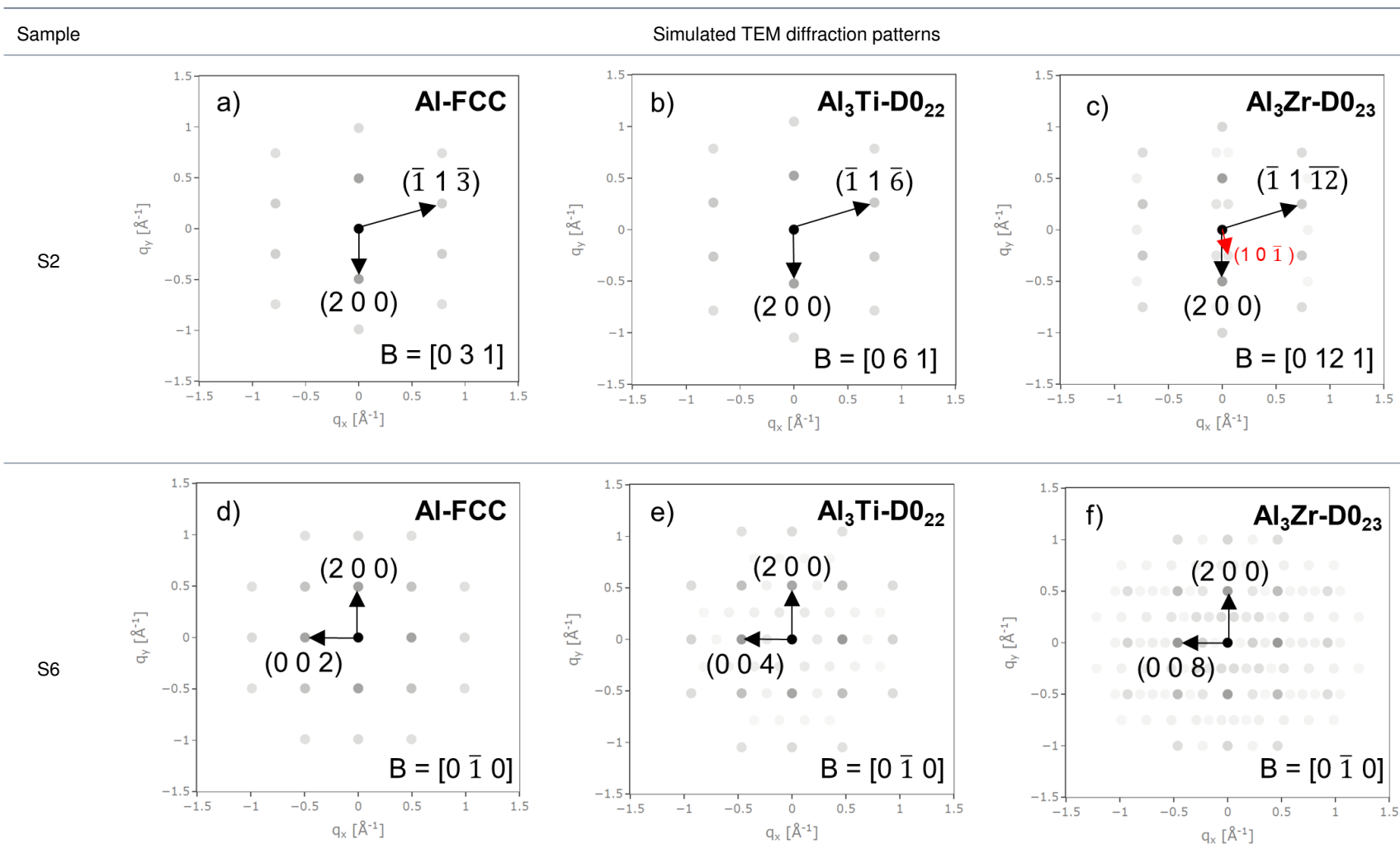
## Electronic Supplementary Material (ESM)

### 1. CRYSTAL SITES OF THE D0<sub>22</sub> AND D0<sub>23</sub> STRUCTURES



**Figure E1.** Schematic distribution of crystal sites in (Al,Si)<sub>3</sub>Ti-D0<sub>22</sub> (i) and (Al,Si)<sub>3</sub>Zr-D0<sub>23</sub> (ii) structures.

## 2. SIMULATED TEM DIFFRACTION PATTERNS



**Table E1.** Simulated electron diffraction patterns (single crystal) of Al-FCC; Al<sub>3</sub>Ti-D0<sub>22</sub> and Al<sub>3</sub>Zr-D0<sub>23</sub> 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<sub>22</sub> AND D0<sub>23</sub> SOLID SOLUTIONS

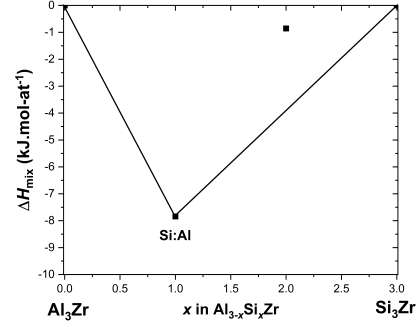
**Table E2.** Total energy ( $E_{tot}$ ) and formation enthalpy ( $\Delta H_f$ ) of the  $(Al,Si)_3Ti$ -D0<sub>22</sub> and  $(Al,Si)_3Zr$ -D0<sub>22</sub> end-member. Reference states are Al (*A1-fcc*), Si (*A4-diamond*), Ti (*A3-hcp*) and Zr (*A3-hcp*) pure elements.

Crystal sites			$E_{tot}$	$\Delta H_f$
2a	2b	4d	eV	kJ/mol-at
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

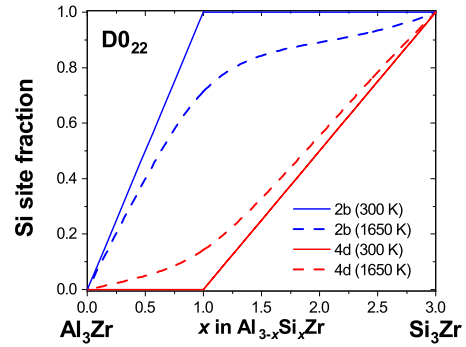
**Table E3.** Total energy ( $E_{tot}$ ) and formation enthalpy ( $\Delta H_f$ ) of the D0<sub>23</sub> end-member. Reference states are Al (*A1-fcc*), Si (*A4-diamond*), Zr (*A3-hcp*) and Ti (*A3-hcp*) pure elements.

Crystal sites				$E_{tot}$	$\Delta H_f$
4c	4d	4e	4e	eV	kJ/mol-at
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

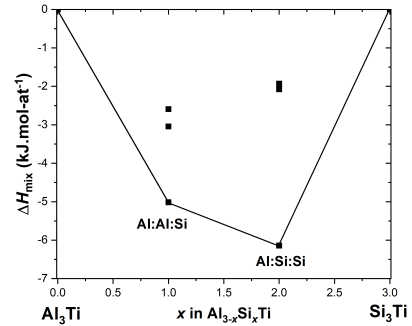
### 4. SITE OCCUPANCY OF METASTABLE END-MEMBERS



**Figure E2.** Mixing enthalpy of  $(Al,Si)_3Zr$ -D0<sub>22</sub> 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<sub>22</sub> structure calculated at 300 K (solid line) and 1650 K (dashed line).



**Figure E4.** Mixing enthalpy of  $(Al,Si)_3Ti$ -D0<sub>23</sub> 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).