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High-pressure synthesis of tetragonal iron aluminide FeAl$_2$

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ABSTRACT

Tetragonal FeAl$_2$ has been predicted a narrow-gap semiconductor stable at ambient pressure. However, only a complex, triclinic FeAl$_2$ has been experimentally observed. We calculated the stability of tetragonal FeAl$_2$ under various pressures and revealed that tetragonal FeAl$_2$ is more stabilized under high pressure. We successfully synthesized tetragonal FeAl$_2$ at 10 GPa and 1873 K with diamond-anvil cell techniques. The X-ray diffraction pattern of the sample was unchanged after releasing the pressure; that is, the pressure-induced transformation is irreversible. We also calculated the transport properties of tetragonal FeAl$_2$. The results indicate that tetragonal FeAl$_2$ is a promising candidate for thermoelectric materials.

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Thermoelectric materials have received a great amount of attention because they can contribute to the global energy demand by waste-heat recovery. The performance of thermoelectric materials is evaluated by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and temperature, respectively. Unfortunately, state-of-the-art materials like Bi$_2$Te$_3$ [1] and PbTe [2] contain highly toxic and/or expensive elements. For wide use of thermoelectric materials, low-cost nontoxic materials with high ZT are highly desirable. Iron aluminides are thus favorable for thermoelectric materials because of their abundance and environmentally benign constituent elements, but none of the experimentally observed Fe-Al intermetallic compounds behave as semiconductors.

A number of intermetallic compounds, such as full- and half-Heusler compounds [3,4], RuGa$_3$ [5,6], RuIn$_3$ [6,7], and RuGa$_2$ [8–11], exhibit semiconducting behaviors and are of interest because of their thermoelectric properties. The group VIII transition metal di-aluminides RuAl$_2$ and OsAl$_2$ are also semiconductors [10–14] crystallized in TiSi$_2$- and MoSi$_2$-type structures [15,16], respectively. Theoretical studies of the electronic structures of FeAl$_2$ crystallized in TiSi$_2$-, CrSi$_2$-, and MoSi$_2$-type structures, which are all relatively simple and similar structures, indicate that these phases are narrow-gap semiconductors [17,18]. Among these three structures, MoSi$_2$-type tetragonal FeAl$_2$ (t-FeAl$_2$, space group $I4/mmm$, Fig. 1(a)) is most energetically stable [18], but none of above FeAl$_2$ phases have been successfully synthesized. Instead, a low-density, disordered phase a-FeAl$_2$ (space group P-1 [19], Fig. 1(b)) is experimentally obtained after heat treatment. This metallic phase, which is slightly less stable than t-FeAl$_2$ in terms of enthalpy, has predicted to be stabilized above 380 K due to the contribution of vibrational entropy [20]. However, if the enthalpy of a-FeAl$_2$ is increased by applying external pressure, t-FeAl$_2$ will become the most stable phase even at the heat treatment temperatures.

High pressure is a useful tool to synthesize new solid-state phases that are not observed at ambient pressure. The features of phases synthesized under high pressure are as follows: (a) the space group and structure of the high-pressure phase should show the same structural trend as the phases containing the same group element at ambient pressure, which is known as the pressure-homology rule [21]; and (b) closely packed structures should be more stable under high pressure, which is known as the pressure-coordination rule [21]. In the case of t-FeAl$_2$, the following two facts satisfy these concepts: (1) RuAl$_2$ and OsAl$_2$ crystallize in the family of MoSi$_2$-type structures; and (2) the atomic volume of t-FeAl$_2$ is 12.7 Å^3/atom, while that of a-FeAl$_2$ is 13.8 Å^3/atom. Thus, it is possible that t-FeAl$_2$ can be synthesized by pressure-induced transformation from a-FeAl$_2$. Here, we report a computational and experimental study of t-FeAl$_2$. We calculated the stability of t-FeAl$_2$ under high pressure, predicted its thermoelectric properties, and synthesized it under high pressure using a laser-heating diamond-anvil cell.

We used Quantum ESPRESSO [22] to perform first-principles total energy calculations under ambient and high pressure at $T = 0$ K. The generalized gradient approximation (GGA) functional with the Perdew–Burke–Ernzerhof (PBE) parameterization [23] was used for

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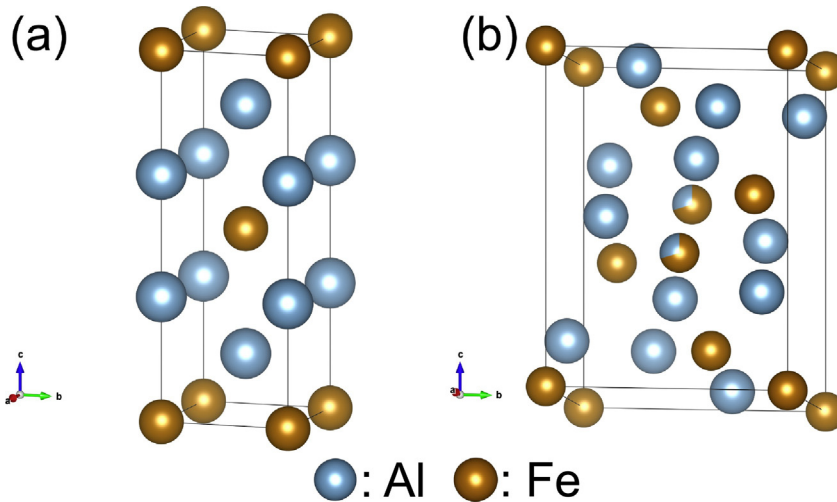E-mail address: t.kazuki52@phys.mm.t.u-tokyo.ac.jp (K. Tobita).

Fig. 1. Crystal structures of (a) *t*-FeAl₂ and (b) *a*-FeAl₂ visualized by VESTA 3 [37]. The blue and yellow spheres represent Al and Fe atoms, respectively. The partially colored spheres represent mixed occupancy sites of Al 29.5% and Fe 70.5%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the exchange and correlation potentials. The projector augmented wave (PAW) method [24] was employed with pseudopotentials Fe.pbe-spn-kjpaw_psl.UPF and Al.pbe-n-kjpaw_psl.UPF available at Quantum ESPRESSO pseudopotential library [25]. We relaxed all of the atomic positions and lattice parameters considering the possibility of spin polarization of Fe atoms. The cutoff energy for the plane wave basis was chosen to be 80 Ry, and we used an $8 \times 8 \times 8$ *k*-mesh based on the Monkhorst–Pack scheme [26]. As shown in Fig. 1(b), *a*-FeAl₂ contains two equivalent sites in a mixed occupancy of 29.5% Al and 70.5% Fe. The three possible arrangements of Al and Fe in a single unit cell [20] were labeled as "AA", "AF" and "FF" by taking the capital of each element. Although molar fractions of these arrangements are out of range of the *a*-FeAl₂ phase in any of the currently available phase diagrams of the Fe-Al binary system [27,28], the use of "FFFA" arrangement for $2 \times 1 \times 1$ supercell does not exhibit further decrease in formation enthalpy [20]. Thus, we only considered three arrangements of Al and Fe (AA, AF, and FF) for single-cell. Given the total energies (E), volume (V) and pressure (P) of a variety of structures, we calculated the enthalpy ($H = E + PV$) at 0, 10 and 20 GPa. We investigated the relative enthalpy of *t*-FeAl₂ and *a*-FeAl₂ at molar fraction of Al $x_{\mathrm{Al}} = 0.6667$ by subtracting enthalpy of *a*-FeAl₂ from that of *t*-FeAl₂. Among the three arrangements of *a*-FeAl₂, we used $1/3 \times H$ (*a*-FeAl₂ (FF)) + $2/3 \times H$ (*a*-FeAl₂ (AF)) as H (*a*-FeAl₂) because we obtained the most energetically stable *a*-FeAl₂ structure with this combination. The neighboring phase composite FeAl + Fe₂Al₅ was also considered in the present study because Krasnowski et al. [29] reported that mechanically alloyed nanocrystalline Fe₃₅Al₆₅ transforms to FeAl + Fe₂Al₅ after compression at 7.7 GPa and 1273 K.

According to the calculation at ambient pressure, *t*-FeAl₂ was the most stable structure, which is in good agreement with previous work [20]. Fig. 2 shows the pressure dependence of the relative enthalpies of the various structures with respect to *a*-FeAl₂. The relative enthalpy of *t*-FeAl₂ decreased from −0.04 eV/atoms (at 0 GPa) to −0.13 eV/atoms (at 20 GPa). Although the contribution of entropic terms destabilizing *t*-FeAl₂ will increase as temperature increasing, the contribution of the relative enthalpy stabilizing *t*-FeAl₂ will also increase as pressure increasing. We can thus say that high pressure effectively expands the temperature range in which *t*-FeAl₂ is stable and be favorable to synthesize *t*-FeAl₂. However, decomposition to FeAl + Fe₂Al₅ was also stabilized under pressure, which can be explained by the smaller average atomic volume of FeAl + Fe₂Al₅ (13.2 Å³/atom) than that of *a*-FeAl₂ (13.8 Å³/atom).

We synthesized the mother ingots of *a*-FeAl₂ from stoichiometric mixtures of iron powder (99.9%, Kojundo Chemical Lab. Co., Ltd.) and

aluminum shot (99.99%, Kojundo Chemical Lab. Co., Ltd.) by arc-melting. For homogenization, the arc-melted ingots were annealed at 1173 K for 72 h by a procedure described in the literature [27]. The ground powder was sandwiched between two MgO pellets and loaded into a sample chamber sealed with a rhenium gasket. A small ruby ball was mounted inside the gasket to serve as an internal pressure marker, and the pressure was estimated by the fluorescence spectrum of ruby [30]. Pressure of 10 or 20 GPa was applied by a diamond-anvil cell with laser heating at 1873 and 2123 K, respectively. Characterization of the samples before and after heating was performed by X-ray diffraction (XRD) with Mo Kα radiation.

Before the heating process, the XRD pattern of the sample compressed at 20 GPa was identified as *a*-FeAl₂ (see Fig. 3(a)). However, the XRD pattern drastically changed after heating at 2123 K. The observed peaks at $2\theta = 9.95°$ and 14.79° were identified as the (002) and (101) reflections of *t*-FeAl₂, respectively. We also observed the same XRD patterns for the sample synthesized at lower pressure and temperature (10 GPa and 1873 K). Fig. 3(b) shows the XRD pattern after the pressure was released from 10 GPa to atmospheric pressure. Most of the peaks were indexed to the computationally optimized structure of *t*-FeAl₂. However, some peaks that cannot be identified as existing Fe–Al intermetallic compounds are present before and after heating, such as those at $2\theta = 16.14°$, 16.74°, and 19.29°. These peaks
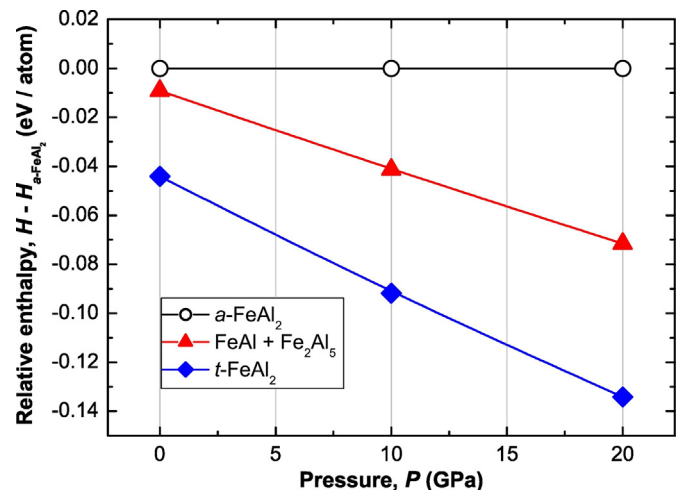

Fig. 2. Relative enthalpies (with respect to *a*-FeAl₂) of *t*-FeAl₂ and FeAl + Fe₂Al₅ as a function of pressure.