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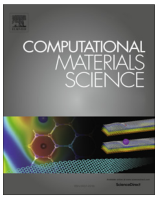

First-principles investigation of mechanical, thermodynamic and electronic properties of $FeSn_5$ and $CoSn_5$ phases

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ABSTRACT

The mechanical, thermodynamic and electronic properties of $FeSn_5$ and $CoSn_5$ intermetallic phases at zero pressure have been systemically investigated by first-principles calculations using ultrasoft pseudopotential and generalized gradient approximation (GGA). The equilibrium lattice constants of $FeSn_5$ and $CoSn_5$ at zero pressure are in good agreement with the available experimental values. Thermodynamic and mechanical properties of $FeSn_5$ and $CoSn_5$ are predicted by calculating formation enthalpy, phonon density of states and elastic constants, respectively. Formation enthalpies calculation indicates that $FeSn_5$ and $CoSn_5$ are energetically unfavorable compare to $FeSn_2$ and $CoSn_2$. This may be the partial reason why $FeSn_5$ and $CoSn_5$ were hidden in the Fe/Co–Sn phase diagrams previously. $FeSn_5$ and $CoSn_5$ exhibit opposite relative incompressible behavior along *a*-axis and *c*-axis. Our results reveal that both $FeSn_5$ and $CoSn_5$ are mechanically and dynamically stable at 0 GPa. The quasi-harmonic model is employed to calculate the temperature dependence of specific heat at constant volume. In addition, the electron density of states and electron density difference are calculated to disclose the underlying electronic structure.

1. Introduction

As the potential anode materials for lithium-ion battery, tin-based materials possess higher theoretical capacity ($Li_{4.4}Sn$: 994 mA h/g) compared to conventional graphite (372 mA h/g) [1–3]. However, it should be noted that the pure tin metal electrode suffers from unfavorable volume expansion–contraction during the lithium-ion alloying–dealloying process, leading to a short cycle life. Much attention has been focused on searching for alternative materials not only maintain the high capacity of tin but reduce the volume change has generated considerable research activity [4]. One promising approach is to introduce an electrochemical inactive metal element (M) as a confining buffer to form M–Sn intermetallic compounds [5–10]. In recent years, Wang and his coworkers prepared uniform nanospheres of the intermetallic $FeSn_5$ and $CoSn_5$ phases by a nanocrystal conversion chemistry method [11,12]. These two intermetallic phases were not established in the existing Fe–Sn and Co–Sn binary phase diagrams [11,12]. The Fe-deficient $FeSn_5$ ($Fe_{0.74}Sn_5$) anode demonstrated best-in-class theoretical capacity of 929 mA h/g among the existing M–Sn alloys [11]. This finding is notable since iron is low-cost and environmentally benign. On the other hand, the Co-deficient $CoSn_5$ ($Co_{0.83}Sn_5$) anode (theoretical capacity of 917 mA h/g) showed a longer cycle life than that of $FeSn_5$ [12]. Structural and electrochemical properties of these phases were characterized experimentally [9,11–14], however, the results of mechanical, thermodynamic and electronic properties were still lacking. Since these properties are important not only for revealing the formation mechanism of these phases but for the application in Li ion batteries, it is necessary to investigate and discuss them thoroughly. In this paper, we performed a systematic density functional theory (DFT) to study the mechanical, thermodynamic and electronic properties of $FeSn_5$ and $CoSn_5$.

2. Computational details

The DFT calculations were carried out using the plane-wave basis-set and Vanderbilt-type ultrasoft pseudopotential [15]. The valence electron configurations for Fe, Co, and Sn are $3d^24s^6$, $3d^24s^7$ and $5s^25p^2$, respectively. The Perdew–Burke–Ernzerhof (PBE) parameterization utilizing spin-polarized generalized-gradient approximation (GGA) scheme was employed for the exchange–correlation functional [16]. A plane wave cut-off energy

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of 450 eV was chosen, and Brillouin zone integration was performed over 10 × 10 × 11 grid points using the Monkhorst–Pack scheme [17]. These parameters ensure sufficient convergence to achieve reliable results for both total energy and the elastic constants. For geometry optimization, the tolerances for difference in total energy, the maximum ionic Hellmann–Feynman force, the stress tensor and the maximum displacement are within 5.0×10^{-7} eV/atom, 0.01 eV/Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively. The elastic stiffness constants c_{ij} ($i, j = 1, 2, 3, 4, 5, 6$) were calculated by $c_{ij} = \sigma_{ij}/\varepsilon_{ij}$, where σ and ε denote elastic stress and strain, respectively, and the subscripts the Cartesian coordinates of the considered structures. In practice, the maximum strain amplitude was set from −0.003 to 0.003 with the step of 0.001. The bulk modulus (B) and shear modulus (G) were calculated via the Voigt–Reuss–Hill average scheme [18]. After directly calculating the phonon frequencies on Monkhorst–Pack q-vector grid of separation of 0.025 $Å^{-1}$ within the finite displacement approach, the results were interpolated onto a very dense q-point set to obtain the phonon density of state. Furthermore, phonon related thermodynamic property such as heat capacity was evaluated in a quasi-harmonic approximation [19]. In addition, the formation enthalpy of MSn_5 (in the following parts, M represents Fe or Co, if not specified otherwise) was estimated by the following equation: $\Delta H_f = E_{tot}(MSn_5) - E_{tot}(M) - 5E_{tot}(Sn)$, where $E_{tot}(MSn_5)$ is the obtained total energy of MSn_5 at equilibrium volume and $E_{tot}(M)$ and $E_{tot}(Sn)$ are the respective total energies of pure M (*bcc*-Fe, or *hcp*-Co) and Sn metals (diamond cubic) at zero pressure. All the total energy calculations were performed in plane-wave code CASTEP [20]. The pressure effect for the properties of MSn_5 will be investigated in the future. In this work, if it is not specified, the calculation is carried out under zero pressure.

3. Results and discussion

3.1. Structural properties and formation enthalpies

$FeSn_5$ and $CoSn_5$ are tetragonal in the *P4/mcc* group (Fig. 1). The atomic coordinates of $FeSn_5$ [Fe (1/2, 1/2, 1/4), Sn_1 (0, 0, 1/2), Sn_2 (0.190, 0.607, 1/2)] and $CoSn_5$ [Co (1/2, 1/2, 1/4), Sn_1 (0, 0, 1/2), Sn_2 (0.191, 0.610, 1/2)] refined by synchrotron powder X-ray diffraction (XRD) [11,12] were used to build the initial structures. The calculated structural parameters of $FeSn_5$ and $CoSn_5$ at zero pressure together with the experimental data are illustrated in Table 1. It can be seen that the calculated lattice parameters within the GGA agree well with the experimental results [11,12]. The slight overestimation is within the permissible range of DFT method, consequently the methodology implemented in this work is reliable.

Table 1
Calculated structural parameters together with the experimental data (a and c in Å, V in $Å^3$) of $FeSn_5$ and $CoSn_5$ at zero pressure.

		a	*c*	*c/a*	*V*
$FeSn_5$	GGA	6.992	5.901	0.844	288.55
	Exp [11]	6.914	5.890	0.852	281.56
$CoSn_5$	GGA	7.052	5.881	0.834	292.45
	Exp [12]	6.933	5.792	0.836	278.40

The distances between Fe/Co and their nearest Sn atoms are 2.708 and 2.727 Å, respectively. Meanwhile, according to the Mulliken charge population [21], the atomic charges of Fe and Co are −0.63 and −0.59, respectively. The atomic charge of Sn atoms around Fe and Co are 0.18 and 0.17, respectively. In fact the absolute magnitude of atomic charge yielded by Mulliken charge population analysis has little physical meaning. However, the relative values can yield useful information [21]. The relative bond length and relative atomic charge population indicates that the bonding strength of Fe–Sn is stronger than that of Co–Sn.

To gain deep insight into the structural stability, the formation enthalpies of $FeSn_5$ and $CoSn_5$ were calculated. A negative value denotes the structural stability with respect to the elemental constituents. Here, the formation enthalpies of $FeSn_5$ and $CoSn_5$ are −0.067 eV/atom and −0.088 eV/atom, receptivity. It can be seen that these phases are thermodynamically stable and can be synthesized at ambient conditions. Furthermore, $CoSn_5$ has the smaller formation enthalpy, which demonstrated that $CoSn_5$ is more thermodynamically stable compared to $FeSn_5$. In order to discuss the formation mechanism of MSn_5, we also calculated the formation enthalpies of $FeSn_2$ and $CoSn_2$ (two existing intermetallic phases in the earlier phase diagrams). It is notable that under the same calculation condition, the obtained formation enthalpies of $FeSn_2$ and $CoSn_2$ are −0.148 and −0.177 eV/atom, which are significant smaller than those of $FeSn_5$ and $CoSn_5$. The formation enthalpy difference between MSn_5 and MSn_2 hints that MSn_5 is not the most thermodynamically stable against decomposition into mixtures of *bcc*-Fe/*hcp*-Co and diamond cubic Sn. In Ref. [11], by comparing the crystal structures of $FeSn_5$ and $FeSn_2$, the authors suggested that FeSn5 may be one intermediate phase between Sn and $FeSn_2$ [11]. In our work, the results based on the formation enthalpies calculation confirm their hypothesis. The unfavorable formation enthalpies might be the partial reason why MSn_5 was hidden in the earlier M–Sn binary phase diagrams.

3.2. Mechanical properties

To obtain the mechanical stability of $FeSn_5$ and $CoSn_5$, elastic constants of these two phases were calculated. Elastic constants

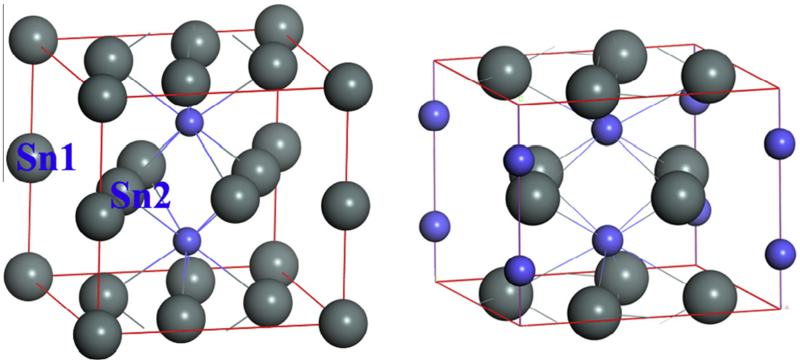

Fig. 1. Crystal structures of MSn_5 (left) and MSn_2 (right), where M is Fe or Co (left graph). The grey ball represents Sn atom, while blue ball represents M atom. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)