Influence of M/A substitution on material properties of intermetallic compounds MSn₂ (M = Fe, Co; A = Li, Na): A first-principles study

Chol-Jun Yu^a, Un-Song Hwang^b, Yong-Chol Pak^a, Kyonga Rim^a, Chol Ryu^a, Chon-Ryong Mun^a, Un-Gi Jong^a,b

^aChair of Computational Materials Design, Faculty of Materials Science, Kim Il Sung University, Ryongnam-Dong, Taesong District, Pyongyang, Democratic People’s Republic of Korea
^bNatural Science Center, Kim Il Sung University, Ryongnam-Dong, Taesong District, Pyongyang, Democratic People’s Republic of Korea

Abstract
Iron and cobalt distannides MSn₂ (M = Fe, Co) are regarded as a promising conversion-type anode material for lithium- and sodium-ion batteries, but their properties are not well understood. In this work, we report a first-principles study of alkali metal (A = Li, Na) substitutional effect on the structural, mechanical, lattice vibrational, electronic and defect properties of these distannides. Special attention is paid to systematic comparison between FeSn₂ and CoSn₂. Our calculations reveal that M/A substitution induces a lattice expansion and decrease of elastic constants, which is more announced with Na substitution than Li, and moreover changes the elastic property of FeSn₂ from ductile to brittle whereas preserves the ductility of CoSn₂. An imaginary phonon frequency mode appears only for FeSn₂ and FeNaSn₂, and M/A substitution provokes a definite gap between high and low frequency regions. We perform a careful analysis of electronic density of states, band structures and Fermi surface, providing an insight into difference of electronic structures between FeSn₂ and CoSn₂. With further calculation of defect formation energies and alkali ion diffusion barriers, we believe this work can be useful to design conversion-type anode materials for alkali-ion batteries.

Key words: Iron distannide, Cobalt distannide, Electronic structure, Defect, First-principles

1. Introduction
Alkali (lithium and sodium) ion batteries have been attracting considerable attention as a promising power source of electronic devices and electric vehicles due to their high energy density and long cycle life. When compared with lithium, sodium has a merit of resource abundance on the Earth’s crust, leading to apparent cost lowering of battery production and thus enabling sodium ion batteries (SIBs) to be commercially viable for electric vehicles and stationary energy storage [1]. However, no optimal electrode materials have yet been developed as some scientific challenges unresolved [2, 3]. In particular, since graphite, the commercial intercalation-type anode material for lithium ion batteries (LIBs), exhibits extremely low specific capacity when reacting with sodium, numerous works have been devoted to finding suitable anode materials for SIBs [4].

The key issues in development of high performance anode materials can be summarized as high reversible capacity, long cycle life, and high rate capability. With these respects, several kinds of anode materials with their own merits and demerits have been found so far, including carbon- and alloy-based materials, metal oxides and 2D materials [5]. Among these, alloy-based materials have earned a remarkable interest because of their high capacity and low redox potential, in spite of their critical problem of poor cycling stability. Typically, metallic β-Sn is a conversion-type anode material for both LIBs and SIBs, exhibiting maximum theoretical capacities of 994 mAh/g for complete conversion of Li₂Sn₃ [6] and 847 mAh/g for Na₃Sn [7, 8, 9]. However, the application of β-Sn as anode material is limited by its fast fading of performance due to the low electronic conductivity of Sn and in particular large volume changes of ~300% for Li and 420% for Na during the charge/discharge processes, leading to crack and pulverization of Sn particles and depletion of electrolyte.

As one way to mitigate such problems, active β-Sn has been proposed to be alloyed with inactive transition metals that do not directly react with lithium and sodium during cycling [11, 12, 13, 14]. The transition metals were known to lessen the volume change by forming a buffer framework, enhance the electric conductivity, limit the coalescence and increase the dispersion of Li− or Na−Sn particles [14, 15]. Accordingly, iron and cobalt have already been used with tin to form FeSn₂ and CoSn₂ alloys as promising anode materials with high capacity and stable cycling performance for SIBs [16, 17, 18, 19, 20] as well as LIBs [21, 22, 23]. Recently, Vogt and Villevielle [17, 18] have reported that these alloys can achieve high capacities of up to 680 mAh/g when fully converted to Na₃Sn (twice larger than hard carbon), demonstrating the significant influence of inactive metals on the reaction mechanism. In addition, their composites with carbon [24, 25, 26, 27] and other materials [28, 29] have been found to exhibit highly stable electrochemical performance as anodes for both LIBs and SIBs. Despite such extensive experimental studies, no theoretical study of FeSn₂ and CoSn₂ in terms of Li or Na reaction has yet reported, except some first-
principles studies of Fe− and Co−Sn alloys [30, 31].

In this work, we have investigated the electronic structures, lattice vibrational and elastic properties, and point defect energetics of FeSn 2 and CoSn 2 as reacting with Li and Na, by using first-principles calculations within the density functional theory (DFT) framework. We first determined the lowest energy spin configurations of FeSn 2 and CoSn 2 by conducting structural optimizations, and using these structures, calculated their electronic band structures with partial density of states (PDOS), elastic constants and phonon dispersion curves. Then we have investigated their chemical reactivity with sodium and lithium by estimating the formation energies of point defects including vacancies and antisites in bulk. Systematic comparison between Fe and Co was provided in each calculation.

2. Theoretical methods

2.1. Structural models

The compounds FeSn 2 and CoSn 2 are known to crystallize in the CuAl 1-type tetragonal structure with a space group of I4/mcm [32]. As shown in Fig. 1a, there are four formula units (12 atoms) in the conventional unit cell, where transition metal atoms occupy the 4a (0, 0, 0.25) sites and Sn atoms locate at the 8h (x, 0.5+x, 0) sites (x = 0.1611 in FeSn 2 and 0.1649 in CoSn 2) [32]. In order to study the influence of reaction with Li and Na on their properties, we consider M/A exchange structural models (M = Fe, Co; A = Li, Na), which were constructed by replacing one Fe or Co atom with Li or Na atom in the conventional unit cell, leading to formation of tetragonal M 3/4 A 1/4 Sn 2 (or simply MASn 2) compound with a space group of P422, as shown in Fig. 1b. Also we constructed the 2×2×2 supercells (96 atoms) to study lattice vibration properties and furthermore point defects including vacancies (V M and V Sn ) and substitutions (A M and A Sn ).

2.2. Computational details

All the DFT calculations have been carried out by applying the pseudopotential plane wave method as implemented in QUANTUM ESPRESSO (QE, version 6.2) package [33]. For a description of the Coulombic interaction between the ionic cores and the valence electrons, we have constructed the ultrasoft pseudopotentials of the atoms by executing LD1 code included in the QE package, using the input files provided in the PS library (1.0). The valence electron configurations of atoms are Na: 3s 2 , Li: 1s 2 2s 1 2p 1 , Fe: 3s 2 3p 6 3d 6 4s 2 , Co: 3s 2 3p 6 3d 7 4s 2 , and Sn: 4d 10 5s 2 5p 2 . The Perdew-Burke-Ernzerhof (PBE) formulation [34] within generalized gradient approximation (GGA) was adopted to describe the exchange-correlation interaction among the valence electrons.

Structural optimizations of the conventional unit cells containing 4 formula units were carried out with the kinetic cutoff energies of 60 Ry for wave function and 600 Ry for electron density, and the special k-points with a (8×8×10) mesh. The atoms were relaxed until the forces converged to 5×10 −4 Ry/Bohr, while the crystalline lattices were allowed to vary until the pressure became less than 0.005 GPa. To achieve a convergence of self-consistent cycle, the Methfessel-Paxton first-smearing method was applied with a gaussian spreading parameter of 0.02 Ry. For the calculation of energy band structures and density of states (DOS), we used a denser k-point mesh of (10×10×12) with a tetrahedron occupation. In these calculations, spin-polarization effect was considered by applying three different magnetic orderings such as ferromagnetic (FM), anti-ferromagnetic (AFM) and non-magnetic (NM) states. The phonon dispersion curves and the corresponding phonon DOS were calculated using the finite displacement method, as implemented in Phonopy code [35]. The 2×2×2 supercells were adopted with reduced k-point sampling of (2×2×2) in accordance to the larger size of supercell, while the (30×30×30) q-point mesh was used for the phonon DOS calculation. The six independent elastic stiffness constants were determined based on the efficient stress-strain method, in which a set of homogeneous deformations with maximum strain amplitude of 0.005 GPa were applied and the resulting stress with respect to the internal degrees of freedom was calculated. Once obtained the elastic stiffness matrix, the elastic compliance constants were also evaluated by calculating the inverse matrix.

In the defect calculations, all the atoms were relaxed while fixing the lattice constants, with reduced computational parameters such as cutoff energy of 30 Ry and k-point mesh of (2×2×2). Moreover, we determined the activation barriers for Li and Na atom diffusion along the vacancy-mediated paths by applying the climbing image nudged elastic band (NEB) method [36]. During the NEB run, the supercell sizes were 2

Figure 1: Crystalline structure of conventional unit cell for (a) MSn 2 (M = Fe, Co) with four formula units and (b) M 3/4 A 1/4 Sn 2 (A = Li, Na). Upper and lower panels show top and perspective views respectively. Blue-colored arrows indicate the spin direction of transition metal atoms, indicating the antiferromagnetic (AFM) configuration here.
fixed at the optimized ones, and all the atoms were allowed to relax. The number of NEB image points was seven, and the convergence threshold for force on the elastic band was 0.05 eV/Å. Visualization of crystalline lattice and volumetric data of charge density was performed by using the VESTA code. 

2.3. Theory

The mechanical properties of a polycrystalline solid are estimated by elastic moduli such as bulk (B), shear (G) and Young’s (E) moduli. These can be determined from the set of elastic stiffness (Cij) and compliance (Sij) constants calculated for a single crystal. There are six independent elastic constants for tetragonal structure: \( ij = 11, 12, 13, 33, 44 \) and 66. The bulk and shear moduli can be determined using the stiffness constants within the Voigt approximation as follows,

\[
B_v = \frac{2C_{11} + C_{33} + 2(C_{12} + 2C_{13})}{9}, \quad G_v = \frac{2C_{11} + C_{33} - (C_{12} + 2C_{13}) + 3(2C_{44} + C_{66})}{15}
\]  

(1)

Meanwhile, they can also be calculated using the compliance constants within the Reuss approach as follows,

\[
B_r = \frac{1}{\frac{2S_{11} + S_{33} + 2(S_{12} + 2S_{13})}{15}}, \quad G_r = \frac{4(2S_{11} + S_{33}) - 4(S_{12} + 2S_{13}) + 3(2S_{44} + S_{66})}{15}
\]  

(2)

As indicated by Hill, the Voigt and Reuss approaches yield the lower and upper limits of the polycrystalline moduli and the real moduli are estimated by arithmetic mean value as follows,

\[
B = \frac{B_v + B_r}{2}, \quad G = \frac{G_v + G_r}{2}
\]  

(3)

Then, the Young’s modulus and Poisson’s ratio (\( \nu \)) are evaluated from the calculated bulk and shear moduli as follows,

\[
E = \frac{9BG}{3B + G}, \quad \nu = \frac{3B - 2G}{6B + 2G}
\]  

(4)

The elastic moduli can be used to determine the longitudinal (\( \nu_l \)) and transverse (\( \nu_t \)) elastic wave velocities as follows,

\[
\nu_l = \sqrt{\frac{3B + 4G}{3\rho}}, \quad \nu_t = \sqrt{\frac{G}{\rho}}
\]  

(5)

where \( \rho \) is the density. Using these values, the average sound velocity \( \nu_m \) is evaluated as follows,

\[
\nu_m = \left[ \frac{1}{3} \left( \frac{2}{\nu_l^3} + \frac{1}{\nu_t^3} \right) \right]^{-1/3}
\]  

(6)

Then, as an important thermodynamic parameter for checking the degree of mechanical properties, the Debye temperature \( \theta_D \) is estimated using the following equation,

\[
\theta_D = \frac{h}{k_B} \left[ \frac{3N}{4\pi V} \right]^{1/3} \nu_m
\]  

(7)

where \( h \) and \( k_B \) are the Plank’s and Boltzmann’s constants, \( N \) the number of atoms in the unit cell and \( V \) the unit cell volume.

The formation energy of point defect \( D \) is calculated using the total energies as follows,

\[
E_f = E[D] - E_{\text{perf}} - \sum_i n_i \mu_i
\]  

(8)

where \( E[D] \) and \( E_{\text{perf}} \) are the total energy of compounds with and without defect, and \( n_i \) is the number of added (\( n_i > 0 \)) or removed (\( n_i < 0 \)) \( i \)-type species with a chemical potential of \( \mu_i \). The chemical potential of metal atoms were estimated as the total energy per atom in their bulk systems: \( \text{bcc-Fe, hcp-Co, diamond cubic-Sn, and bcc-Li or -Na.} \)

To check the thermodynamic stability of the compound with defect, its formation enthalpy per formula unit was calculated as follows,

\[
\Delta H_{\text{m-A}_x}\text{Sn}_y = \frac{E_{\text{M}_{n\text{A}_x}\text{Sn}_y} - mE_M - nE_A - 2E_{\text{Sn}}}{m + n + 2}
\]  

(9)

where \( E_{\text{M}_{n\text{A}_x}\text{Sn}_y} \), \( E_M \), \( E_A \) and \( E_{\text{Sn}} \) are the total energy of \( \text{M}_{n\text{A}_x}\text{Sn}_y \) compound, pure transition, alkali and Sn metals, and \( m \) and \( n \) are the corresponding number of atoms in the unit cell.

3. Results and discussion

3.1. Structural properties with magnetic ordering

Firstly we determined the favorable spin configuration for transition metal atoms in \( \text{MSn}_2 \) and \( \text{MASn}_2 \) with crystalline lattice optimization. It was found that for the case of \( \text{FeSn}_2 \) the AFM configuration was energetically favorable with the best agreement of lattice constants to the experiment (see Table S1 in Supplementary Information). In this AFM state, the Fe atoms have the magnetic moment of \( \pm 1.89 \mu_B \), while the total magnetization was confirmed to be zero (see Table S2). For the case of \( \text{CoSn}_2 \), however, the NM state was always observed though the three different spin configurations of AFM, FM and NM were initially imposed. In fact, Co atoms with these different initial impositions were found to have zero magnetic moment after lattice optimization and SCF cycle. When replacing M (Fe, Co) atom by A (Li, Na) atom, although we initially imposed the AFM configurations on the resultant unit cell of \( \text{MASn}_2 \), the FM state was observed for \( \text{FeASn}_2 \) while also the NM state was realized for CoASn\(_2\) (see Table S2).

To determine the optimized lattice parameters of the unit cells with these magnetic orderings, we plotted the energy-volume curves by calculating the total energies as gradually increasing the unit cell volume. Here, the optimized tetragonal ratio \( c/a \) at each volume was determined by calculating total energy as varying \( c/a \) with allowing the relaxation of atomic positions and by interpolating the data to the third-order polynomial (see Fig. S1). The obtained energy-volume curves for all the intermetallics studied in this work are shown in Fig. 2(a) and the optimized tetragonal ratios as increasing the cell volume are plotted in Fig. 2(b). Table lists the determined lattice parameters and mass density of these intermetallics. For the cases of FeSn\(_2\) and CoSn\(_2\), the calculated lattice constants were
Table 1: Optimized lattice constants $a$ and $c$, tetragonal ratio $c/a$, unit cell volume $V$, Sn position $x_{Sn}$, mass density $\rho$, M–M interatomic distance $d_{M-M}$, cohesive energy per atom $E_{c}$ and formation energy per atom $E_{f}$ of intermetallics.

| Compound      | $a$ (Å) | $c$ (Å) | $c/a$ | $V$ (Å$^3$) | $x_{Sn}$ | $\rho$ (g/cm$^3$) | $d_{M-M}$ (Å) | $E_{c}$ (eV/atom) | $E_{f}$ (eV/atom) |
|---------------|---------|---------|-------|-------------|----------|-------------------|----------------|-------------------|-------------------|
| FeSn$_2$      | 6.3533  | 5.3271  | 0.8153| 227.38      | 0.1623   | 8.566             | 2.663          | -5.135            | -0.221            |
| Fe$_{1/2}$Li$_{1/2}$Sn$_2$ | 6.3531 | 5.3202 | 0.8144| 227.07      | 0.1611   | 8.577             | -0.148         |                   |                   |
| Fe$_{1/2}$Na$_{1/2}$Sn$_2$ | 6.0831 | 5.7633 | 0.8409| 253.39      | 0.1539   | 7.561             | 2.576          | 4.650             | 0.164             |
| CoSn$_2$      | 6.3442  | 5.4723  | 0.8626| 220.25      | 0.1669   | 8.936             | 2.736          | -4.416            | -0.183            |
| Co$_{1/2}$Li$_{1/2}$Sn$_2$ | 6.3617 | 5.4582 | 0.8580| 220.90      | 0.1649   | 8.910             | 2.798          | -4.416            | -0.141            |
| Co$_{1/2}$Na$_{1/2}$Sn$_2$ | 6.4781 | 5.5963 | 0.8639| 234.86      | 0.1608   | 8.013             | 2.798          | -4.416            | -0.141            |
| Co$_{1/2}$Na$_{1/2}$Sn$_2$ | 6.5733 | 5.7381 | 0.8729| 247.93      | 0.1520   | 6.798             | 2.869          | -4.416            | -0.141            |

$^a$ X-ray diffraction data at $T = 295$ K. $^b$ DFT calculation data with PBE functional [30]

Figure 2: (a) Total energy difference per atom $\Delta E$ and (b) optimized lattice constants ratio $c/a$ as a function of cell volume per atom in tetragonal intermetallics FeSn$_2$, FeLiSn$_2$, FeNaSn$_2$, Co$_{1/2}$Sn$_2$, Co$_{1/2}$LiSn$_2$ and Co$_{1/2}$NaSn$_2$.

found to be agreed well with the experimental values $^3$ with very low values of relative error under 1%.

It was found that replacing one M atom in the MSn$_2$ unit cell with A atom induces an increase of lattice constants, tetragonal ratio and thus unit cell volume and decrease of density. The volume expansion rate $V/V_0 \times 100\%$ ($V_0$ the volume of MSn$_2$ unit cell) for FeASn$_2$ were estimated to be smaller (104.5% for Li and 111.4% for Na) than those for CoASn$_2$ (106.6 and 112.6%). Accordingly, the relative density decrease rates ($\rho - \rho_0)/\rho_0 \times 100\%$ for FeASn$_2$ (–8.3% for Li and –12.8% for Na) were found to be smaller than those for CoASn$_2$ (–10.3 and –13.8%). Such volume expansion is mainly associated with an increase of interatomic distance between the M atoms from 2.663/2.736 Å in MSn$_2$ to 2.736/2.798 Å for Li and to 2.837/2.869 Å for Na exchanges respectively, indicating a weakening of interatomic reaction by alkali metal exchange. Note that the M–Sn distance also increases but the Sn–Sn distance slightly decreases by such exchange (see Table S3). The volume expansion and relative interatomic distance indicate that the bonding strength of Fe–Fe is stronger than that of Co–Co, and replacing Fe or Co with Li atom makes the bonding strength weaker than with Na atom.

To gain insight into the structural stability, we evaluated the cohesive energy $E_{c} = E_{tot} - \sum_i E_{i}^{atom}$ and the formation energy $E_{f} = E_{tot} - \sum_i E_{i}^{bulk}$, where $E_{i}^{atom}$ and $E_{i}^{bulk}$ are the total energies of isolated atom and elementary bulk of $i$-th species. As shown in Table 1, the calculated cohesive and formation energies are negative for all the compounds, indicating that these phases are thermodynamically stable and can be formed at ambient condition from their elemental constituents. The formation energy of FeSn$_2$ (–0.221 eV/atom) is lower than that of CoSn$_2$ (–0.183 eV/atom), demonstrating that the Fe-related intermetallics is more stable than the Co-related ones, which is consistent with the bonding strength analysis though being contrast to the previous DFT calculation [30]. It was also observed that substituting Li or Na for Fe or Co atom makes the compounds less stable, and this effect is more pronounced for Na substitution compared to Li substitution.

3.2. Elastic and mechanical properties

The mechanical stability of intermetallics can be estimated by its elastic constants, which play an important role in describing the resistance of material against mechanical deformation. The calculated six independent elastic stiffness constants for MSn$_2$ and MASn$_4$ in the tetragonal phase, namely $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$ and $C_{66}$, are listed in Table 2. For the cases of MSn$_2$, our calculated data is in overall agreement with the previous first-principles calculation [30]. These independent elastic constants were found to satisfy the well-known Born stability criteria for tetragonal crystal [38], expressed by $C_{11}$ > 0, $C_{33}$ > 0, $C_{44}$ > 0, $C_{66}$ > 0, $C_{11} - C_{12}$ > 0, $C_{11} + C_{33} - 2C_{13}$ > 0, $2(C_{11} + C_{12}) + C_{33} + 4C_{13}$ > 0, thereby implying their mechanical stability at zero pressure. For all these alloys, $C_{11}$ is larger...
Table 2: Elastic stiffness constants \( C_{ij} \), bulk modulus \( B \), shear modulus \( G \), Young’s modulus \( E \), Pugh’s ratio \( B/G \), Poisson’s ratio \( \nu \), average sound velocity \( v \), and Debye temperature \( \theta_D \) of the considering intermetallics.

| Compound     | \( C_{11} \) (GPa) | \( C_{12} \) (GPa) | \( C_{13} \) (GPa) | \( C_{44} \) (GPa) | \( B \) (GPa) | \( G \) (GPa) | \( E \) (GPa) | \( B/G \) | \( \nu \) | \( v \) (m/s) | \( \theta_D \) (K) |
|--------------|---------------------|---------------------|---------------------|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| FeSn\(_2\)   | 202.4               | 48.6                | 73.5                | 178.5               | 53.4           | 69.2           | 108.3          | 60.3           | 152.6          | 1.796          | 0.265          | 2950.6         | 706.8 |
| FeSn\(_2\)*  | 184.9               | 22.8                | 43.7                | 190.6               | 42.8           | 62.7           | 86.6           | 57.7           | 142.7          | 1.501          |                |                |
| Fe\(_2\)Li\(_3\)Sn\(_2\) | 164.1               | 41.4                | 45.7                | 141.7               | 45.2           | 54.9           | 81.6           | 51.2           | 127.0          | 1.595          | 0.241          | 2830.6         | 668.2 |
| Fe\(_2\)Na\(_3\)Sn\(_2\) | 146.1               | 43.1                | 40.9                | 123.9               | 42.6           | 51.0           | 73.7           | 46.5           | 115.2          | 1.587          | 0.240          | 2765.2         | 638.9 |
| CoSn\(_2\)   | 204.1               | 52.9                | 58.3                | 190.1               | 42.7           | 67.0           | 104.1          | 57.4           | 145.4          | 1.815          | 0.267          | 2818.3         | 682.3 |
| CoSn\(_2\)*  | 208.5               | 53.8                | 62.4                | 178.7               | 43.2           | 68.3           | 105.8          | 57.1           | 145.2          | 1.853          |                |                |
| Co\(_2\)Li\(_3\)Sn\(_2\) | 151.0               | 37.8                | 44.3                | 130.5               | 28.1           | 46.0           | 76.1           | 39.3           | 100.5          | 1.937          | 0.280          | 2466.7         | 584.6 |
| Co\(_2\)Na\(_3\)Sn\(_2\) | 136.7               | 36.9                | 41.8                | 107.7               | 25.6           | 39.7           | 68.8           | 34.4           | 88.4           | 2.002          | 0.286          | 2356.5         | 548.4 |

* DFT calculation data with PBE functional [30].

than \( C_{33} \), indicating that their deformation resistance along the \( a \)-axis is stronger than that along the \( c \)-axis. In accordance with the above discussion, substituting Li or Na atom was confirmed to reduce the mechanical stability and deformation resistance along both the \( a \)- and \( c \)-axes, due to lowering of elastic constants, and this effect was more influential in Na replacement than Li one. It should be noted that the shear deformation resistance is weakened as well by such substitution due to smaller values of \( C_{44} \) in MASn\(_2\) than in MSn\(_2\).

As the strength of a polycrystalline solid is estimated by its elastic modulus, which can be readily evaluated from the elastic constants (see Table S4 for elastic compliance constants), we present the bulk, shear and Young’s moduli in Table 2. The bulk and shear moduli within the Voigt (\( B_V, G_V \)) and Reuss (\( B_R, G_R \)) approximations are shown in Table S5. Since the calculated elastic moduli are much lower than 360 GPa, these alloys are not said to be incompressible [39]. It was known that the bulk, shear and Young’s moduli describe the material response to uniform pressure, shear and uniaxial stress respectively. In accordance with this fact, Table 2 shows that the elastic moduli of Fe-related intermetallics are larger than those of Co-related ones, indicating that the former has stronger resistance to volume compression and more prominent directional bonding between the constituent atoms than the latter.

According to the Pugh criteria for ductility of solid [40], the critical values of Pugh’s ratio \( B/G \) and Poisson’s ratio \( \nu \) are 1.75 and 0.26; when the \( B/G \) value is greater than 1.75 or the \( \nu \) is larger than 0.26, the crystal is considered as a ductile material, otherwise it is a brittle material [41]. It was found that FeSn\(_2\) and CoSn\(_2\) are ductile materials due to their \( B/G \) values of 1.796 and 1.815 being larger than 1.75 and \( \nu \) values of 0.265 and 0.267 being larger than 0.26. Interestingly, Li or Na substitution for Fe in FeSn\(_2\) induces decreases of \( B/G \) and \( \nu \) values to 1.595 or 1.587 and 0.241 or 0.240 respectively, thereby indicating a transition from ductile to brittle property. However, an opposite trend is observed in CoSn\(_2\); Li or Na substitution increases the \( B/G \) and \( \nu \) values to 1.937 or 2.002 and 0.280 or 0.286 respectively, suggesting that Li or Na substitution increases the ductility.

In Table 2 we also present the average sound velocity and Debye temperature (see Table S5 for longitudinal and transverse elastic wave velocities). The Debye temperature \( \theta_D \) is known to be associated with the vibration of atoms and hardness of a solid; the higher \( \theta_D \) value implies the stronger interaction between atoms and the higher hardness. Our calculation result shows that FeSn\(_2\) (706.8 K) has higher Debye temperature than CoSn\(_2\) (682.3 K), and moreover, Li or Na substitution reduces the \( \theta_D \) values. Such tendency indicates that FeSn\(_2\) is harder than CoSn\(_2\) and Li or Na substitution lowers the hardness, which is consistent with the variation of elastic modulus.

### 3.3. Lattice vibrational properties

To further discuss the dynamic stability of the intermetallic compounds, the phonon dispersion curves and the corresponding phonon DOS were plotted. Figure 3 depicts those for FeSn\(_2\) and CoSn\(_2\). It turned out that there is no imaginary phonon mode in CoSn\(_2\) but a non-degenerate optical phonon mode with imaginary phonon frequency values appears around the zone-center \( \Gamma \) point for the case of FeSn\(_2\), suggesting that at ambient conditions FeSn\(_2\) is not stable.

Figure 3: Phonon dispersion curves and the atomic resolved phonon density of states for (a) FeSn\(_2\), which has soft mode with imaginary phonon frequency indicated by red color, and (b) CoSn\(_2\). The primitive unit cell including two formula units was used in the calculation.
3.4. Electronic properties

In order to understand the electronic properties, we calculated the electronic density of states (DOS) and energy band structures of MSn2 and MASn2 with spin-polarization. Figure 5 shows the atomic resolved total DOS around the Fermi level $E_F$, which is set to zero as indicated by vertical dashed line, in the energy range from −5 eV to 2 eV (see Fig. S2 for orbital resolved partial DOS). We show the spin-up band structures in the energy range of interest (−2 eV to 2 eV) along the high-symmetry lines of the first Brillouin zone in Fig. 7. It should be condition CoSn2 is dynamically stable but FeSn2 should transformed to another phase. From the analysis of phonon DOS for FeSn2, the imaginary soft phonon was found to be mainly caused by the relative vibration among Fe atoms. When allowing atom movement along the soft phonon vector, the Fe atoms moved along the c-axis direction, resulting in an extension of Fe–Fe interatomic distance and furthermore phase transition from tetragonal $I4/mcm$ to $I4/m$ space group phases. Such space group change has been already illustrated for Mo3B with first-principles calculations by Zhou and co-workers [42].

Then the influence of M/A substitution on lattice vibrational properties of FeSn2 and CoSn2 was explored along the above discussion. Figure 4 shows the phonon dispersion curves with phonon DOS for MASn2 in tetragonal $P4_22$ space group phase, containing 12 atoms. One interesting finding is that for FeNaSn2, an imaginary phonon mode originated from acoustic phonon appears around A, R and X points, indicating that this phase is dynamically unstable like FeSn2. However, other intermetallic compounds were found to be stable at ambient condition due to no imaginary phonon mode. For each MASn2, there is a gap in the region between low frequency and high frequency. The gaps in Li-substituted compounds are larger than those in Na-substituted ones. The high frequency region above 6 THz is predominantly contributed by Li or Na atoms, while the contribution is derived from vibrations of Fe or Co and Sn atoms below 6 THz.
noted that for the compounds with spin-ordering of AFM and NM, which are FeSn$_2$, CoSn$_2$, CoLiSn$_2$ and CoNaSn$_2$, the spin-down bands perfectly coincide with the spin-up bands, while for FeLiSn$_2$ and FeNaSn$_2$ in the FM state the spin-down bands are strikingly different from the spin-up bands (see Fig. S3 for comparison between spin-up and spin-down bands in FeLiSn$_2$ and FeNaSn$_2$).

For all the compounds, we can see 2~4 bands crossing the Fermi level, denoted by red- and cyan-colored thick lines in Fig. 6 accounting for the metallic behavior. The number of crossing bands and atomic contribution characteristics vary with the compound. For the case of FeSn$_2$, one hole (cyan color) and one electron (red color) bands appear across the Fermi level, of which the hole band is contributed from Fe-3$d$ and Sn-5$s$, 5$p$ states almost equally but the electron band above $E_F$ is dominated by Fe-3$d$ state, as shown in Fig. 6(a) and Fig. S2(a). Contrastingly, CoSn$_2$ exhibits two hole and two electron bands across the Fermi level, of which the hole bands below $E_F$ are dominated by Co-3$d$ with a slight contribution from Sn-5$p$ states but the electron bands are contributed equally from Co-3$d$ and Sn-5$s$, 5$p$ states, as shown in Fig. 6(d) and Fig. S2(d). For M/A exchange, FeLiSn$_2$ has 3 crossing (two electron and one hole) bands (Fig. 6(b)), and others also have 4 (two hole and two electron) bands crossing the Fermi level (Fig. 6(c), (e), (f)). Similar contribution characteristics to MSn$_2$ is observed for MASn$_2$. However, since one M2 atom with minus magnetization was replaced by alkali atom, enhanced contribution from M1 atom with plus magnetization compared to M2 atom can be seen in Fig. 6 for total DOS. It is worth noting that from the total DOS plot, FeSn$_2$ is clearly in AFM state and FeAsSn$_2$ is in FM state, whereas CoSn$_2$ and CoAsSn$_2$ have NM feature.

These band structure features yield a multi-sheet Fermi surface, as shown in Fig. 7. There are several kinds of shape for the Fermi surface, including round corner polyhedron, rugged ring, quasi-2D sheet, and wrinkled and branched cylinder. The relatively simple topology of Fermi surface, Fermi hole pocket with a shape of round polyhedron at zone center around Γ point and bent cylinder for electron at zone boundary going from Z to R, is observed for FeSn$_2$, while complicated shapes appear for CoSn$_2$. For the case of FeAsSn$_2$, we can see wavy-like 2D sheet for holes and electron pockets at the center of zone boundary, while for CoAsSn$_2$ the electron Fermi surface with a shape of wrinkled cylinder is characteristically observed.

Figure 6: Energy band structures in (a) FeSn$_2$, (b) FeLiSn$_2$, (c) FeNaSn$_2$, (d) CoSn$_2$, (e) CoLiSn$_2$ and (f) CoNaSn$_2$, calculated by using the PBE exchange-correlation functional. Spin polarization is considered and only spin-up bands are shown here. Blue- and orange-colored lines indicate the occupied and empty bands, while cyan- and red-colored thick lines denote the bands crossing the Fermi level $E_F$, which is set to zero as indicated by horizontal dotted line.

Figure 7: Fermi surface for MSn$_2$ (M = Fe, Co) and MASn$_2$ (A = Li, Na). Pink-colored labels indicate the high-symmetry point of first Brillouin zone.
3.5. Defect formation and alkali atom migration

In order to simulate the initial interaction of alkali metal with MSn₂, we considered the point defect such as vacancies of V_M and V_Sn and substitutional solutes of A_M and A_Sn. The defect formation energy was calculated using Eq. 8 and the formation enthalpy of the compound with such defect was calculated using Eq. 9. Table 3 presents the calculated energetic values for defect were calculated to be negative for both FeSn₂ and CoSn₂, indicating that the compounds with defect can be formed in exothermic way. The reactivity of CoSn₂ with Li or Na was found to be higher than that of FeSn₂ due to smaller values of formation enthalpy. It was found that for both FeSn₂ and CoSn₂, the formation energy of Sn vacancy is lower than those of Fe or Co vacancies, and Li substitutional solute has lower formation energy than Na one. In particular, for the case of CoSn₂, Sn-related defects such as V_Sn, Li_Sn, and Na_Sn have negative formation energies of −0.662, −2.307 and −1.539 eV respectively. These suggest that Sn atom has higher reactivity with Li or Na than Fe or Co atom and moreover lithium is more reactive with MSn₂ than sodium.

Finally we estimated the activation barrier for alkali atom diffusion mediated by M vacancy, which occurs through the exchange positions between the solute atom A and M vacancy. Figure 8 shows the calculated activation barrier with depiction of migration path. It turned out that in FeSn₂, the activation barriers (0.17 and 0.44 eV for Na and Li) are lower than those in CoSn₂ (0.83 and 0.88 eV). Also Li diffusion occurs with lower activation barrier than Na diffusion.

4. Conclusions

In conclusion, we have performed first-principles calculations to study the effect of M/A substitution on structural, mechanical, lattice vibrational and electronic properties of intermetallic compounds MSn₂ (M = Fe, Co; A = Li, Na). The main conclusions can be summarized as follows:

1. M/A substitution leads to lattice expansion along the a- and c-axis. With this substitution, tetragonal ratio and unit cell volume also increase and thereby mass density decreases. Na substitution has more announcement effect than Li. FeSn₂ has less volume expansion than CoSn₂.

2. The calculated elastic constants of MSn₂ and MASn₂ satisfy the mechanical stability criteria for tetragonal crystal. M/A substitution reduces the mechanical stability and deformation resistance of MSn₂, which is more announced with Na substitution. The Pugh’s and Poisson’s ratios decrease with M/A substitution for Fe in FeSn₂, leading to its phase change from ductile to brittle, but increase for Co in CoSn₂, keeping its ductility.

3. Phonon dispersion curve of FeSn₂ in primitive unit cell exhibits imaginary frequency (soft) mode around Γ point, which might lead to phase transition from I4/mcm to I4/m, whereas CoSn₂ has all the real phonon frequencies. With M/A substitution for Fe, the soft mode of FeSn₂ disappears for FeLiSn₂ but is still preserved for FeNaSn₂. In phonon DOS, the gap between low and high frequency regions appears with this substitution.

4. In electronic band structures, there are two or four bands crossing the Fermi level E_F. For FeSn₂, the hole bands below E_F is contributed equally from Fe-3d and Sn-5s, 5p states and the electron band above E_F is dominated by Fe-3d states. In contrast, the hole bands are dominated by Co-3d states while the electron bands are contributed equally from Co-3d and Sn-5p states.

5. Formation enthalpy of FeSn₂ compound with Fe vacancy or substitutional substitutional solute alkali atom is higher than that of CoSn₂. Li substitutional defect has lower formation energy than Na one. The activation barrier of vacancy-mediated Li diffusion is higher than Na one. The activation barriers in FeSn₂ are lower than those in CoSn₂.

Acknowledgments

Computations in this work have been performed on the HP Blade System C7000 (HP BL460c) managed by Faculty of Materials Science, Kim Il Sung University.

Notes

The authors declare no competing financial interest.

Table 3: Defect formation energy (E_f) and formation enthalpy per atom (ΔH) of compound with defect, including vacancies (V_M, V_Sn) and substitutional solutes (A_M, A_Sn) in intermetallic compounds MSn₂ (M = Fe, Co; A = Li, Na).

| Defect | E_f (eV) | ΔH (eV) | E_f (eV) | ΔH (eV) |
|--------|---------|---------|---------|---------|
| V_M    | 2.876   | −1.487  | 4.590   | −2.136  |
| V_Sn   | 2.193   | −1.494  | −0.662  | −2.191  |
| Li_M   | 2.146   | −1.479  | 4.067   | −2.119  |
| Na_M   | 3.998   | −1.460  | 5.643   | −2.103  |
| Li_Sn  | 0.784   | −1.493  | −2.307  | −2.186  |
| Na_Sn  | 1.511   | −1.486  | −1.539  | −2.178  |

Figure 8: Activation energy barrier for vacancy-mediated Li/Na migration in FeSn₂ and CoSn₂. Inset shows the migration path denoted by yellow-colored balls in 2 × 2 × 2 supercell including 96 atoms.
References

[1] C. Vaalma, D. Buchholz, M. Weil, S. Passerini, A cost and resource analysis of sodium-ion batteries, Nat. Rev. Mater. 3 (2018) 18013.

[2] S. Mukherjee, S. B. Mujib, D. Soares, G. Singh, Electrode materials for high-performance sodium-ion batteries, Materials 12 (2019) 1952.

[3] Q. Bai, L. Yang, H. Chen, Y. Mo, Computational Studies of Electrode Materials in Sodium-Ion Batteries, Adv. Energy Mater. 8 (2017) 1702998.

[4] W. Luo, F. Shen, C. Bommier, H. Zhu, X. Ji, L. Hu, Na-ion battery anodes: materials and electrochemistry, Acc. Chem. Res. 49 (2016) 231–240.

[5] L. Li, Y. Zheng, S. L. Zhang, J. P. Yang, Z. P. Shao, Z. P. Guo, Recent progress on sodium-ion batteries: potential high-performance anodes, Energy Environ. Sci. 11 (2018) 2310–2340.

[6] B. Huang, Z. Pan, X. Su, L. An, Tin-based materials as versatile anodes for alkali (earth)-ion batteries, J. Power Sources 395 (2018) 41–59.

[7] J. M. Stratford, M. Mayo, P. K. Allan, O. Pecher, O. J. Borkiewicz, K. M. Meisner, E. J. Crumlin, X. Liu, W. Yang, G. M. Veith, The local atomic structure and chemical bonding in sodium tin phases, J. Mater. Chem. A 7 (2019) 18959–18973.

[8] J. W. Wang, X. H. Liu, X. Su, M. Walter, S. Doswald, M. V. Kovalenko, Inexpensive colloidal SnSb nanocrystals as high-capacity alloy electrodes for Li-ion rechargeable batteries, Electrochem. Acta 52 (2007) 4853–4857.

[9] W. Sun, L. Zhang, J. Liu, H. Wang, Y. Bu, First-principles investigation of mechanical, thermodynamic and electronic properties of FeSn2 and SnSb phases, Comput. Mater. Sci. 111 (2016) 175–180.

[10] M. de Jong, W. Chen, T. Angsten, A. Jain, R. Notestine, A. Gamst, Charting the complete elastic properties of inorganic crystalline compounds, Sci. Data 2 (2015) 150009.

[11] M. Armbruster, M. Schmidt, R. Cardoso-Gil, H. Bornmann, Y. Grin, Crystal structures of iron distannide, FeSn2, and cobalt distannide, CoSn2, Z. Kristallogr. NCS 222 (2007) 83–84.

[12] P. Giannoni, S. Baron, N. Bonini, M. Calandra, R. Car, et al., QUANT-UM ESPRESSO: A modular and open-source software project for quantum simulations of materials, J. Phys.: Condens. Matter 21 (2009) 395502.

[13] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865.

[14] A. Togo, F. Oba, I. Tanaka, First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures, Phys. Rev. B 78 (2008) 134106.

[15] G. Henkelman, B. P. Uberuaga, H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, J. Chem. Phys. 113 (2000) 9901–9904.

[16] K. Momma, F. Izumi, VESTA 3 for three-dimensional crystal visualization, crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (2011) 1272–1276.

[17] B. Max, H. Kun, Dynamical theory of crystal lattices, Clarendon, Oxford, UK, 1956.

[18] S. Chiado, H. J. Gotsis, N. Russo, E. Sicilia, OsB₂ and RuB₂, ultra incompressible, hard materials: First-principles electronic structure calculations, Chem. Phys. Lett. 425 (2006) 311–314.

[19] S. F. Pugh, XCII. Relations between the elastic moduli and the plastic deformations, Phil. Mag. 45 (1954) 823–843.

[20] M. A. Hadi, M. Roknuzzaman, A. Chroneos, S. H. Naqib, A. K. M. A. Islam, R. V. Vovk, K. Ostrikov, Elastic and thermodynamic properties of new (Zr₁₋ₓTiₓ)AlC₂ MAX-phase solid solutions, Comput. Mater. Sci. 137 (2017) 318–326.

[21] D. Zhou, J. Wang, Q. Cui, Q. Li, Crystal structure and physical properties of Mo₅B₂: First-principles calculations, J. Appl. Phys. 115 (2014) 113504–113508.