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Linear thermal expansion coefficients of higher manganese silicide compounds

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Abstract

The linear thermal expansion coefficients α_L of the higher manganese silicide compounds are calculated using a combined approach involving Density-Functional Theory calculations, an empirical relation and experimental data. Since it has been reported that the linear thermal expansion coefficient and the cohesive energy are inversely proportional to each other, we calculated by DFT methods the cohesive energies of a set of selected disilicide compounds and using the corresponding experimental data for α_L we determined the coefficient of proportionality. From the empirical relation so obtained, the linear thermal expansion coefficients of the HMS in the 'a' and '*c*' directions were calculated.

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Keywords: linear thermal expansion coefficient ; Density-Functional Theory; semi-empirical model; thermoelectrics; semiconductors

1. Introduction

The semiconductors Higher Manganese Silicides $MnSi_x$ (x = 1.72 – 1.75) also known as HMS are the highest silicon-rich intermediate phases in the manganese-silicon binary phase diagram. These compounds have attracted much attention in recent years because of their applications in spintronics, such as ferromagnetic semiconductors, and in thermoelectrics due to their large Seebeck coefficient, low

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resistivity, and high oxidation resistance [1-3]. Several HMS, namely Mn_4Si_7 [4], $Mn_{11}Si_{19}$ [5], $Mn_{15}Si_{26}$ [6], and $Mn_{27}Si_{47}$ [7] are reported in literature. These phases are referred to as the "Nowotny chimney ladder" phase being derived from a $TiSi_2$ parent structure [8]. They all possess a tetragonal unit cell with high anisotropy. These structures differ mainly by the *c*-parameter which is in all cases very large in comparison to the *a*-parameter, and hence these phases are difficult to distinguish from one another.

The cohesive energy is among the most fundamental physical quantity as it shows the strength of the chemical bond between atoms in solids. It corresponds to the energy gained by the crystal when arranging the atoms into the crystalline lattice from the gas phase. As a consequence, at absolute zero Kelvin the cohesive energy is a measure of the crystal stability. To the best of our knowledge, the cohesive energy of the Higher Manganese Silicides has not been studied so far. From a theoretical viewpoint they can be obtained from ab initio calculations using either wavefunction-based methods (Hartree-Fock and post-Hartree-Fock) or the density functional theory.

Another important factor, especially for controlling the hetero-epitaxial growth of materials, is the linear thermal expansion coefficient. Tsuru *et al.* [9] showed that the linear thermal expansion coefficient is inversely proportional to the cohesive energy. Using experimental linear thermal expansion coefficients and the calculated cohesive energies for a set of compounds these authors determined the coefficient of proportionality between both two properties. However, Tsuru's set of compounds does not comprise silicide ones. Thus, the aim of this work is to calculate the cohesive energy for a set of silicide compounds for which the experimental linear thermal expansion coefficients are known so as to obtain the empirical relation between these properties. The silicides that we selected in our set are disilicide so as to have silicon to metal content ratio close to that of the HMS. Finally, using the empirical relation, we determined the linear thermal expansion coefficient of the HMS.

2. Computational details

The cohesive energies were calculated by Density-Functional Theory [10,11] method using the *Quantum Espresso* [12] package. The generalized gradient approximation (GGA) approach that accounts for the local electron density and its gradient at each point in space was used to calculate the exchange and correlation energies. The exchange-correlation functional is the Perdew-Burke-Ernzerhof (PBE) one [13]. A cutoff energy of 30 Ry for the plane wave expansion and 300 Ry for the electronic charge density was found to be sufficient to obtain converged results. The stationary state structures for the atoms and cell parameters were optimized using the Quasi-Newton Broyden-Fletcher-Goldfarb-Shanno BFGS generalized algorithm. The structure was considered as being converged when forces on atoms and pressure were below 0.0001 Ry/Bohr and 0.2 kbar, respectively. The 12 x 12 x 4 grid of the Monkhorst-Pack *k*-points was utilized in the case of Mn_4Si_7. Because of the relatively large *c* lattice parameter of $Mn_{11}Si_{19}$ we used the 6 x 6 x 1 *k*-point grid, while for $Mn_{15}Si_{26}$ and $Mn_{27}Si_{47}$, the *k*-point mesh was set to 2 x 2 x 1. The calculated cohesive energy per atom is defined as

$$E_{coh} = (\sum E_{atom} - E_{total}) / N \quad (1)$$

where E_{coh} is the cohesive energy (in eV/atom), E_{tot} is the total energy of the compound, E_{atom} is the total energy of a neutral atom, and N is the number of atoms in the compound.

3. Results

The silicide compounds that we used in our set to obtain the empirical relation between the cohesive energies and the linear thermal expansion coefficients α_L are presented in Table 1 with their cell parameters, symmetry point group and cohesive energy calculated at the DFT-PBE level of