

Structural Disorder in TiFeSb Half-Heusler Antimonide

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Abstract – The DFT modeling of the $TiFe_{1+x}Sb$ solid solution revealed that composition $TiFe_{1.375}Sb$ with $MnCu_2Al$ structure type is more preferable than equiatomic $TiFeSb$ which crystallizes in $MgAgAs$ -type. At $T > 873$ K the formation of the two phase region containing both half-Heusler and full-Heusler phases is predicted. The composition dependence of the lattice parameter shows deviation from linearity. The calculations explain the difficulties in solid solutions formation based on $TiFeSb$ intermetallic.

Key words – DFT modeling, half-Heusler phases, structural disorder, thermoelectric material, thermodynamics.

I. Introduction

Recent experimental and theoretical investigations of full- and half-Heusler compounds have attracted a lot of attention due to their thermoelectric properties and ability to directly transform thermal energy into electrical current. The crystal structure of full-Heusler $TiFe_2Sb$ (structure type $MnCu_2Al$, space group $Fm-3m$) can be derived from the half-Heusler structure of $TiFeSb$ (structure type $MgAgAs$, space group $F-43m$) by filling the vacant $4d$ site with Fe atoms. According to [1] the $TiFeSb$ intermetallic is characterized by Curie-Weiss behavior [1]. Evers et al. [2] assumed Pauli paramagnetism for this compound. The TB-LMTO-ASA calculations [3] predicted paramagnetic behavior of $TiFeSb$ antimonide, while KKR-CPA-LDA investigations in [4] and FP-LAPW in [5] revealed half-metallicity with ferromagnetic behavior. The investigation of the Ti-Fe-Sb phase diagram [6] showed the presence of the homogeneity region of the $TiFeSb$ compound toward the Ti-corner. Recently the ability to accumulate additional Ni atom in $4d$ vacant sites of $ZrNiSn$ was found that had a positive effect on the thermoelectric performance of this material. In order to check the possible solubility of additional Fe atoms in $TiFeSb$ structure the $TiFe_{1+x}Sb$ solid solution was investigated and the results are presented in the current paper.

II. Computational Details

The DFT calculations were carried out using the Elk v2.3.22 package [7] – an all-electron full-potential linearized augmented-plane wave (FP-LAPW) code with Perdew-Burke-Enzerhoff (PBE) exchange-correlation functional in generalized gradient approximation (GGA) [8]. The k -point mesh size was equal to $10 \times 10 \times 10$ for a single unit cell and $20 \times 10 \times 10$ for the doubled. The ground state calculations were carried out for the following

concentrations of $x(Fe)$ in the $TiFe_{1+x}Sb$ solid solution: 0, 0.125, 0.25, 0.375, 0.5, 0.75, and 1. For the concentration of $x(Fe) = 0.125$ and 0.375 the symmetry of the unit cell was reduced to $P1$ and the unit cell was doubled in the a -direction. Prior to the final total energy calculations the geometry of the initial structure (lattice vectors) was optimized using the 11 values of the lattice parameter in the range 0.55-0.65 nm and universal equation of state [9]. The proper values of the muffin-tin radii were selected automatically at the initial stage of the calculations. For the thermodynamic calculations the ground state energies of each concentration of the $TiFe_{1+x}Sb$ solid solution and pure metals (Ti, Fe, Sb) were used.

III. Results and Discussion

The DFT calculations consisted of several stages. At the first stage the ground state calculations for the pure equiatomic $TiFeSb$ with different distributions of Fe atoms were carried out. For this purpose two structure types were used – 1 combination with $MgAgAs$ -type and 6 combinations with $MnCu_2Al$ -type. The results clearly showed that the distribution of the Fe atoms which corresponds to the $MgAgAs$ structure type is characterized by the lowest ground state energy. To model the $TiFe_{1+x}Sb$ solid solution the Fe atoms were placed in the vacant $4d$ site of the $MgAgAs$ structure type (Fig. 1). This leads to the two possible structure types – $MnCu_2Al$ or $MgAgAs$. Partial filling of the vacant site increases the entropy of alloy which was taken into account using the entropy of mixing for the ideal solution.

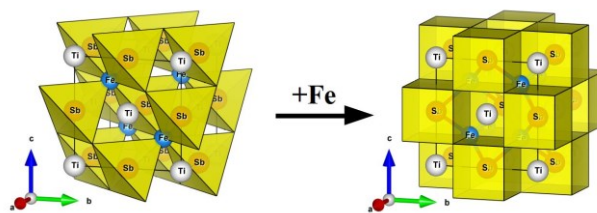


Fig. 1. Half-Heusler $TiFeSb$ to full-Heusler $TiFe_2Sb$ structure transition

Calculation of the enthalpy of formation of the $TiFe_{1+x}Sb$ showed that in the region of $x(Fe) = 0.125-0.75$ more favorable is $MnCu_2Al$ structure type, while for the $TiFe_2Sb - MgAgAs$ (Fig. 2).

With increasing the temperature to 873 K and counting the entropy contribution into the thermodynamic Gibbs potential the dependencies significantly change. At $x(Fe) < 0.5$ the $MnCu_2Al$ structure type is preferable, but at $x(Fe) = 0.5$ the situation becomes opposite. At this temperature a narrow two-phase region (coexistence of $TiFe_{1+x}Sb$ with two different structure types) at $x = 0.4-0.5$ could be expected. Further temperature growth leads to the narrowing of the two-phase region.

In all cases the minimum on the concentration dependence of the thermodynamic potential occurs at $x(Fe) = 0.375$. This $TiFe_{1.375}Sb$ composition with $MnCu_2Al$ -type is more favorable than equiatomic $TiFeSb$ with $MgAgAs$ -type and the compound position on the

Ti-Fe-Sb phase diagram should be at least revised. This result shed a light on the reason of unsuccessful attempts to obtain continuous solid solutions like $\text{TiFe}_{1-x}\text{Co}_x\text{Sb}$ by simple substitution one transition element on another.

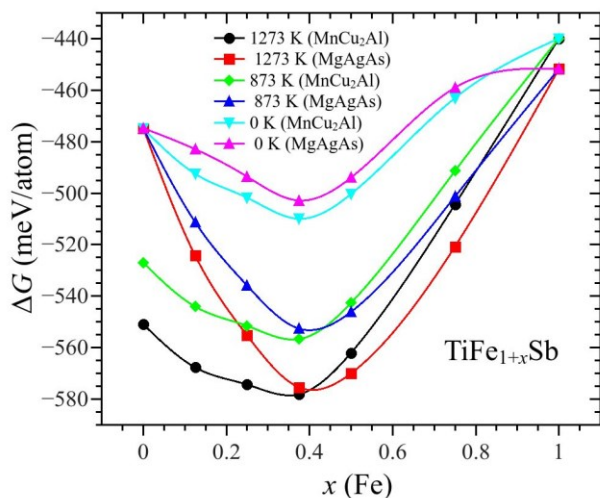


Fig. 2. Concentration dependence of Gibbs potential of $\text{TiFe}_{1+x}\text{Sb}$ solid solution at 0, 873, and 1273 K for different structure types

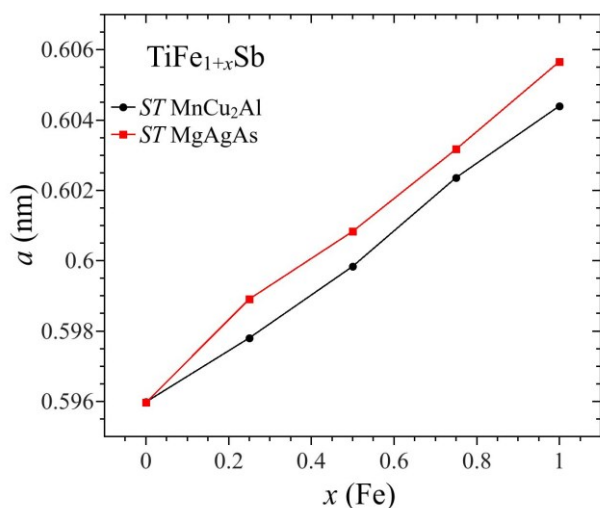


Fig. 3. Composition dependence of the lattice parameter of $\text{TiFe}_{1+x}\text{Sb}$ solid solution for different structure types

Conclusions

The concentration dependence of the lattice parameter (a) shows that with increasing of Fe atoms concentration the lattice parameter also increases (Fig. 3) and corresponds with interstitial solid solution formation. Taking into account the preferable structure type for each

concentration at $T > 0$ K the negative deviation from linearity could be observed. The deviation could be explained by the strong covalent bonding with electron density localization between Sb and Fe atoms in the [FeSb] sublattice.

The DFT modeling of the $\text{TiFe}_{1+x}\text{Sb}$ solid solution showed that the composition of the equiatomic TiFeSb half-Heusler phase should be shifted to full-Heusler $\text{TiFe}_{1.375}\text{Sb}$. Strong interaction between Sb and Fe atoms in the [FeSb] sublattice was revealed from the negative deviation of the lattice parameter in the $\text{TiFe}_{1+x}\text{Sb}$ solid solution. The structural disorder gives an advantage and a new degree of freedom in tuning the thermoelectric performance of both half-Heusler and full-Heusler materials.

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