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Experimental and DFT study of the V–Co–Sb ternary system

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ABSTRACT

The phase diagram of the V–Co–Sb ternary system was constructed at 870 K over the whole concentration range using X-ray powder diffraction and electron probe microanalysis. The formation of one ternary compound VCoSb with MgAgAs type structure (half-Heusler phase, space group *F*-43*m*, $a = 0.57838(2)$ nm) was confirmed. The influence of V doping on electrical transport property behavior of the binary skutterudite $CoSb_3$ ($CoAs_3$-type, space group *Im*-3) was studied by measurements of electrical resistivity and Seebeck coefficient as well as ab initio DFT calculations.

1. Introduction

The problem of the efficient heat conversion into electrical power could be partially solved by developing new thermoelectric materials. The class of clathrates, skutterudite, half-Heusler phases and related multicomponent alloys are intensively studied as perspective thermoelectric materials [1–11]. The $CoSb_3$ binary skutterudite has formed the basis for a wide variety of materials (so called filled skutterudite) exhibiting exceptional thermoelectric properties [12]. The structure of the $CoSb_3$ skutterudite ($CoAs_3$-type, space group *Im*-3) is characterized by icosahedral voids where other elements can be included [12]. Inclusion of additional atoms into $CoSb_3$ structure (atomic position 2*a*) results in the formation of the filled-type of skutterudites described with $LaFe_4P_{12}$-type (space group *Im*-3) [13]. This is a good way to improve thermoelectric performance of the already known materials. Semiconducting compounds crystallizing in MgAgAs structure type, known as half-Heusler phases, and containing Sn and Sb show comparable thermoelectric performance and are suitable for the mid-temperature applications [7–11]. The previously studied V–Fe–Sb system [14] has shown that VFeSb half-Heusler compound exhibits semiconducting behavior below 1070 K, while above this temperature it crystallizes in the hexagonal Ni_2In structure type with typical metallic-like electrical properties. Another related system with Zr, Co, and Sb is characterized by the formation of disordered half-Heusler compound $Zr_{1+x}Co_{1-x}Sb$ [15]. The deviation from equiatomic composition leads the change of conductivity type from semiconducting to metallic.

In our work we have performed an investigation of the phase relations in the system V-Co-Sb at 870 K to obtain the information on the homogeneity ranges of the intermediate phases and solubility of the third components in the binary compounds. The study of electrical properties of the V-doped skutterudite $CoSb_3$ was performed. The obtained results are discussed within the results of the DFT calculations.

2. Experimental

Samples of ~1 g were prepared by arc melting of vanadium (purity 99.96 wt %), cobalt (purity 99.99 wt %), and the antimony (purity 99.999 wt %) under purified, Ti-gettered, argon atmosphere with non-consumable tungsten electrode on a water-cooled copper hearth. The addition of 3–5 wt% of Sb was required to compensate the evaporation losses. The overall weight losses of buttons were generally less than 1 wt %. After that alloys were sealed in evacuated quartz tubes and annealed at 870 K for 1400 h. The temperature of annealing was chosen based on a) melting temperature of Sb (904 K); b) increasing of liquidus range in Co-Sb system from the

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Sb-part at the temperature higher than melting temperature of Sb; c) quality of the samples at high Sb content (fragility and porosity of the alloys). Taking into account these factors an optimal temperature 870 K for investigation of V-Co-Sb over the whole concentration range was chosen. After annealing the samples were water-quenched.

For the characterization of the annealed samples X-ray powder diffraction on DRON-4.0 with Fe $K\alpha$ radiation was performed. Lattice parameters were refined from the peak positions of the powder patterns using the WinCSD program package [16]. The compositions of the obtained samples were examined by Scanning Electron Microscopy (SEM) using REMMA 102-02 electron microscope with a Link EDX system operated at 20 kV and 60 μA. Quantitative electron probe microanalysis (EPMA) of the samples was carried out using an energy-dispersive X-ray analyzer with the pure elements as standards (an acceleration voltage was 20 kV; *K*- and *L*-lines were used).

The electrical resistivity was measured in the temperature range 80–380 K employing four-probe method on millimeter-scale, well-shaped pieces cut by spark erosion from the polycrystalline samples. Seebeck coefficient measurements were carried out using a standard differential method with pure copper as a reference material in the temperature range 80–390 K.

An all-electron full-potential linearized augmented-plane wave (FP-LAPW) method was used in the DFT calculations within the Elk v2.3.22 program package [17]. Calculations were carried out in the generalized gradient approximation (GGA) with Perdew-Burke-Enzerhoff exchange-correlation functional [18]. The high quality *k*-point mesh size was selected automatically depending on the crystal structure of compound and was kept constant during geometry optimization procedure, which was carried out using calculation of the Hellman-Feynman forces with core and incomplete basis set corrections and equation of state [19] for the set of 11–13 values of the lattice parameter with a step of 0.01 nm. The muffin-tin radii of each element were adjusted before the first iteration on each geometry optimization step. The enthalpy of formation (ΔH) was calculated using the general formula:

$$\Delta H = \left[E_{tot}(V_aCo_bSb_c) - a\left(\frac{E_{tot}(V)}{j}\right) - b\left(\frac{E_{tot}(Co)}{k}\right) - c\left(\frac{E_{tot}(Sb)}{l}\right)\right] \times (a+b+c)^{-1}$$

where a, b, c – are the number atom types; j, k, l – are the number of V, Co, and Sb atoms in the crystal structure; E_{tot} – is the total energy of the system (eV). The calculation of the density of states was performed by a trilinear method for 1000 *k*-point grid size for integrating functions in the Brillouin zone and 1000 energy points in the DOS plot. The interstitial DOS is included into the total DOS distribution, while the partial DOS for each atom type was obtained only within the volume of the appropriate muffin-tin sphere. The charge density (ρ) as well as electron localization function (Υ) distributions were calculated for the 60 × 60 × 60 point grid and plotted by the VESTA software package [20].

3. Results and discussion

3.1. The ternary system V-Co-Sb at 870 K

The isothermal section of the V-Co-Sb system was constructed at 870 K based on the results of the X-ray powder diffraction and electron probe microanalysis of 12 binary and 28 ternary alloys, the phase compositions of the most samples are listed in Table 1.

All binaries of the V-Co and Co-Sb systems [21–23] that were reported to exist at 870 K were confirmed. According to literature data in Co-Sb system the CoSb and $CoSb_2$ phases are characterized by small homogeneity ranges confirmed in our work by EPM analysis ($Co_{48.8\text{-}51.7}Sb_{51.2\text{-}48.3}$, $Co_{32.2\text{-}34.4}Sb_{67.8\text{-}65.4}$, respectively). Data of homogeneity range of VCo_3 and $V_{0.6}Co_{0.4}$ binaries were used from Ref. [22]. The composition with maximal V content for VCo_3 ($V_{31.3}Co_{68.7}$) and minimal V content for $V_{0.6}Co_{0.4}$ ($V_{47.7}Co_{52.3}$) was established from EPM data of $V_{35}Co_{50}Sb_{15}$ ternary sample (sample N4, Table 1). Taking into account the recently studied V–Sb system and performed analysis of the previously known binaries [24], a batch of samples with compositions corresponding to the reference data was synthesized and analyzed by X-ray powder diffraction. The analysis confirmed the formation of VSb_2 ($CuAl_2$-type), $V_{7.46}Sb_9$ (own structure type), V_3Sb_2 (Fe_3Sn_2-type), and V_3Sb (Cr_3Si-type) binary compounds (Table 1). However, two binaries VSb and V_5Sb_4 were not observed at annealing temperature and samples contained only V_3Sb_2 and $V_{7.46}Sb_9$ phases. Homogeneity range for V_3Sb binary determined by EPMA data was limited by $V_{81.52}Sb_{18.48}$ and $V_{76.41}Sb_{23.59}$ compositions. According to EPM analysis the solubility of Sb in VCo_3 and $V_{0.6}Co_{0.4}$ is less than 3 at. %. To study the solubility of vanadium in the binary skutterudite $CoSb_3$ with formation of $V_xCo_4Sb_{12}$ interstitial solid solution the V-containing samples with x(V) = 0.02; 0.04; 0.08; 0.12; 0.20 and 0.28 were prepared, annealed at 870 K and examined by X-ray analysis. X-ray analysis confirmed the existence of the cubic $CoSb_3$ binary with $CoAs_3$-type (a = 0.90357(2) nm). First step of analysis of V-containing samples using X-ray powder diffraction showed single phase up to content of V $x = 0.20$. A sample at composition $x = 0.28$ contained additional phases - $CoSb_2$ and VCoSb. Analysis of the lattice parameters do not shows considerable change of their values indicating insignificant solubility of V (a = 0.90387(1) nm for maximal content of V) (Table 2). However, the EPM analysis showed that V atoms substitute Co in $CoSb_3$ (up to ~1 at. %) and thus do not fill the voids of the initial $CoSb_3$ structure. All other binaries do not show some significant solubility of the third component at 870 K.

In the V–Co–Sb system at 870 K the formation of one ternary half-Heusler phase VCoSb (a = 0.57838(2) nm) is observed (Fig. 1). SEM pictures of $V_{60}Co_{10}Sb_{30}$, $V_{60}Co_{20}Sb_{20}$, $V_{20}Co_{50}Sb_{30}$, and $V_{50}Co_{10}Sb_{40}$ samples (Fig. 2) revealed the presence of VCoSb ternary phase in equilibrium with binary compounds. In contrast to the related $Zr_{1+x}Co_{1-x}Sb$ compound the observed VCoSb is characterized by single-point composition with no deviation from the equiatomic stoichiometry.

3.2. Electrical properties of the V-doped $CoSb_3$

As reported in the literature the $CoSb_3$ binary formed in the Co-Sb system shows semiconducting behavior [25]. We studied the electrical properties of V-doped samples based on $CoSb_3$ phase in the temperature interval 80–380 K (electrical resistivity) and 80–390 K (thermopower). Among all prepared samples we have chosen only three with a good quality to cut well-shaped pieces for electrical properties measurement. A brittleness of the rest samples made it impossible to cut well-shaped pieces. For the chosen V-doped samples the resistivity decrease with temperature increasing revealing semiconducting behavior in the investigated temperature range (Fig. 3). All studied samples are characterized by negative Seebeck coefficient (Fig. 3, Table 2) indicating the dominance of the electron-type of conductivity. Obtained experimental data exhibit that doping of the basic $CoSb_3$ skutterudite allows to considerably increase the power factor value Z^* at higher temperatures for V-doped samples in comparison with binary $CoSb_3$ (Table 2). Both resistivity ($\ln\rho(1/T)$) and Seebeck coefficient $S(1/T)$ dependencies are characterized by two activation regions proving the presence of at least two carrier activation mechanisms. The