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Half-Heusler phase related structural perturbations near stoichiometric composition FeZnSb

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ABSTRACT

Half-Heusler phases *XYZ* (Pearson symbol cF12) are chemically versatile and rich in physical properties. The half-Heusler phase in the Fe–Zn–Sb ternary system was reported in the year 2000. In this work, two new ternary phases are identified in the vicinity of the equiatomic composition FeZnSb in the same system: $Fe_{1-x}ZnSb$ (tetragonal, space group *P*4/*nmm*, Pearson symbol tP6$-\delta$, $Z=2$: $a=4.1113(6)$ Å, $c=6.0127(12)$ Å for $x=0.08$ (**1**), and $a=4.1274(6)$ Å, $c=6.0068(12)$ Å for $x=0.12$ (**2**)); and $Fe_{7.87}Zn_{6.72}Sb_8$ ($Fe_{0.98}Zn_{0.84}Sb$) (**3**) (cubic, space group *Fm*-3*m*, Pearson symbol cF96$-\delta$, $Z=4$, $a=11.690(13)$ Å). **1** and **2** crystallize in the PbFCl-type structure, and **3** adopts a unique $2\times2\times2$ supercell of a normal half-Heusler structure. The structures of both the tetragonal and cubic phases can be described as assemblies of half-Heusler structure related subunits. Electrical resistivity measurement on the pure sample of **2** shows it has metallic-like behavior, and its thermal and magnetic properties are also characterized.

1. Introduction

Half-Heusler phases have the general form *XYZ* and crystallize in the $C1_b$ structure, which consists of four interpenetrating face-centered cubic sublattices occupied by the three atoms *X*, *Y* and *Z* and a vacant site. Half-Heusler phases are known to combine with a wide variety of different elements. Typically, *X* and *Y* are the alkali metal, transition metal or rare-earth metal, and *Z* is the main group element. Different combinations result in half-Heusler phases exhibiting a great variety of electronic states and physical properties. Most studies of the half-Heusler phases seem to simply postulate an equiatomic composition. However, experiments indicated that the phases with compositions in the vicinity of the ideal equiatomic composition can be prepared, and the deviations from the equiatomic composition made a significant difference to their physical properties, such as the electrical transport properties of TiCoSb [1] and the magnetic properties of the half-metallic ferromagnet NiMnSb [2]. Offernes and Kjekshus et al. systematically investigated the homogeneity regions of a series of half-Heusler phases [3–6]. Their results indicated that the phases calculated to be stable semiconductor (such as NiTiSn, PtTiSn and TiCoSb with valence–electron concentration (VEC)=18) all take the euqiatomic composition, while the other phases show deviation from the euqiatomic composition [6].

Besides the influence of VEC on the composition deviation of a phase, structural perturbation can modify the electronic band structure acting as a substitute for a change in VEC [6], such as CaF_2-type structure in the disordered PtMnSn [7] and the $2\times2\times2$ supercell of a normal half-Heusler structure in CoMnSb [8]. We are interested in exploring the variations of structure and property with composition in half-Heusler phases. Ru–Zn–Sb system was investigated in our previous studies [9]. The equiatomic phase RuZnSb has VEC of 15, which is in the VEC gap in the structure map of half-Heusler phases [9]. Investigations showed that only the phase with a $2\times2\times2$ supercell of a normal half-Heusler structure existed in the solid solution range $Ru_{9-x}Zn_{7+x}Sb_8$ $(0\leq x\leq1)$ and no normal half-Heusler phase was observed. Both CoMnSb and $Ru_{9-x}Zn_{7+x}Sb_8$ $(0\leq x\leq1)$ adopt a $2\times2\times2$ supercell of a normal half-Heusler structure, but the ratios of the number of two different transition metals *X* and *Y* in respective ordered phases are different, namely $Co_8Mn_8Sb_8$ and $Ru_9Zn_7Sb_8$ [8,9]. In this work, as a result of our ongoing investigations on half-Heusler phases, we report the structural variation in the vicinity of the equiatomic composition in the Fe–Zn–Sb ternary system. Two new non-stoichiometric phases are identified, one is $Fe_{1-x}ZnSb$ [$x=0.08$ **(1)** and 0.12 **(2)**] with a PbFCl-type structure and the other is $Fe_{7.87}Zn_{6.72}Sb_8$ ($Fe_{0.98}Zn_{0.84}Sb$) **(3)** with a $2\times2\times2$ supercell of a normal half-Heusler structure. Physical properties for the pure sample of **2** are also characterized.

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2. Experimental section

2.1. Synthesis

All samples were prepared on about 300 mg scale via high-temperature reaction of iron (99.9%), zinc (99.99%) and antimony (99.8%) in evacuated fused-silica tubes. As shown in Table 1, five reactions with three different atomic ratios of Fe:Zn:Sb were carried out, 1:1:1, 0.95:0.99:1 and 0.91:0.97:1. The loaded non-stoichiometric compositions in the reactions **II**–**V** were decided according to the elemental analyses and single-crystal X-ray diffraction (XRD) refinements. In reactions **I**, **II** and **III**, the samples were heated to 1273 K at a rate of 60 K/h, maintained at 1273 K for 3 h, then cooled to 873 K at a rate of 50 K/h, and maintained at 873 K for four days. The loss of Zn and Sb due to condensation outside the reaction zone was reduced by placing the reactants at the least hot site of the ampoules, and the furnace was placed on small slope to make sure the elements contact thoroughly. Thereafter the ampoules were taken out from the furnace and cooled to room temperature in air. The products from the reaction **III** were then used as precursors without any treatment in the reactions **IV** and **V**. They were annealed again at 873 K for four days in the reaction **IV** and at 570 K for two weeks in the reaction **V**.

Powder XRD patterns were recorded with an X'pert MPD diffractometer (Philips) operating in Bragg–Brentano geometry with Cu $K\alpha$ radiation. The purities were checked by comparing the experimental patterns and the theoretical patterns calculated from the single-crystal refinement results. Chemical compositions of selected crystals were examined in a scanning electron microscope (CS 4DV, CamScan) providing an energy dispersive X-ray spectrometer (EDS, Si(Li)-detector, Noran Instruments).

2.2. Crystal structure determination

Crystals of **1**, **2** and **3** were selected from the reactions **III**, **IV** and **V**, respectively, and used for single-crystal XRD analyses. The diffraction intensities were recorded with an imaging plate diffractometer (IPDS, Stoe & Cie) operating with Mo Kα radiation (λ=0.71069 Å) at 293(2) K. Numerical absorption corrections based on the sizes and shapes of the crystals were applied to the data sets with the programs of *X-SHAPE* [10] and *X-RED* [11]. All structures were successfully solved by applying a direct method and subsequently refined on F^2 with a full-matrix least-square algorithm with the aid of the program of *SHELXTL*, version 6.1 [12].

Table 1
Reaction compositions, products in the Fe–Zn–Sb System.

Sample	Loaded Fe:Zn:Sb	Conditions (T_1/T_2)[a]	Products and estimated yields[b]	Single-crystal diffraction
I	1:1:1	1273/873	95% tetragonal phase+5% β-Zn_4Sb_3	
II	0.95:0.99:1	1273/873	95% tetragonal phase+5% β-Zn_4Sb_3	
III	0.91:0.97:1	1273/873	90% tetragonal phase+10% β-Zn_4Sb_3	**1**
IV		**III**@873	>98% tetragonal phase	**2**
V		**III**@570	90% superstructure phase+10% $Zn_{1+\delta}Sb_{1-\delta}$	**3**

[a] Loaded elements were melt at temperature T_1 at first, and then annealed at temperature T_2.

[b] Percentages were estimated according to observed peak intensities in powder patterns.

2.2.1. $Fe_{0.92}ZnSb$ (1) and $Fe_{0.88}ZnSb$ (2)

The extinction conditions led to the space groups of *P*4/*n* (No. 85) and *P*4/*nmm* (No. 129). Refinements with both space groups resulted in qualitatively identical structure models, therefore the higher symmetry space group *P*4/*nmm* (No. 129) was chosen for the detailed structure analysis. At this stage the refinements for both structures converged smoothly at *R*(*F*) values smaller than 5% and gave a composition of FeZnSb, and the structures were subsequently refined with anisotropic displacement parameters. Site occupancies were checked for deviations from unity by freeing the site occupancy factor (SOF) of an individual atom while the remaining SOFs were kept fixed. Iron positions in both structures were found with less than full occupancy (92% in **1** and 88% in **2**), while zinc and antimony with full occupancy. The crystal structure of FeZnSb was similar to MnZnSb [13] and was isotypic with PbFCl. As like in the refinement of MnZnSb, X-ray diffraction analysis did not allow to unambiguously determine whether iron and zinc atoms occupy only their respective sites or have a tendency for disorder. Neutron diffraction method indicated no mixed distribution of manganese and zinc [14], but magnetization measurements strongly suggested structural disorder of manganese and zinc [13,14]. In this work, based only on single-crystal XRD data, both structures were refined without mixed distribution of iron and zinc.

2.2.2. $Fe_{7.87}Zn_{6.72}Sb_8$ (3)

The structure was solved in the space group of *Fm*-3*m* (No. 225) and identical with $Ru_9Zn_7Sb_8$ [9]. At this stage the refinement converged smoothly at *R*(*F*) value smaller than 5% and gave a composition of $Fe_9Zn_7Sb_8$, and the structure was subsequently refined with anisotropic displacement parameters. Site occupancies were checked for deviations from unity by freeing the site occupancy factor (SOF) of an individual atom while the remaining SOFs were kept fixed. All positions are fully occupied except one of two zinc positions and one of two iron positions were found with less than full occupancy (72% for Zn1 and 86% for Fe2), resulting in the refined composition $Fe_{7.87}Zn_{6.72}Sb_8$. As like in **1** and **2**, the structure was refined without mixed distribution of iron and zinc.

Additional details concerning data collection and crystallographic data, atomic coordinates, and interatomic distances are summarized in Tables 2–4. Further details of the crystal structure

Table 2
Crystallographic and technical data of the single-crystal structure refinements of the compounds in the Fe–Zn–Sb system.

	1	**2**	**3**
Formula	$Fe_{0.92}ZnSb$	$Fe_{0.88}ZnSb$	$Fe_{7.87}Zn_{6.72}Sb_8$
Space group (No.), *Z*	*P*4/*nmm* (129), 2	*P*4/*nmm* (129), 2	*Fm*-3*m* (225), 4
Pearson symbol	$tP6-\delta$	$tP6-\delta$	$cF96-\delta$
a (Å)	4.1113(6)	4.1274(6)	11.690(13)
c (Å)	6.0127(12)	6.0068(12)	
V (Å^3)	101.63(3)	102.33(3)	1597.5(3)
D_c (g cm^{-3})	7.94	7.89	7.68
μ (mm^{-1})	31.43	31.21	29.93
θ_{max} (deg)	32.9	32.8	32.65
refl. coll. *R*(int)	1038/0.0528	998/0.1149	4331/0.1452
data/parameter	135/11	129/11	187/16
R1/wR2 $[I_o > 2\sigma(I_o)]$[a,b]	0.0336/0.0337	0.0315/0.0315	0.0811/0.0850
[all data]	0.0942/0.0942	0.0864/0.0864	0.1499/0.1513
Goodness of fit (F^2)	1.296	1.308	1.320
$\Delta\rho_{min}/\Delta\rho_{max}$/e (Å^{-3})	−1.872/1.342	−1.358/2.335	−3.129/5.546

[a] $R=\sum||F_o|-|F_c||/\sum|F_o|$,

[b] $wR=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.