

Preparation and Crystal Structure of $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$ and $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_2$ ($0 \leq x \leq 1$)

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Complete solid solutions of $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$ and $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_2$ with marcasite or pseudomarcasite structures have been synthesized. Lattice parameters a , b , and c follow Vegard's law in both series. From the results of crystallographic data, it is expected that the iron and cobalt ions change their apparent valence state from 4 to 2 due to anion replacement of Sb by Te.

Introduction

In recent years many investigators have been interested in the preparation and characterization of compounds with marcasite and arsenopyrite structures (1-5). Bjerkelund and Kjekshus (2) synthesized a considerable number of binary and ternary transition metal pnictides.

Although many experimental data on the preparation and properties of the binary and ternary transition metal pnictides with marcasite structure have been reported, there has been little investigation into the effect of replacement of the anion such as $M(Y_{1-x}X_x)_2$, where M is a transition element, X is a chalcogen, and Y is a pnictogen. Recently, Baghdadi and Wold (6) synthesized the compounds $\text{FeAs}_{2-x}\text{Se}_x$ ($0 \leq x \leq 0.13$) and from the results of electrical and magnetic measurement, they reported that the substitution of selenium for arsenic in the diamagnetic semiconductor FeAs_2 resulted in metallic and paramagnetic behavior. For the preparation of compounds with the chemical formula $M(Y_{1-x}X_x)_2$, the complete range of solid solutions with full replacement of the anion in $M(Y_{1-x}X_x)_2$ has not been synthesized, but only the end members, $\text{CoAs}_x\text{S}_{2-x}$ ($0 \leq x \leq 1$) (7) and $\text{CoP}_x\text{S}_{2-x}$ ($0 \leq x \leq 0.5$) (8) with the pyrite structure.

We have undertaken the study of the full anion-substituted system $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$, in which iron atoms change their apparent valence state from 4 to 2 depending on the x value, in order to investigate the phase relation of the marcasite structure in detail. In the present study, an attempt was made to synthesize a series of compounds with chemical compositions $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$ and $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_2$ ($0 \leq x \leq 1$) to see the effects of replacement of the Sb ion by Te ion on their crystal structure.

Experimental

Eleven compounds were prepared for both solid solutions by mixing stoichiometric quantities of the elements Fe(99.99%), Co(99.99%), Sb(99.999%), and Te(99.99%). Compositions were made up at 10 mole% intervals as shown in Table I and II. They were fired in evacuated and sealed silica tubes. Samples of the $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$ solid solutions were maintained for 12 hr at 1100°C and quenched in ice water. All samples were subsequently annealed at 600°C for 2 weeks, and finally quenched to room temperature. The solid solution of $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_2$ was prepared as mentioned below. The samples whose chemical compositions were in the range of $0 \leq x \leq 0.3$ were reacted at 800°C

TABLE I

UNIT CELL PARAMETERS AND THE AXIAL RATIOS OF c/a AND c/b IN THE SYSTEM $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$ ($0 \leq x \leq 1$)

Sample	a (Å)	b (Å)	c (Å)	c/a	c/b
FeSb ₂	5.829	6.535	3.196	0.548	0.489
FeSb _{1.8} Te _{0.2}	5.779	6.519	3.239	0.561	0.497
FeSb _{1.6} Te _{0.4}	5.719	6.491	3.302	0.577	0.509
FeSb _{1.4} Te _{0.6}	5.657	6.458	3.381	0.598	0.524
FeSb _{1.2} Te _{0.8} ^a	5.580	6.424	3.472	0.622	0.541
FeSbTe ^a	5.525	6.393	3.539	0.641	0.554
FeSb _{0.8} Te _{1.2} ^a	5.464	6.362	3.622	0.663	0.569
FeSb _{0.6} Te _{1.4}	5.414	6.336	3.699	0.683	0.584
FeSb _{0.4} Te _{1.6}	5.358	6.312	3.776	0.705	0.598
FeSb _{0.2} Te _{1.8}	5.308	6.288	3.830	0.722	0.609
FeTe ₂	5.275	6.269	3.872	0.734	0.618

^a Pseudo-orthorhombic symmetry.

TABLE II

UNIT CELL PARAMETERS AND THE AXIAL RATIOS OF c/a AND c/b IN THE SYSTEM $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_2$ ($0 \leq x \leq 1$)

Sample	a (Å)	b (Å)	c (Å)	c/a	c/b
CoSb ₂ ^a	5.583	6.388	3.377	0.60 ₅	0.52 ₉
CoSb _{1.8} Te _{0.2}	5.515	6.365	3.474	0.63 ₀	0.54 ₆
CoSb _{1.6} Te _{0.4}	5.425	6.317	3.588	0.66 ₁	0.56 ₈
CoSb _{1.4} Te _{0.6}	5.331	6.287	3.696	0.69 ₃	0.58 ₈
CoSb _{1.2} Te _{0.8}	5.278	6.253	3.787	0.71 ₈	0.60 ₆
CoSbTe	5.257	6.248	3.844	0.73 ₁	0.61 ₅
CoSb _{0.8} Te _{1.2}	5.256	6.248	3.875	0.73 ₇	0.62 ₀
CoSb _{0.6} Te _{1.4}	5.272	6.268	3.881	0.73 ₆	0.61 ₉
CoSb _{0.4} Te _{1.6}	5.296	6.283	3.891	0.73 ₅	0.61 ₉
CoSb _{0.2} Te _{1.8}	6.307	6.298	3.894	0.73 ₄	0.61 ₈
CoTe ₂	5.328	6.320	3.904	0.73 ₃	0.61 ₈

^a Pseudo-orthorhombic symmetry.

for 1 month. In the case of $0.4 \leq x \leq 1.0$, the materials were fired for 12 hr at 1100°C and quenched in ice water, and then annealed at 600°C for 2 weeks. After annealing, the samples were air quenched. In both cases of preparation for these solid solution series, the last step of the annealing processes was repeated until the products were homogeneous. Each product was identified by X-ray powder diffraction using silicon as internal standard.

Results and Discussion

(a) $\text{Fe}(\text{Sb}_{1-x}\text{Te}_x)_2$ Solid Solution Series

The X-ray powder diffraction patterns of the products in this system were completely indexed on the basis of a marcasite structure, except in case of $x = 0.4$, $x = 0.5$, and $x = 0.6$. In the composition range, $0.4 \leq x \leq 0.6$, the products were considered to be the arsenopyrite structure with monoclinic symmetry. However, the difference in symmetry between the orthorhombic pseudocell and the monoclinic cell is so slight that the lattice parameters of these three samples were calculated on the basis of pseudo-orthorhombic symmetry. The unit cell parameters and the axial ratios c/a and c/b are listed in Table I. The lattice parameters of both FeSb₂ and FeTe₂ corresponding to the end members in this solid solution series were in quite good agreement with those reported by Fan *et al.* (5) and Brostigen and Kjekshus (9). As seen in Table I, the lattice parameters a , b , and c follow Vegard's law. The fact that the FeSbTe had the arsenopyrite structure suggests that the electron configuration of the iron atom for the FeSbTe was $3d^5$ in the low spin state because the monoclinic arsenopyrite type structure is demonstrated only by compounds with d^5 low spin state configuration of transition metal ions such as FeAsSe, CoSb₂, and CoAs₂. However, in the present study, the monoclinic arsenopyrite structure appears only in the composition range $0.4 \leq x \leq 0.6$. This result indicates that the structural deformation from marcasite to arsenopyrite is introduced not only by the formal d^5 low spin configuration, but also by the low spin-configuration between $d^{4.8}$ and $d^{5.2}$.

(b) $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_2$ Solid Solution Series

In this system, CoSb₂ ($x = 0$) belonged to the monoclinic arsenopyrite structure and the lattice parameters of CoSb₂ were in good agreement with those reported by Kjekshus (3). In the composition range $0.1 \leq x \leq 1$, the X-ray diffraction patterns of the products were completely indexed as a marcasite structure and the lattice constants of the CoTe₂, which is one of the end members, agreed well with those reported by Brostigen

et al. (9). The crystal structure data are tabulated in Table II. As seen in this table, the lattice constants follow Vegard's law.

The axial ratios c/a and c/b are constant in the composition range $0.5 \leq x \leq 1.0$ and these values are in quite agreement with those for the anomalous marcasite compounds with d^6 and d^7 electron configurations (1). This result suggests that the apparent valence state of the cobalt ion changes from 4 to 2, corresponding to anion replacement of Sb by Te. In case of the Fe(Sb_{1-x}Te_x)₂ solid solution series, it is expected that the iron ion changes its valence state, as does the cobalt ion, since in this system FeSbTe belongs to the monoclinic arsenopyrite structure.

In summary, the complete solid solutions of Fe(Sb_{1-x}Te_x)₂ and Co(Sb_{1-x}Te_x)₂ ($0 \leq x \leq 1$) can be synthesized. The results of axial ratios indicate that both iron and cobalt ions change their valence state from 4 to 2,

corresponding to anion replacement of Sb ion by Te ion in these series.

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