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Synthesis and Structural Evolution of $RuSb_3$, a New Metastable Skutterudite Compound

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A thin-layer synthesis technique was used to synthesize bulk amounts of the metastable phase, $RuSb_3$, a novel compound with the skutterudite structure. The compound crystallized at 350 °C and was stable to 525 °C. When annealed above 550 °C, it decomposed into $RuSb_2$ and Sb. Rietveld refinement of X-ray diffraction data showed the presence of excess Sb residing in the interstitial site in the skutterudite structure. X-ray diffraction and thermal analysis experiments allowed us to examine the evolution of the sample as a function of annealing and determine the reaction pathway. The activation energy for the crystallization of the compound was determined to be 3 eV/nucleation event, while the activation energy for decomposition was approximately 8 eV.

Introduction

The field of solid state chemistry is continually faced with the challenge of how to make new, useful compounds. Unlike the fairly gentle temperatures and techniques used in organic chemistry, most solid state chemistry reactions take place at high temperatures to overcome the diffusion difficulties inherent in reacting solids. The resulting compounds, many of them very useful, are the thermodynamic products of these reactions. In recent times, the focus has changed from high temperature, thermodynamic products, to searching for metastable products, which are usually synthesized at lower temperatures. Several schemes have been used to achieve this, including flux and hydrothermal methods,[1] high-pressure techniques,[2] and thin film techniques.[3]

In addition to the reactivity challenges due to slow solid state diffusion rates, and unlike in organic chemistry, there are few guidelines in materials chemistry for predicting the stability and structure of unknown solid state phases. In solid state chemistry, the multiple coordination geometries possible even within binary systems are so large that it makes accurately predicting the coordination and structure of unknown compounds very difficult.[4] One approach to predicting undiscovered compounds is to use analogous phase diagrams as guides to identify potential local energy minima for particular structures in related phases. We used this predictive technique to target and prepare $RuSb_3$, a new compound with the skutterudite structure.

Skutterudites have been of interest to the materials science community for some time, since they have been identified as potentially useful for thermoelectrics applications. The skutterudite structure consists of a transition metal atom octahedrally coordinated to six pnictide atoms. The octahedra are shared by the metal atoms, creating a 1:3 metal-to-pnictide ratio. The linking of the octahedra creates a 12 coordinate interstitial site, belted by four pnictides bound in a ring. The interstitial site is empty in the thermodynamically stable binary skutterudite compounds, $CoSb_3$, $RhSb_3$, and $IrSb_3$. Although the electrical properties of these compounds are highly favorable for thermoelectric materials, their thermal conductivities are too high,[5] and so there have been consistent attempts to optimize their electronic and thermal properties. Two main procedures have been suggested to decrease the thermal conductivity in skutterudites. The first, suggested by Slack, is to insert rare earth atoms into the void in the structure. These interstitial atoms will "rattle" in the void and scatter phonons.[6] The second method is to use larger metal or pnictide atoms in the compound, which provides a larger, more complex unit cell.[7] As a result of Slack's

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suggestions, the binary compounds have been modified to make the related filled compounds, $A_xM_4Sb_{12}$ (A = rare earth; M = Co, Rh, and Ir), where the A atoms occupy the 12 coordinate "void" site in the skutterudite structure.

The ternary compounds, $A_xM_4Sb_{12}$ (A = rare earth; M = Fe, Ru, Os), have also been extensively studied. In these compounds, the atom A, in the interstitial site, is necessary to donate electrons to the compound, stabilizing the structure.[8] The related binary compounds, $FeSb_3$, $RuSb_3$, and $OsSb_3$, lack filler atoms and are not thermodynamically stable. Although the binary compound $FeSb_3$ has been formed, it is metastable,[9] and there have been no reports to date of the synthesis of binary skutterudites formed from the remaining elements in this column of the periodic table. The antimony-rich part of the Ru−Sb system has been previously investigated, but the synthesis of a binary skutterudite was not reported.[10]

There are extensive similarities among the phases formed by Sb with the group 8 and 9 transition metals. All six elements form 1:2 compounds with Sb, and all but Os form 1:1 compounds. All the 1:2 compounds have the marcasite FeS_2 structure, FeSb, CoSb, and IrSb all have the NiAs structure, and RuSb and RhSb both have the MnP structure.[11,12] These similarities have lead us to attempt to synthesize $RuSb_3$, both in the hopes that it will prove to be useful for thermoelectric applications and to provide further insight into the factors that control or affect metastable phase formation.

Experimental Section

All samples were synthesized in a custom-built ultrahigh vacuum deposition system, described elsewhere.[13] Samples were synthesized in a 10^{-6}−10^{-7} Torr atmosphere. Ruthenium was deposited from an electron beam gun at a rate of 0.2 or 0.5 Å/s, and antimony was deposited from an effusion cell at a rate of 1 Å/s. The ruthenium and antimony layers were deposited alternately for 80 repeats, resulting in repeat layer thicknesses of 10−15 Å and total sample thicknesses of 800−1200 Å. A computer-controlled quartz crystal monitoring system was used to control layer thickness. Samples were deposited on a 4 in. diameter silicon wafer coated with poly(methyl methacrylate) (PMMA), a silicon chip, and a 1 in. square piece of zero-background cut quartz. The coated wafers were soaked in acetone to dissolve the polymer, which lifted the powder sample off of the wafer. The powder sample was collected by vacuum filtration using a Teflon filter.

X-ray diffraction studies were conducted on the quartz piece and the silicon chip using a Philips X'Pert diffractometer and a Scintag XDS-2000 θ−2θ diffractometer. X-ray reflectivity and diffraction studies were conducted on both as-deposited and annealed samples and on both film and powder samples. The powder samples were combined with NIST silicon powder standard reference material number 604b to verify lattice parameters and for quantitative analysis using Rietveld refinement. Unless indicated otherwise, samples were annealed for 30 min at a time in a Thermolyne 1500 box furnace under nitrogen atmosphere. Annealing temperatures ranged from 300 to 600 °C. Compositional studies were conducted on a Cameca S-50 electron probe microanalysis (EPMA) instrument using 20 nA beam current and beam voltages of 8, 10, and 15 keV. Differential scanning calorimetry measurements were conducted on a Netsch DSC 200 PC. 0.5−1 mg of powder material was used for all DSC experiments, and the samples were heated from 50 to 550 or 600 °C, at a rate of 2, 5, 10, or 20 °C/min.

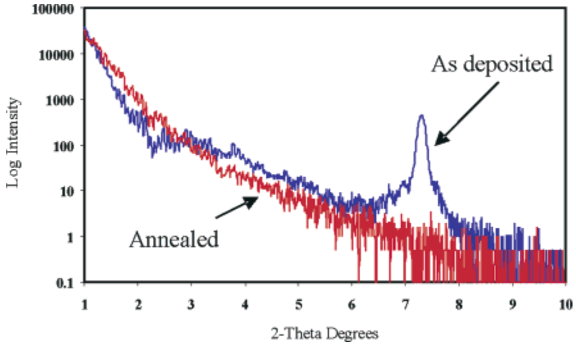

Figure 1. Representative low-angle X-ray diffraction pattern of the unannealed and annealed (to 335 °C) samples. The Bragg reflection has disappeared during annealing, indicating complete interdiffusion.

Table 1. Compositional Data and Intended and Actual Thicknesses for All Samples

name	at. % Ru	at. % Sb	intended layer thickness (Å)	actual layer thickness (Å)	actual tot. thickness (Å)
A1	4.29	95.71	15	14.5	474
A2	6.77	93.23	16	15.6	795
A3	8.29	91.71	16	15.9	684
A4	16.42	83.58	15	11.9	1045
A5	17.68	82.32	15	14.4	no peaks
A6	21.97	78.03	15	12.1	1051
A7	35.73	69.27	15	14.5	1145
A8	40.61	59.39	15	15.8	no peaks

Results and Discussion

We synthesized a series of samples that varied in composition from Sb-rich to Ru-rich, as presented in Table 1. Layer and total thicknesses were calculated from the Bragg reflections and the Kiessig fringes, respectively. In some cases the samples were sufficiently rough that no Kiessig fringes were discernible, and we could not calculate the total thickness (indicated by "no peaks" in Table 1). These samples were synthesized with total thicknesses similar to the other samples. The samples are completely X-ray amorphous before annealing, indicating that no crystalline material is present. Figure 1 shows a representative X-ray reflectivity pattern for a sample before and after annealing to 335 °C. The Bragg reflection in the unannealed sample results from the modulation of electron density in the sample due to sequential deposition of the elements rather than any crystalline character. The Kiessig fringes are visible in both scans, but the first Bragg reflection has disappeared during annealing, indicating that the layers have completely inter-

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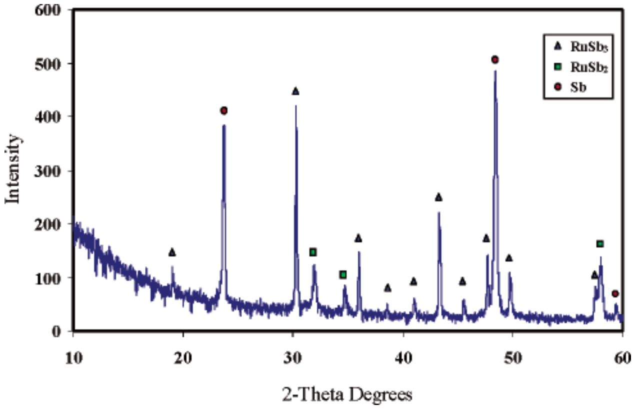

Figure 2. High-angle X-ray diffraction data collected from a powder that was heated in the DSC to 550 °C showing three crystalline phases: $RuSb_3$, $RuSb_2$, and Sb. The peaks were distinct enough to allow calculation of the $RuSb_3$ lattice parameter: 9.338(1) Å.

diffused. Before complete interdiffusion, the position of the Bragg reflection shifted, reflecting a contraction in the layer thickness from 12.1 to 11.8 Å. This layer contraction is frequently observed during annealing of thin film samples and is attributed to the increase in sample density as vacancies and other defects are eliminated.[14] A summary of the total and layer thicknesses for the unannealed samples can be found in Table 1.

The samples with greater than 90 at. % antimony did not show any irreversible events in the differential scanning calorimetry experiments. X-ray diffraction analysis of these samples indicated that the only phase to crystallize was antimony. The lack of an exotherm for the crystallization of antimony is likely due to it crystallizing gradually, rather than all at once, which has been observed in a number of cases.[14,15] Differential scanning calorimetry experiments conducted on nearly all the samples with less than 90 at. % antimony showed one irreversible exotherm in the temperature range under 450 °C. This peak occurred between 290 and 390 °C. In ~10% of the samples, a second exotherm with very small amplitude occurred within 50 °C of the first exotherm. We were unable to identify any structural changes that pertained to this exotherm. High-angle X-ray diffraction studies were conducted on powder samples from the DSC experiments, each of which had been annealed to 550 or 600 °C. When annealed to 550 °C, all samples where the composition was less than 90% Sb showed mixed phases of $RuSb_2$, Sb, and in some cases $RuSb_3$. The targeted skutterudite phase was visible in samples A4, A5 (see Figure 2), and A7. The lattice parameter of the skutterudite phase of A5 was calculated to be 9.338(1) Å, which is significantly larger than the reported values for $CoSb_3$ ($a = 9.034$ Å)[16] and $IrSb_3$ ($a = 9.2503$ Å)[17] and is similar to values for $BaRu_4Sb_{12}$ ($a = 9.315$ Å).[18]

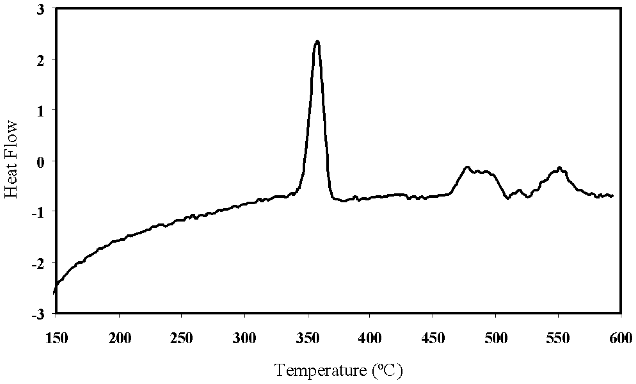

Figure 3. Differential scanning calorimetry data for sample A6, with a heating rate of 10 °C/min. The exotherm at 350 °C is due to crystallization, and the exotherms between 475 and 550 °C are due to decomposition into $RuSb_2$ and Sb.

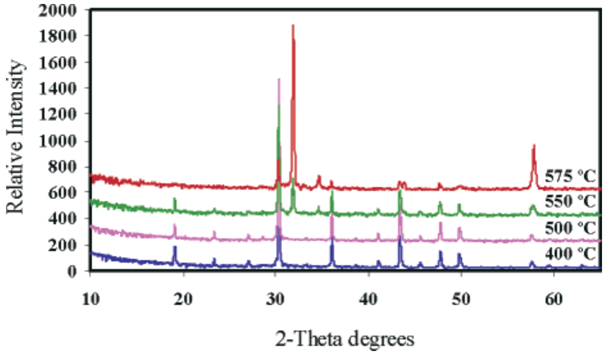

Figure 4. Selected high-angle X-ray diffraction scans for sample A6, showing the change in phases from pure $RuSb_3$ (500 °C and below) to a mixed phase of $RuSb_3$ and $RuSb_2$ at 550 °C and then a mixed phase of $RuSb_2$ and Sb at 575 °C.

To determine the structural changes taking place during the observed exotherms, detailed annealing studies were conducted, using the thermal analysis data as a guide. Figure 3 contains the DSC data for sample A6, which has the closest stoichiometry to the ideal 1:3 ratio. High-angle X-ray diffraction data collected below the exotherm at 350 °C revealed that the sample remained X-ray amorphous. Figure 4 summarizes the diffraction data collected as a function of annealing temperature from 400 to 575 °C, with the sample held at each temperature for 30 min. All scans through the 525 °C annealing (not shown) show a phase-pure skutterudite diffraction pattern, which indicates that the large exotherm is associated with the crystallization of the skutterudite phase. The scan of the sample annealed to 550 °C reveals a mixed phase of $RuSb_3$ and the thermodynamically stable phase $RuSb_2$; the skutterudite phase has completely disappeared after the sample was annealed at 575 °C. This decomposition is confirmed by exothermic peaks in the DSC experiments where the sample was heated to 600 °C (Figure 3). Exothermic decomposition peaks indicate that the compound is metastable; this metastability confirms the findings of higher temperature syntheses, in which this phase was unable to be formed.[10] The differences between the temperatures for the structural transitions viewed using X-ray diffraction and the exothermic peaks observed in the thermal analysis of these samples is due to several differences in the treatment of the samples. First, the thermal analysis was conducted on powder samples, while the annealing studies for X-ray diffraction were conducted on thin films that had been

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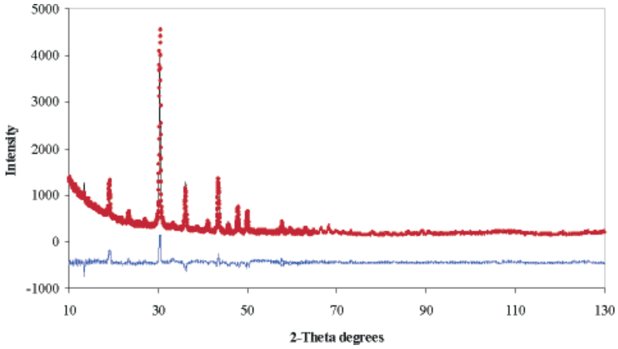

Figure 5. Representative Rietveld refinement. Red points are experimental data, the black line is the calculated curve, and the blue is the difference curve which is offset for clarity. The lattice size is 9.336 Å, Ru atoms are located at (0.25, 0.25, 0.25), and Sb atoms are at (0, 0.16, 0.34) and (0, 0, 0). The thermal parameters and occupancy for Ru and Sb1 were held constant at $U = 0.01$ and $F = 100\%$, respectively. Both parameters were refined for Sb2 (interstitial), giving $U = 0.41$ and $F \sim 57\%$. $X^2 = 2.7$, $R_{wp} = 0.094$, and $R_p = 0.071$.

Table 2. Sample Rietveld Refinement Data[a]

atom	x	y	z	occ.	U (Å^2)
Ru	0.25	0.25	0.25	1	0.01
Sb1	0	0.1607	0.3424	1	0.01
Sb2	0	0	0	0.57	0.41

[a] U values and occupancies for Ru and Sb1 are fixed; all other values are refined. $X^2 = 2.658$. $R_{wp} = 0.0935$. $R_p = 0.0714$. Lattice size = 9.325 Å.

deposited on off-cut quartz. In addition, the DSC samples were heated at a constant rate through a range of temperatures, while the X-ray samples were held at one constant temperature for a longer period of time. Kissinger analysis demonstrates the effect of heating rate on the temperature at which a thermal event occurs, so it is not surprising that the temperatures vary somewhat between the two methods.

A more careful look at the high-angle diffraction data showed changes in the lattice parameter as a function of annealing temperature. We suspect that this shift is a result of defects being removed from the structure during annealing. Rietveld refinement was employed to provide more in depth structural information, including the atomic positions and occupancies. The standard skutterudite crystal structure, with $Im\bar{3}$ symmetry, 8 Ru atoms and 24 Sb atoms per unit cell, and an empty interstitial site, was not able to reproduce the peak intensities. Several structural and experimental variables can affect the peak intensities, including crystallite size and strain, sample transparency to the X-ray beam, diffractometer alignment, and sample position in the X-ray beam. Modeling these parameters moderately improved the fit but did not correct the intensity mismatches. Since the samples had been synthesized with excess Sb present, we added Sb to the interstitial site (0, 0, 0), and this solved the intensity problem. There are two interstitial sites/unit cell, giving a maximum of two additional Sb atoms/unit cell. The refined occupancy of Sb at (0, 0, 0) was approximately 55% and resulted in a significantly improved fit for intensity (see Figure 5). The large thermal parameter ($U = 0.41$) is typical of the interstitial atoms in skutterudites. Table 2 summarizes the structural parameters. We conclude that although we have synthesized binary $RuSb_3$, it would be better expressed as $Sb_\delta Ru_4Sb_{12}$ to reflect the Sb in the interstitial site. In previously reported filled $RuSb_3$ compounds, several rare earth atoms (Ba, La, Ce, Pr, Nd, Eu) have been included to donate charge and stabilize the structure.[18-20] These filled skutterudites were designed to have 100% filling of the interstitial site. The coincidental filling that we observe, of Sb in the interstitial site, is therefore not surprising, since Sb should be able to donate charge to stabilize the $RuSb_3$ structure. We are not aware of other cases in which Sb is used as a filled atom, other than that which we observed being incorporated into the $CoSb_3$ interstitial site in a recent study.[21]

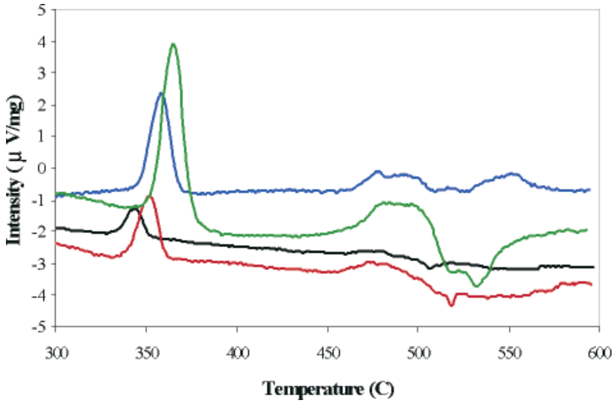

Figure 6. Superimposed differential scanning calorimetry data for the scans used in Kissinger analysis. The black scan is 2 °C/min, the red is 5 °C/min, the blue is 10 °C/min, and the green is 20 °C/min.

In a broader context, it is instructive to examine the structural evolution of the initially modulated reactants to determine the factors that control metastable phase formation. In bulk reactions, interdiffusion and interfacial nucleation determine which compounds form. In contrast, the Ru−Sb samples investigated here were deposited with angstrom-thick layers, which allowed interdiffusion to be completed during gentle heating, before nucleation could occur at the evolving interfaces, as confirmed by the diffraction data in Figure 1. After interdiffusion, only a small amount of additional heating was required to induce the samples to nucleate and crystallize. The composition of the amorphous intermediate determined which compounds crystallized. Samples with 75−85% Sb crystallized $RuSb_3$. The activation energy of crystallization of $RuSb_3$, 3 eV/nucleation event, was calculated from thermal data collected at scan rates of 2, 5, 10, and 20 K/min, (see Figure 6) via a method first suggested by Kissinger.[22] The presence of distinct, exothermic decomposition peaks allowed us to determine the activation energy for transforming $RuSb_3$ into the thermodynamically favored products, $RuSb_2$ and Sb. This energy was calculated to be approximately 8 eV, significantly higher than the activation energy to form $RuSb_3$. Since the temperatures of the two decomposition peaks did not correspond exactly to the decomposition temperature we observed using

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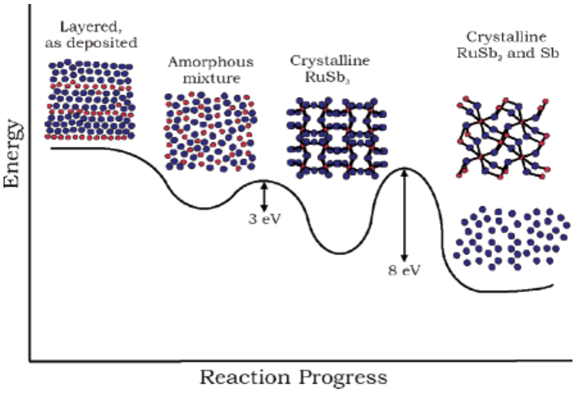

Figure 7. Schematic of proposed reaction pathway, from mixing of the layered compound, to crystallization, and to decomposition.

X-ray diffraction, and at some scan rates we only clearly observed one decomposition peak, we used the average between the two energies calculated to provide an approximate decomposition energy.

The fact that this decomposition is exothermic and results in two stable phases indicates that $RuSb_3$ is thermodynamically unstable at all temperatures. This confirms Caillat's investigations into the Ru−Sb system, since their syntheses were conducted at temperatures too high for $RuSb_3$ to form.[10] The formation of an amorphous phase, followed by crystallization of $RuSb_3$ and eventually decomposition into $RuSb_2$ and Sb, might follow a reaction pathway similar to that in Figure 7. This reaction pathway is specific to one in which nucleation, not diffusion, is the rate-limiting step and in which only enough heat is input to allow movement between the kinetic steps in the reaction pathway.

Summary

Using a thin layer vacuum deposition technique, we have synthesized bulk amounts of the novel, metastable, binary skutterudite phase, $RuSb_3$. The initially amorphous, layered mixture crystallizes at low temperatures to selectively form this phase. The lattice size of $RuSb_3$ is even larger than the filled $A_xRu_4Sb_{12}$ samples that have been previously synthesized.[19] This partially results from the presence of excess Sb in the "voids" in the skutterudite structure. Differential scanning calorimetry data indicate that this metastable phase has a window of kinetic stability, decomposing if annealed past 525 °C. The exothermic decomposition of $RuSb_3$ into $RuSb_2$ and Sb demonstrates that this novel phase is metastable at all temperatures.

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