Rational Synthesis of Metastable Skutterudite Compounds Using Multilayer Precursors

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Abstract: A new metastable binary compound and a series of new, metastable ternary crystalline compounds with the skutterudite crystal structure have been prepared through controlled crystallization of amorphous reaction intermediates formed by low-temperature interdiffusion of modulated elemental reactants. Discussed in this paper are $La_{1-x}Fe_4Sb_{12}$, $FeSb_3$, $Hf_{1-x}Fe_4Sb_{12}$, and $Y_{1-x}Fe_4Sb_{12}$. The amorphous reaction intermediate for each system crystallizes exothermically near 200 °C forming the desired skutterudite structure. At temperatures above 500 °C, they decompose exothermically forming a thermodynamically more stable mixture of binary compounds and elemental components. We propose that the desired compounds nucleate from the amorphous precursor because slow solid state diffusion rates hinder disproportionation into the more stable mix of binary compounds and elements. This general synthetic approach to prepare new metastable compounds gives control of both the *composition and structure* of the product compounds.

Introduction

The chemistry of extended inorganic solids has largely been the study of thermodynamically stable phases. This is a consequence of the high temperatures and long reaction times used to obtain reasonable diffusion rates in solid state reactions.[1,2] A phase diagram is a summary of the resulting information regarding phase stability as a function of temperature and composition. For example, early studies of the reactions between iron and antimony resulted in the iron antimony phase diagram shown in Figure 1. This phase diagram contains two compounds, a defect NiAs phase with a broad composition range labeled ϵ and $FeSb_2$ with a narrow stoichiometry range.[3] With regard to the title compounds, this diagram shows that at equilibrium, a mix of one part iron and three parts antimony would consist of a mixture of $FeSb_2$ and elemental antimony.

Solid state chemists have long sought reaction routes which give the ability to prepare materials by design—where structural and chemical characteristics are rationally planned for and controlled.[2] This ability would be particularly important when trying to modify a property of a known family of materials to optimize technological performance within that group. For example, the quaternary alloys of rare earth iron−cobalt antimonides known as "filled skutterudites" have recently been reported to be promising thermoelectric materials, potentially permitting thermoelectrics to approach the efficiency of vapor-compression-based cooling units.[4] These materials are promising thermoelectric materials because they have low thermal conductivity while still maintaining good electrical properties. The low thermal conductivity is thought to result from the large vibrational amplitude of the lanthanum atoms. There are several obvious modifications, such as optimizing the doping and
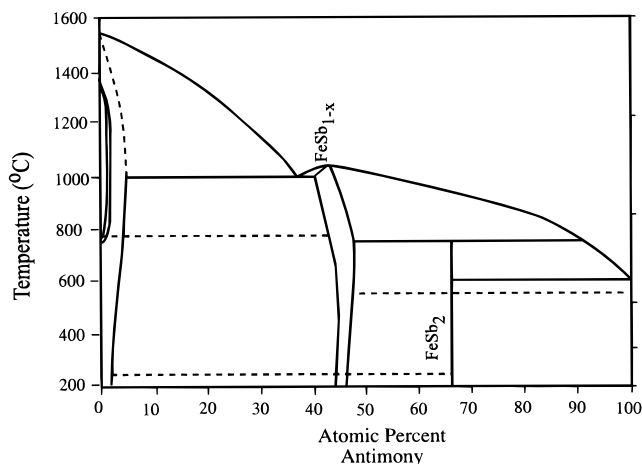

Figure 1. A schematic of the iron−antimony phase diagram. Reprinted with permission from ref 16 from data in Copyright 1986 ASM International.

replacing the lanthanum cation with a cation with a smaller ionic radius and higher mass, which have been predicted to result in the skutterudites having the highest efficiencies of any known thermoelectric material.[4] Unfortunately, while the modifications suggested are simple substitutions, preparing these target compounds is a significant synthetic challenge using standard solid state chemistry techniques.[1]

One solution to this challenge is a synthetic approach which replaces diffusion as the rate limiting step with nucleation, a kinetic phenomenon. This approach has been used successfully in exploratory synthetic studies to prepare many new compounds at low temperatures out of solutions or reactive fluxes. Unfortunately, these systems can be exceedingly complicated and little is known regarding the speciation in the intermediate solutions. Replacing one species in the reacting system with another, even if it is isoelectronic, often leads to completely unexpected products. This lack of background information makes it impossible to rationally design experimental conditions to yield a particular product.

We have been developing a general synthetic strategy based on using modulated elemental reactants in which the layers are

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thin enough that the layers interdiffuse before nucleation occurs.[5,6] By changing the ratio of the initial elemental layer thicknesses, the composition of the amorphous reaction intermediate formed by low-temperature interdiffusion of the layers can be controlled.[7,8] Nucleation is now the rate limiting step in compound formation.[9,10] The slow diffusion rates are now advantageous, because the nucleation of the desired compounds which have the same composition as the amorphous intermediate is easier than disproportionation to more thermodynamically stable compounds.[5] In this paper we demonstrate for the first time the ability of this synthetic approach to prepare new metastable compounds with desired *composition and structure*. We report on the synthesis of a series of metastable ternary iron skutterudites as well as a new binary compound, the metastable compound $FeSb_3$.

Experimental Section

Sample Preparation. A custom built deposition system with independently controlled deposition sources was used to prepare the multilayer samples. All of the elements were deposited at a rate of 0.5 Å/s using Thermionics electron beam gun sources which were controlled by Leybold-Inficon XTC quartz crystal thickness monitors. The background pressure was kept below 1×10^{-7} Torr during deposition. Multilayer films were simultaneously deposited on two adjacent substrates, one polished (±3 Å rms) silicon wafer (or miscut quartz zero-background plate) and one poly(methyl methacrylate) (PMMA) coated wafer. The samples deposited on the polished wafers were used for low-angle X-ray diffraction measurements. The samples deposited on the miscut quartz zero-background plate were used to collect high-angle X-ray diffraction data for Reitveld refinement. The films on the PMMA coated wafers were removed from the substrates by immersing the wafers in acetone. The suspended sample was filtered and washed to remove dissolved PMMA and then dried on the Teflon filters.

Compositional Analysis. Electron probe microanalysis (EPMA) was used to determine the composition of all as-deposited samples. Portions of the sample collected on the Teflon filters (approximately 9 mm^2) were adhered to a glass substrate by double-sided conductive carbon tape. The microprobe data were collected on a Cameca S-50 using a 10 keV accelerating voltage, a 10 nA beam current, and a 1 μm spot size.

X-ray Diffraction. Diffraction data were collected using copper k-α radiation on a Scintag SDS-2000 $\theta-\theta$ diffractometer with a sample stage modified to allow rapid and precise alignment for low-angle measurements. The low-angle diffraction pattern resulting from the periodic layered structure of the as-deposited sample was used to determine modulation thicknesses and widths of the composition profiles between elemental layers. High-angle diffraction data were used to identify crystalline elements or compounds in the as-deposited films, as free-standing samples, and as a function of annealing temperature and time. A quartz zero-background plate was used as a sample support for all high-angle work.

Differential Scanning Calorimetry (DSC). The evolution of the samples as they were subjected to elevated temperatures was monitored using a TA Instruments TA9000 calorimeter fitted with a 910 DSC cell. Approximately 1 mg of sample was placed into an aluminum pan and sealed by crimping for each experiment. The sample was heated from ambient temperature to 550 °C at rates of 10 °C/min under flowing nitrogen and then allowed to cool back to room temperature.

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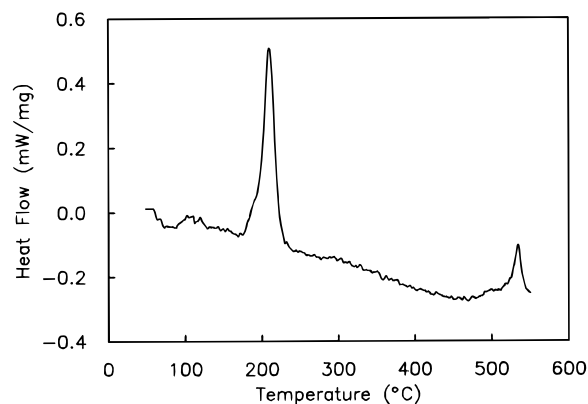
Figure 2. Differential scanning calorimetry data for a representative La−Fe−Sb sample. The exotherm at 210 °C is from crystallization of $La_{1-x}Fe_4Sb_{12}$. The exotherm at 535 °C is from decomposition into $LaFe_4Sb_{12}$, La, Sb, and $FeSb_2$.

Without disturbing the sample or instrument, this cycle was repeated to measure reversible transitions in the sample as well as the cell background. The net heat flow associated with the irreversible changes occurring in the sample during the initial heating cycle was determined by subtracting the data collected during the second cycle from those for the first.

Results and Discussion

We initiated this study by preparing several La−Fe−Sb multilayer films. These samples were prepared by sequential evaporation of the elements from three electron beam evaporation sources. The multilayer repeat distance was chosen to be small enough that the elements could be reasonably expected to interdiffuse before crystallizing. Before any annealing, the samples were characterized using low-angle X-ray diffraction and elemental analysis by energy dispersive X-ray analysis in an electron microscope (microprobe). For the sample discussed in the following paragraph, low-angle X-ray data indicated that the multilayer repeat distance was 21 Å and that the elements were significantly interdiffused but still layered on deposition. Microprobe analysis indicated that the average composition of this sample was La:Fe:Sb 0.81:4.17:12.

The sample was annealed in a differential scanning calorimeter at a scan rate of 10 °C/min, and the results are shown in Figure 2. The data show two irreversible exotherms on heating, one at 210 °C and one at 535 °C. Diffraction data collected after each of these exotherms as shown in Figure 3 indicate that the first exotherm results from the formation of the desired skutterudite compound while the second exotherm results from the decomposition of the skutterudite compound into a mixture of binary compounds and elemental components. After this second exotherm, the sample contains the distribution of products observed from conventional high-temperature synthesis. From these calorimetry data, an energy diagram as a function of the reaction progress can be created as shown in Figure 4. The energy difference between the reactants and the initial skutterudite compound is the integrated heat from the low-temperature exotherm. This product is only kinetically stable, however, being metastable relative to a mix of binary compounds by the integrated heat of the second exotherm. This provides the necessary information to optimize the crystallinity of the metastable skutterudite. Indeed, plan view TEM images show that substantial grain growth occurs between 250 and 400 °C without any evidence for decomposition of this metastable product.

To further characterize the skutterudite compound formed after the initial exotherm, a Rietveld refinement of the structure was undertaken. The results of this structural refinement are
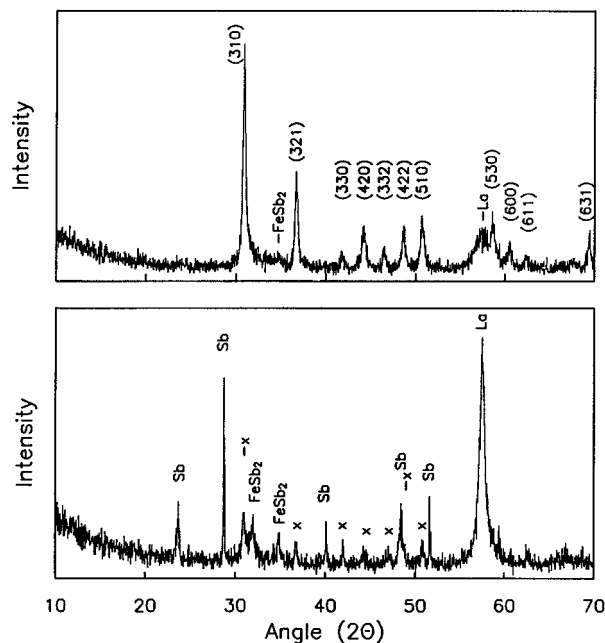
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Figure 3. X-ray diffraction scans taken on the La−Fe−Sb sample shown in Figure 2 after heating to 250 °C (top) and 550 °C (bottom). The top diffraction pattern is that of $La_{1-x}Fe_4Sb_{12}$ with a small amount of lanthanum and $FeSb_2$ impurities. The bottom diffraction pattern is that of a mixture of La, Sb, and $FeSb_2$ with a minor component of $LaFe_4Sb_{12}$ indicated by the diffraction maxima marked with X's.
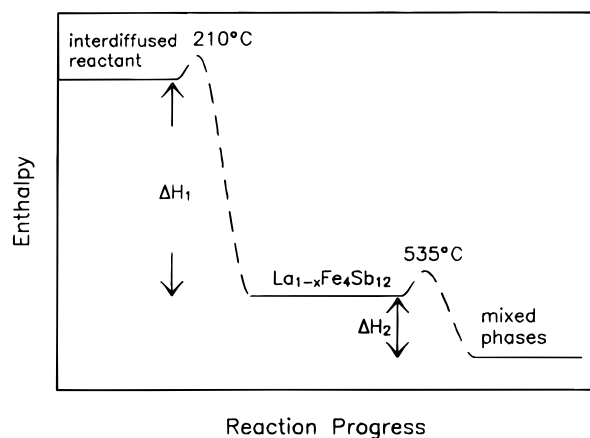

Figure 4. Energy diagram showing enthalpy changes of a La−Fe−Sb sample during heating from room temperature. The enthalpy of formation of $La_{1-x}Fe_4Sb_{12}$ from the interdiffused initial reactant, ΔH_1, is 126 kJ/mol. The enthalpy associated with the decomposition of $La_{1-x}Fe_4Sb_{12}$ into a mixture of La, Sb, and $FeSb_2$ with a minor component of $LaFe_4Sb_{12}$, $\Delta H_2 = 34$ kJ/mol.

Table 1. Positional and Thermal Parameters for $La_{1-x}Fe_4Sb_{12}{}^a$

$Im\bar{3}$	La 2(a)	Fe 8(c)	Sb 24(g)
x	0	1/4	0
y	0	1/4	0.3335(5)
z	0	1/4	0.1572(5)
B	10(2)	1.7(3)	1.9(1)
occupancy	0.4−0.7	1	1

^{a} Unit cell size is $a = 9.1957(8)$ Å. $R_{wp} = 10.5$, $R_p = 8.1$. Standard deviations for least significant digits are given in parentheses for refined parameters. Thermal parameters are estimated to be a factor of 7.5 too large due to a systematic error in the absorption correction. La occupancy is estimated by fixing the La thermal parameter at high and low values and refining the occupancy.

shown in Table 1. The structure of our low-temperature skutterudite is very similar to that previously determined for $LaFe_4Sb_{12}$.[11,12] Our low-temperature product, however, had a

partial occupancy of the lanthanum sites and a significantly larger unit cell than reported for the high-temperature product (9.1957 versus 9.1395 Å). We believe the lanthanum non-stoichiometry arose from the low lanthanum content of the initial reactant, and the difference in lattice parameters can be understood by considering the lanthanum as a source of bonding electrons for the iron−antimony framework. A reduction in the number of these electrons due to partial occupancy of the lanthanum will cause the framework to expand. Interestingly, it is not possible to prepare this low-temperature, partially filled skutterudite via the conventional high-temperature methods; during the 535 °C exotherm the lattice parameter of the skutterudite is observed to contract, forming the previously reported high-temperature product as part of a mixture containing $FeSb_2$, elemental antimony, and elemental lanthanum.

The low nucleation temperature found in synthesizing the new metastable $La_{1-x}Fe_4Sb_{12}$ compound indicates that the skutterudite structure nucleates easily, which led us to explore the possibility of preparing structurally related compounds. The partial occupancy of the lanthanum led us to attempt to prepare the thermodynamically unstable parent binary compound, $FeSb_3$. We also decided to replace the trivalent lanthanum with either a smaller trivalent cation or a tetravalent cation as suggested previously to further reduce the thermal conductivity of these promising thermoelectrics. For a smaller trivalent cation, we chose yttrium which has an ionic radius of 0.90 Å compared with 1.03 Å for lanthanum. For a tetravalent cation, we chose hafnium which has an ionic radius of 0.71 Å.[13,14] As in the synthesis of the lanthanum compound, we began by layering the desired elements to yield an initially layered reactant with a repeat thickness approximately 20 Å and a composition near that of the desired compound. In the yttrium containing sample, calorimetry data of the free-standing films show a single exotherm on heating (at 205 °C). In both the binary sample and the hafnium sample, the DSC trace from the free-standing film shows two irreversible exotherms on heating (at 145 and 360 °C for the binary sample and 240 and 400 °C for the hafnium sample). Diffraction data collected after the initial exotherms in each sample again showed the quantitative formation of the desired skutterudite compound. Figure 5 contains the diffraction patterns of these three new compounds: $FeSb_3$, $Hf_{1-x}Fe_4Sb_{12}$, and $Y_{1-x}Fe_4Sb_{12}$. All of these compounds decomposed to a mix of binary compounds on heating to 550 °C.

The ability to prepare the new binary compound, $FeSb_3$, led us to explore the reaction pathway in more detail. The low-angle diffraction pattern of a binary sample on deposition showed diffraction maxima resulting from front surface−back surface interference of the Cu Kα X-rays used as well as a first-order Bragg diffraction maxima from the repeating unit of the multilayer. After the film was annealed at 100 °C, the intensity of the Bragg diffraction maxima is significantly reduced as a result of interdiffusion of the deposited layers. Annealing the film has also made it smoother; the front surface−back surface interference pattern continues out to significantly higher diffraction angles. High-angle diffraction studies indicated that the film is still amorphous after this 100 °C anneal. The compound $FeSb_3$ nucleates soon after the elements interdiffuse, which supports the observation that this structure nucleates easily from an amorphous mixture of the elements. Annealing a film at higher temperatures, 250 °C for 7 h, resulted in a film suitable

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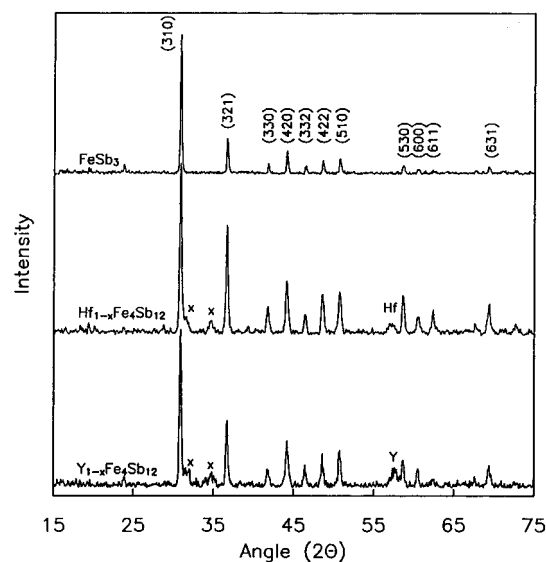(14) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

Figure 5. X-ray diffraction scans taken after the first exotherm showing the formation of the new ternary compounds $Y_{1-x}Fe_4Sb_{12}$ and $Hf_{1-x}Fe_4Sb_{12}$ as well as the new binary compound $FeSb_3$. The small amount of $FeSb_2$ and ternary element in the yttrium and hafnium samples (as well as the lanthanum sample shown in Figure 3) can be avoided by adjusting the iron–antimony ratio of the initial reactant and optimizing the annealing as was done for the binary compound, $FeSb_3$.
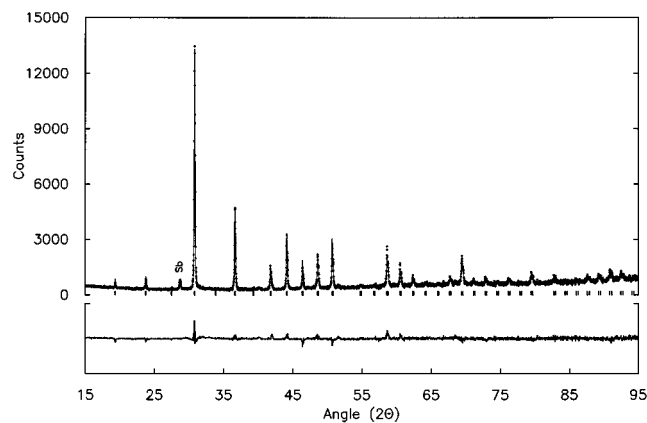

Figure 6. Results of Reitveld refinement on the binary compound $FeSb_3$. Diffraction peaks from the skutterudite structure are marked with vertical bars below the data. The line through the data is the calculated pattern and a difference plot is given underneath. The structural parameters from the fit are summarized in Table 2.

for Rietveld structural refinement. These diffraction results support our proposed reaction pathway summarized in Figure 4.

The diffraction pattern of the film deposited and annealed on a miscut quartz plate is shown in Figure 6 along with the simulated diffraction pattern from the structural refinement. The resulting structural parameters are summarized in Table 2. The structure of this new binary skutterudite is very similar to that previously determined for $CoSb_3$.[12,15] This binary compound has a significantly larger unit cell than reported previously for the filled skutterudites (9.1763 Å versus 9.1395 Å for $LaFe_4$-Sb_{12}), which supports our early conjecture that a reduction in the number of framework electrons resulting from reducing the

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Table 2. Positional and Thermal Parameters for $FeSb_3{}^a$

$Im\bar{3}$	Fe 9(c)	Sb 24(g)
x	1/4	0
y	1/4	0.3400(2)
z	1/4	0.1618(2)
B	0.21(17)	0.95(7)

^{a} Unit cell size is $a = 9.1762(3)$ Å. $R_{wp} = 9.3$, $R_p = 7.1$. Standard deviations for least significant digits are given in parentheses for refined parameters.

occupancy of the lanthanum site (now to zero) causes the framework to expand. Since the lattice parameter of $FeSb_3$ is intermediate between that of $LaFe_4Sb_{12}$ and $La_{1-x}Fe_4Sb_{12}$, however, an additional factor must be involved. One possibility is that there is a static displacement of the lanthanium cation from the ideal position. Unfortunately, the quality of the data is insufficient to refine such a displacement.

The synthesis of $M_{1-x}Fe_4Sb_{12}$, where M = La, vacancy, Y, and Hf, highlights a number of advantages to the use of thin-film multilayers as precursors in exploratory solid state chemistry. Low-angle diffraction provides a valuable means of quantifying the initial structure of the multilayer as well as monitoring the interdiffusion of the layered structure. This information is complemented by the ability to further follow the course of reactions using differential scanning calorimetry in conjunction with low- and high-angle diffraction. This approach is especially useful as a means of determining the existence of metastable phases which can only be formed at low temperatures. As shown in this paper, these techniques provide detailed information on the formation and decomposition of compounds formed from low-temperature reactions.

Summary

In this paper we have shown the ability to synthesize new metastable binary and ternary compounds with the skutterudite structure. In this work, we have taken advantage of the ability to control nucleation kinetics using the average composition of the reactant. At the low nucleation temperature observed for the skutterudite structure, the low diffusion rate prevents disproportionation of the amorphous intermediate into more stable binary components. The instability of the low-temperature amorphous intermediate is clearly significant in the case of the new binary compound, $FeSb_3$. This compound is metastable with respect to a mixture of $FeSb_2$ and Sb as found in our work and summarized in the accepted phase diagram shown in Figure 1. This synthetic approach has also given us access to new ternary compounds which would be very difficult or impossible to prepare using conventional high-temperature synthesis, where elements must be heated above 600 °C to obtain measurable reaction. The ability to prepare these compounds with small-radius cations enhances our ability to search for efficient new thermoelectric materials based on the skutterudite structure. In general, the ability to use thin-film multilayer reactants to prepare derivatives of a known structure in a rational manner opens new opportunities to optimize the properties of technologically important materials.