Synthesis of Metastable Post-Transition-Metal Iron Antimony Skutterudites Using the Multilayer Precursor Method

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Modulated elemental reactants were used to form amorphous ternary reaction intermediates of the desired compositions. The amorphous reaction intermediate for each system crystallizes exothermically below 200 °C forming kinetically stable "filled" skutterudites of general formula $M_{1-x}Fe_4Sb_{12}$ where M = Sn, Al, Ga, In, and Zn. These metastable compounds can only be prepared by controlling the reaction intermediates, avoiding the formation of more thermodynamically stable binary compounds. 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. If modulated elemental reactants are prepared with layer thicknesses above a critical value (∼40 Å), the thermodynamically stable binary compound $FeSb_2$ interfacially nucleates, preventing formation of the desired metastable ternary compounds. The use of low-angle X-ray diffraction and calorimetry provide the data necessary to develop an understanding of the reaction mechanism.

Introduction

The emerging field of materials chemistry is a blend of solid-state chemistry, solid-state physics, and materials science.[1] The goal of this field is to design and synthesize new compounds to meet a specific engineering need. This approach requires an understanding of structure−property relationships which has been the main focus of solid-state physics and chemistry. One typically attempts to determine the structural features which are important in producing the desired properties. Once the proposed structural features have been identified, one needs the ability to design new compounds with the desired structure. While some progress has been made in the ability to predict both stable and metastable new structures,[2] usually analogies are drawn to known compounds to predict possible compounds which might have the desired structure.

Once the new compound has been designed, it is necessary to figure out a method to synthesize it. This synthesis is often the rate-limiting step in this process. The synthesis of a new extended inorganic solid has been referred to as being as much an art as a science, even by solid-state chemists.[3] As recently pointed out by Schollhorn, developing an understanding of reaction mechanisms is a necessary precursor to predictive ability in these solid-state synthesis routes.[4] However, the rate-limiting step in a typical solid-state reaction

is diffusion. Under these reaction conditions, there is little understanding of reaction mechanisms. This is due in part to the fact that most reactions either begin as heterogeneous reactions or progress through heterogeneous intermediates.[5] What is lacking in solid-state chemistry is a simple, general synthesis route which provides kinetic rather than thermodynamic access to new compounds. Ideally such a synthesis route would require only low reaction temperatures so that metastable structures can be produced. This ideal synthesis route would also have a "generic" reaction mechanism − one which stays similar in a wide variety of reacting systems. The rate-limiting step of this synthetic route should involve a kinetic process which can be controlled to access compounds beyond just the thermodynamically most stable set.

Toward the development of such a general synthetic route, we have been exploring elementally modulated precursors as reactants. An idealized structure of an elementally modulated reactant is shown in Figure 1. Early efforts concentrated on elucidation of the reaction mechanisms and the effect of experimental parameters on the formation of known binary compounds. The thicknesses of the elemental layers was found to be an important synthetic variable.[6] Above a critical layer thickness, heterogeneous nucleation of crystalline compounds was observed at the reacting interfaces and diffusion was found to be the rate-limiting process. Below this critical layer thickness, the elements inter-

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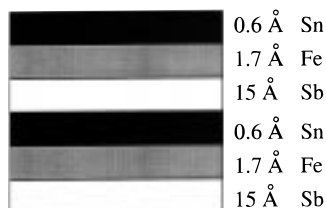|	
	0.6 Å Sn
	1.7 Å Fe
	15 Å Sb
	0.6 Å Sn
	1.7 Å Fe
	15 Å Sb

Figure 1. An idealized structure of an elementally modulated reactant. In the actual sample, the interfaces between the elemental layers are not abrupt due to interdiffusion of the elements.

diffuse at low temperature forming an amorphous mixture. The rate-limiting step for the formation of a crystalline compound from this amorphous intermediate was found to be nucleation.[7] Subsequent studies showed that relative nucleation energies of different compounds in a system are a function of the composition of the amorphous intermediate.[8] Thus, elementally modulated reactants can be used to prepare compounds which are thermodynamically metastable by avoiding stable binary compounds as reaction intermediates.[9] This promising synthetic route has now been extended to ternary systems. Again a critical thicknesses is found below which the three elements will mix to form an amorphous reaction intermediate. These ternary amorphous mixtures can be directly crystallized to form ternary compounds without ever forming any binary compounds.[10,11]

This paper focuses on our attempt to use elementally modulated reactants to synthesize new compounds for application as thermoelectrics. In a recent paper, compounds with the formula $LaFe_xCo_{4-x}Sb_{12}$ having the filled skutterudite structure were found to be promising thermoelectric materials.[12] These quaternary alloys of rare earth iron−cobalt antimonides have low thermal conductivity while still maintaining good electrical properties. The low thermal conductivity is thought to result from phonon scattering caused by a large vibrational amplitude of the lanthanum atoms. In the spirit of a materials chemistry approach to improved performance, there are several obvious chemical modifications one would like to perform, such as optimizing the electrical properties through doping and replacing the lanthanum cation with a cation of smaller ionic radius and higher mass. Unfortunately, while the modifications suggested are simple substitutions, preparing these target compounds and controlling doping levels is a significant synthetic challenge using standard solid-state chemistry techniques. Even for stable skutterudites, conventional high-temperature synthesis yields a mix of the desired skutterudite phase with approximately 10−20% impurities consisting of binary compounds and elemental antimony.[13,14] There is also

a limited ability to substitute other elements for the lanthanum in the structure using conventional synthetic methods.

Our goal in these studies was to make compounds which are isostructural to the known "filled" skutterudites, replacing the ternary lanthanum atom with post-transition-metal elements. The latter group IIIB and IVB cations are considerably more polarizable, and the aluminum cation is significantly smaller than the rare earth cations. We were interested in how these changes in the cation change the thermal conductivity of the skutterudite and whether the dynamic displacement of the lanthanum cation is replaced by a static structural distortion as the size of the ternary cation is reduced. We have already shown that the entire rare earth sequence can be synthesized[15] and so were also interested in investigating the limits of our ability to control the nucleation and growth of a particular ternary structure which is metastable relative to a mixture of binary compounds.

Experimental Section

The multilayer samples were prepared in a high-vacuum evaporation system which has been described in detail elsewhere.[16] Briefly, the elements were sequentially deposited in high vacuum (approximately 5×10^{-7} Torr) under the control of a personal computer. The elements were deposited from electron beam evaporation sources at a rate of 0.5 Å/s. Each source was independently monitored by quartz crystal thickness monitors. The thickness of each elemental layer was controlled to the nearest angstrom. The repeat thicknesses for all of the samples were kept below 25 Å to increase the probability that the films would interdiffuse at low temperatures without nucleating binary compounds at the reacting interfaces. The elemental composition of the samples were found to be repeatable to within about 5%. The films were simultaneously deposited on silicon, off-cut quartz, and photoresist-coated silicon wafers. The silicon substrates were used for low-angle diffraction studies. The films on the off-cut quartz were annealed and used to collect diffraction data for structural refinement. The coated substrates were used to allow the sample to be removed from the substrate by soaking in acetone and collecting with Teflon filters.

Low-angle X-ray diffraction was used to characterize the multilayer periodicity and to study the interdiffusion of the elements. The repeat thickness was determined from the position of the Bragg diffraction maxima. The total film thickness was determined from the higher frequency oscillations resulting from interference from the front and back of the films. High-angle X-ray diffraction was used to identify crystalline compounds. Copper Kα radiation was used in both the low- and high-angle diffraction studies which were done on a Scintag XDS 2000 $\theta-\theta$ diffractometer. The average composition of the multilayer films was determined by electron microprobe analysis using an energy-dispersive X-ray detector.

Samples were annealed in a nitrogen atmosphere or in a dynamic vacuum better than 10^{-5} Torr. Substrate-free samples were annealed in a differential scanning calorimeter. Measured exotherms were correlated with X-ray results to identify and track the interdiffusion of the elements and the crystallization of any compounds.

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Table 1. Summary of Samples Prepared[a]

sample	intended ternary metal thickness (Å)	intended iron thickness (Å)	intended antimony thickness (Å)	measured repeat thickness (Å)	measured composition T:Fe:Sb
Sn-1	0.95	1.65	15	19.8 ± 0.1	1.1:4.1:12
Al-1	0.6	1.65	15	18.5 ± 0.1	1.0:4.1:12
Ga-1	0.7	1.65	15	20.2 ± 0.1	1.1:3.7:12
In-1	0.9	1.65	15	20.4 ± 0.1	1.3:3.7:12
Zn-1	0.55	1.65	15	19.3 ± 0.1	1.1:3.2:12

[a] The repeat thickness was measured using low-angle X-ray diffraction. The composition was measured using electron probe microanalysis. The symbol "T" represents the amount of ternary metal in the sample. The uncertainties in the measured compositions are less than 0.1 for the ratio of ternary metal and iron to antimony.
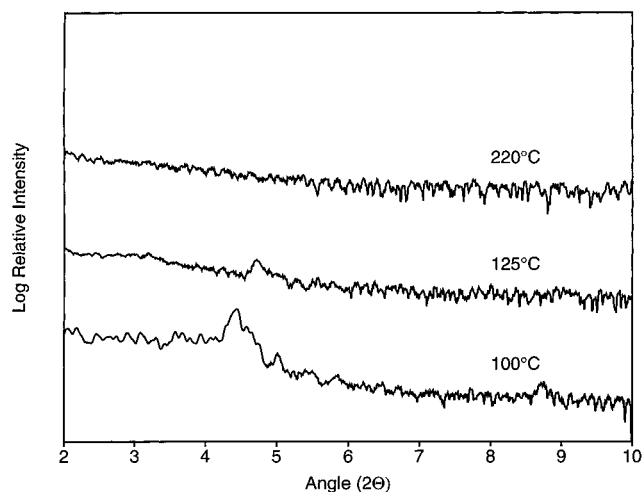

Figure 2. The low-angle X-ray diffraction pattern of sample Sn-1, a Sn–Fe–Sb multilayer on top of silicon. The curves are after successive 1 h anneals at the indicated temperature. Each curve is offset by a factor of 1000 for clarity.

Results and Discussion

Table 1 contains a list of the samples made as part of this investigation. Samples were prepared with five different post-transition-metal elements as the ternary cation. The structures of the as-deposited samples were probed using low-angle X-ray diffraction and the repeat thicknesses determined as summarized in Table 1. The agreement between the intended and actual repeat thicknesses for the samples in this table is within the errors of the calibrations. The compositions, determined via microprobe analysis, are close to the intended compositions (MFe_4Sb_{12}) determined by the relative thickness of the deposited layers except for the zinc-containing sample which was iron deficient. All of the samples in this table were investigated using differential scanning calorimetry (DSC) to determine the temperatures at which exotherms corresponding to the solid-state reaction of the layers were observed. X-ray diffraction was used to investigate the structure of the samples before and after any observed exotherms.

The tin sample is representative of our results. Figure 2 shows the evolution of the low-angle diffraction pattern as a function of annealing temperature and time. The Bragg diffraction maxima indicate that the sample is layered with a repeat spacing of 19.8 Å for the repeating unit of the initial reactant. The ability
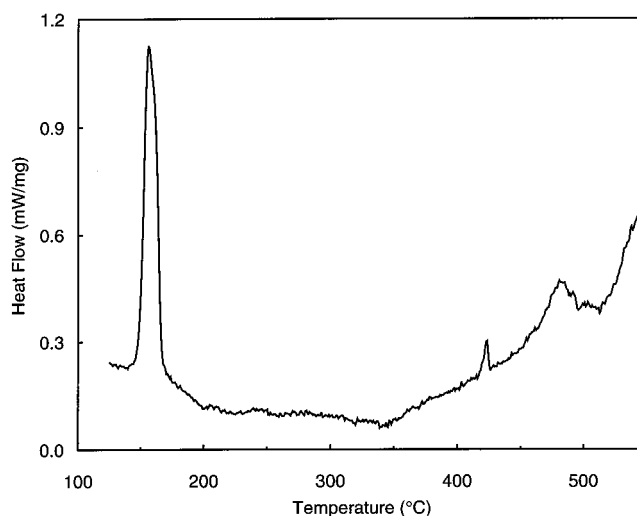

Figure 3. The differential scanning calorimetry data collected on a portion of sample Sn-1. The curve shows two irreversible exotherms for the formation (155 °C) and decomposition (475 °C) of a metastable skutterudite structure.

to observe front–back interference in this sample (the higher frequency maxima in the diffraction pattern) out to approximately 6° indicates that these two surfaces are smooth to within 4 Å (about the initial roughness of the silicon substrate).[17] The data clearly shows that annealing at low temperatures leads to interdiffusion and eventual loss of the composition gradients present in the starting sample. The sample surface also becomes smoother during this annealing, and the sample contracts slightly. Figure 3 contains the DSC of a portion of sample Sn-1 which has been removed from the substrate. Two exotherms are clearly identifiable in these data. Figure 4 contains high-angle diffraction pattern collected on a portion of sample annealed to the indicated temperatures. These data suggest that the low-temperature exotherm in Figure 3 results from the crystallization of a skutterudite phase from the previously X-ray amorphous sample. The diffraction data also show that the higher temperature exotherm results from the decomposition of the ternary skutterudite into a mixture of binary compounds including $FeSb_2$, $SnSb$, and elemental Sb.

The decomposition temperature of the ternary compound is lower than the temperatures used in the conventional synthesis of skutterudite compounds. Therefore, the synthesis of this kinetically stable new compound depends on the ability to control the kinetics of the reaction route at low temperatures. Elementally modulated reactants permit us to control the interdiffusion distances, allowing nucleation rather than interdiffusion to be the rate-limiting step. Table 2 contains a series of tin samples prepared to determine the thickness dependence of the reactivity.

Figure 5 contains the DSC data collected on this series of samples with increasing repeat layer thickness. There are distinct changes in the exotherm shape and onset temperature as the thickness of the repeating layer increases. In the thinnest sample, there is a single exotherm at 155 °C which diffraction data show is caused by the crystallization of $SnFe_4Sb_{12}$ from the

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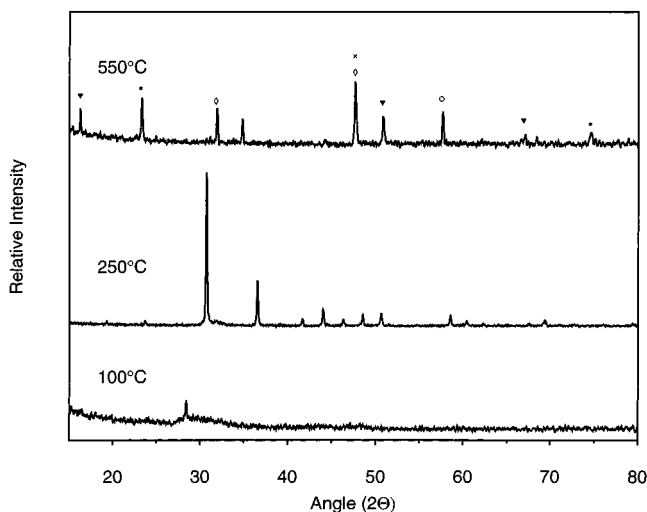
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Figure 4. The high-angle diffraction data collected as a function of annealing temperature. The temperatures were chosen on the basis of the calorimetry data shown in Figure 2. The lowest scan indicates that the sample is amorphous with respect to X-ray diffraction. The small diffraction maximum at approximately 28° is due to a small amount of silicon contamination. The middle diffraction scan is that of a cubic skutterudite. The top scan is that of the product after the decomposition of the metastable skutterudite. It shows that the sample is a mixture of (*) $FeSb_2$, (×) $SnSb$, (◊) Fe_3Sb_2 and (▼) Sn. The diffraction peak at approximately 34° is unidentified.

Table 2. Summary of Tin Samples Prepared[a]

sample	intended tin metal thickness (Å)	intended iron thickness (Å)	intended antimony thickness (Å)	measured repeat thickness (Å)	measured composition Sn:Fe:Sb
Sn-1	0.95	1.65	15	19.8 ± 0.1	1.1:4.1:12
Sn-2	1.9	3.3	30	28.4 ± 0.1	1.2:4.3:12
Sn-3	2.85	4.95	45	46.7 ± 0.1	1.3:4.3:12
Sn-4	3.8	6.6	60	58.1 ± 0.1	1.3:4.6:12

[a] The repeat thickness was measured using low-angle X-ray diffraction. The composition was measured using electron probe microanalysis. The uncertainties in the measured compositions are less than 0.1 for the ratio of tin and iron to antimony.

amorphous precursor. In the thickest sample, there is also a single exotherm at 220 °C, this time from the crystallization of the binary compound $FeSb_2$ from the still partially layered reactant. The intermediate thickness samples each have broader exotherms, with the sample having 28.4 Å thick repeating layers still nucleating the ternary skutterudite compound while the sample with 46.7 Å thick layers nucleating $FeSb_2$. Thus there is a critical thickness in this system of approximately 40 Å below which one nucleates the ternary compound and above which one nucleates binary compounds heterogeneously at the reacting interfaces.

The stability of the amorphous reaction intermediate formed by samples layered below this critical thickness was studied by collecting differential scanning calorimetry data as a function of scan rate to estimate the activation energy of the nucleation and growth process. Figure 6 contains an overlay of the DSC data collected at different scan rates. Such nonisothermal DSC data are typically analyzed using a Kissinger analysis[18] in which the activation energy can be obtained from the
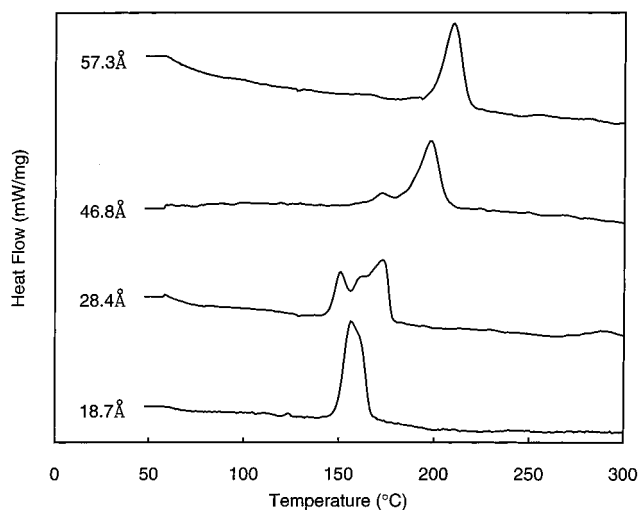

Figure 5. Differential scanning calorimetry data collected on samples Sn-1 through Sn-4.
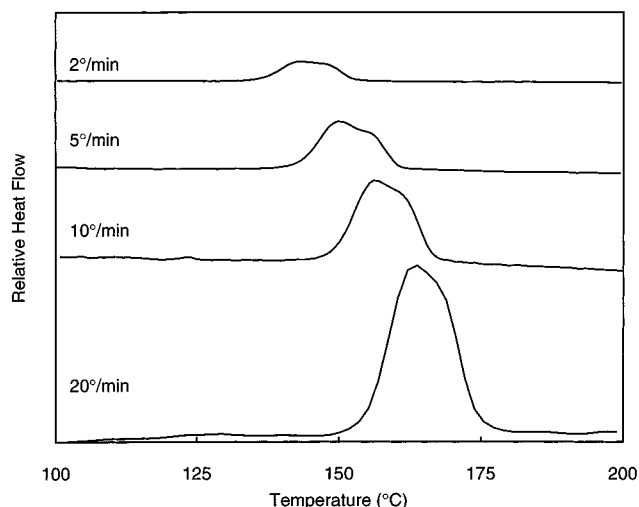

Figure 6. DSC data from sample Sn-1 as a function of scan rate. The shift in exotherm position is used to determine the activation energy as shown in Figure 6.

peak temperature, T_p, as a function of scan rate, Q

$$\frac{d \ln\left[\dfrac{Q}{T_p^{2}}\right]}{d\left[\dfrac{1}{T_p}\right]} = \frac{-E_{crystallization}}{R}$$

where R is the gas constant 8.314 J K^{-1} mol^{-1}. Graphing ln $[Q/T_p^2]$ versus $1/T_p$, as shown in Figure 7, gives a straight line with slope $-E/R$ yielding a value of 2.0 eV for the activation energy. This calorimetry data clearly illustrate the metastable nature of $SnFe_4Sb_{12}$ with respect to binary compounds and the nucleation controlled nature of the reaction.

Since a mixture of tin and germanium has been used to replace the antimony in the skutterudite structure, a film of $Sn_{1-x}Fe_4Sb_{12}$ was prepared which was designed to allow structure analysis by Rietveld refinement using a program developed by Young and Sakthevel (DBWS-9006PC).[19] The initial multilayer was directly deposited

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Table 3. Summary of Data Obtained on the New Skutterudites Prepared as Part of This Study

sample	temperature of formation exotherm	temperature of decomposition exotherm	lattice parameter of skutterudite (Å)	decomposition products
Al-1	177	494	9.177 ± 0.001	Sb, Fe_3Sb_2, Fe, AlSb
Ga-1	181	362	9.165 ± 0.001	Sb, Fe_3Sb_2, Fe, GaSb
In-1	146	463	9.201 ± 0.001	$FeSb_2$, Sb, Fe_3Sb_2, Fe, InSb
Zn-1	161	416	9.172 ± 0.001	$FeSb_2$, Sb, Fe_3Sb_2, Fe, ZnSb
Sn-1	160	484	9.186 ± 0.001	Sb, SnSb, $FeSb_2$, Fe_3Sb_2
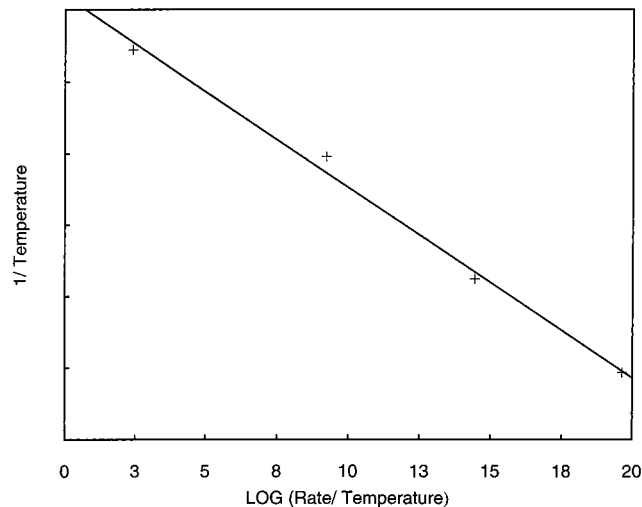
Figure 7. Kissinger analysis of the data shown in Figure 6 used to derive the activation energy for nucleation of $SnFe_4Sb_{12}$.

on an off-cut, single-crystal quartz substrate. The substrate was off-cut to provide a uniform, featureless background for the diffraction experiment. The low-angle X-ray diffraction was used to determine the film thickness (1200 Å) so an accurate absorption correction could be applied to the Rietveld refinement. Care was taken to ensure that the incident beam did not extend beyond the edges of the sample at the lowest angle in the scan and that the detector field of view contained the entire illuminated area of the sample. The data are shown in Figure 8 along with the calculated profile based on our refined structure. The refined parameters from this analysis are given in the figure caption to Figure 8. The refined structure is isostructural to that of $LaFe_4Sb_{12}$. There is a systematic error in the refined thermal parameters, despite the accurate absorption correction used. The refinement program overestimates the background intensity and underestimates peak intensity in the high-angle region of the diffraction pattern. The large background intensity results from the film thickness being a small fraction of the penetration depth of the X-ray beam. This leads to a large fluorescence background from the substrate which increases as a function of angle. The refinement suggests that most of the tin goes in ternary atom position since its occupancy is near 1. We have been unable to insert antimony into the ternary position, so this electron density most likely is due to tin.

Our success in preparing the new metastable filled skutterudite $SnFe_4Sb_{12}$ prompted us to explore whether we could prepare this structure with the group IIIb elements and zinc as the ternary cation. Aluminum, gallium, and indium provide a smooth progression in size and polarizability and would be a significant test of the ability of this synthetic approach to prepare an isostructural progression of metastable compounds. Zinc
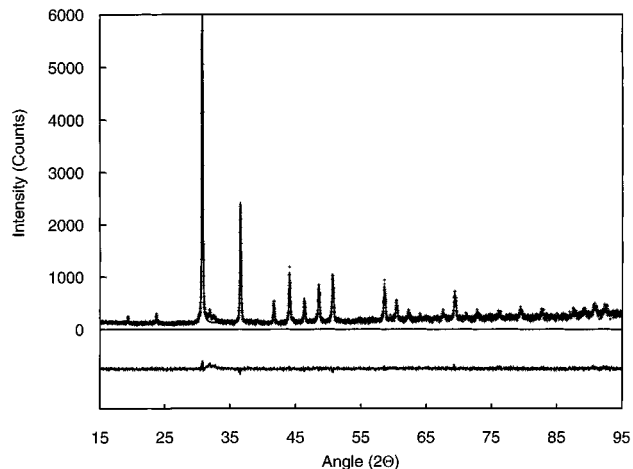
Figure 8. Diffraction data for sample Sn-1 along with the calculated intensities from a Reitveld refinement of $SnFe_4Sb_{12}$. Space group, $Im\bar{3}$. $a = 9.1862(4)$. $R_{wp} = 13.59$ with atomic positions Sn, $16f$ ($x = 0$, occ $= 0.65(8)$); Fe, $8c$; Sb, $24g$ ($y = 0.3363(4)$, $z = 0.1594(3)$). Thermal parameters Sn, 28.(3); Fe, 3.0(2); Sb, 3.4(1). Errors for least significant digits given in parentheses. Data are shown as filled circles; line is refined pattern. Difference plot is shown underneath on the same scale.

was chosen to determine if the structure could be prepared with a small divalent cation. Ternary multilayer elemental reactants were prepared, as summarized in Table 1, containing the desired elements layered below the critical thickness found in our study of the tin-containing system. The differential scanning calorimetry data of all of these samples were similar, containing a single low-temperature exotherm below 200 °C and a higher temperature exotherm below 500 °C. Diffraction data collected as a function of annealing temperature confirmed that the low-temperature exotherm resulted from the formation of the desired skutterudite structure as a single-phase product. Diffraction data collected after the higher temperature exotherm showed the decomposition of these metastable compounds into a mix of binary compounds and elements. There are no obvious trends in either the formation or decomposition temperatures of these new compounds as summarized in Table 3. The data shown earlier for the tin-containing compound suggests that the formation temperature reflects the nucleation barrier for the transformation of the amorphous intermediate to the final crystalline compound. Its lack of variability with respect to the identity of the electropositive element suggests that the nucleation barrier is governed mainly by the assembly of the iron–antimony octahedra. The insensitivity of the decomposition temperature with respect to the size or valence of the ternary cation also suggests that decomposition is also mainly a function of the strength of the bonding in the iron–antimony framework.

Lattice parameters of the cubic skutterudite determined from this diffraction data show little change in cell size with cation size as summarized in Table 3. This was expected because the ternary cation fits in the holes formed by the rigid iron−antimony framework and previous studies of rare earth compounds suggest that the ternary cation donates its valence to the iron−antimony framework.[12] The lattice parameter therefore depends on the charge transfer as well as size of the ternary cation. The picture is further complicated by the possibility of variable occupancy of the ternary cation. The lone surprise in the lattice parameters is the large unit cell size observed for the indium compound. This suggests that the indium may be monovalent. Experiments measuring the Seebeck coefficient as a function of x in $InFe_{4-x}Co_xSb_{12}$ to determine the valance of the indium are planned.

Conclusions

A series of new filled skutterudite compounds containing post-transition-metal cations were prepared using modulated elemental reactants. Calorimetry data demonstrate that the prepared compounds are thermodynamically unstable with respect to decomposition into a mix of binary compounds. A "critical thickness" for the modulated elemental reactants was found, below which the reactants interdiffuse forming an amorphous intermediate and subsequently nucleate the desired ternary filled skutterudite structure. Above this critical thickness, the thermodynamically more stable binary compounds nucleate at the reacting interfaces, preventing formation of the thermodynamically unstable skutterudite compounds.

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