Suppression of Binary Nucleation in Amorphous La−Fe−Sb Mixtures

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Abstract: The nucleation energy of a series of $La_xFe_ySb_z$ modulated elemental reactants was measured as a function of the Fe/Sb ratio over a large composition range while holding the La content constant. The nucleation energy of the ternary compound $La_{0.5}Fe_4Sb_{12}$ with the skutterudite crystal structure was found to depend very strongly on the Fe/Sb ratio in the modulated elemental reactant, with a higher nucleation energy as the Fe/Sb ratio is moved away from the 1:3 stoichiometric value. When the results of this study are compared with those from Fe_ySb_z modulated reactants, the addition of lanthanum was found to suppress the nucleation of $FeSb_2$, thereby broadening the Fe/Sb composition range in which the ternary skutterudite compound $La_xFe_4Sb_{12}$ nucleates. This suppression of nucleation of a binary phase on addition of a ternary component to an amorphous intermediate is in agreement with theoretical arguments. The observed suppression of nucleation also provides rational for the observed nucleation of metastable ternary and higher-order compounds from homogeneous amorphous reactants.

Introduction

Nucleation is an important issue in the study of materials and materials synthesis, as it plays the critical role in determining which phases form. Nucleation is also an important parameter in organic synthesis and pharmaceutical chemistry, as, for example, different crystallographic polymorphs of a drug have different properties (such as solubility) that effect dose and activity. Most organic chemistry students have opened up a reaction vessel after refluxing to discover a viscous, yellow oil rather than the fluffy white crystals their lab manual described. This frustrating experience is a great example of an impurity suppressing crystal nucleation. The fundamental importance of nucleation has prompted many experimental and theoretical studies of nucleation-related parameters, including nucleation rates,[1,2] activation energies,[3−6] crystallization temperature, and kinetics studies.[6−9] Indeed, even the suppression of nucleation

has become a popular area of research with the synthesis of metallic glasses.[10,11]

It is generally thought that nucleation involves a competition between surface energy and the stabilization per unit volume from forming a crystal in a supersaturated solution. For very small crystal "embryos", which have a large surface area-to-volume ratio, the surface energy dominates and it is more energetically favorable for the embryo to redissolve than to continue growing. Statistically, however, there is a finite probability that an embryo will reach a sufficient size that the volume term begins to dominate the free energy. At this point, continued growth of the embryo is thermodynamically favored and spontaneous crystal growth occurs.[12]

Nucleation is an especially important issue in the area of solid-state synthesis. Since most solid-state reactions are heterogeneous, composition gradients form at the reactant interfaces, resulting in areas where all possible binary compounds can nucleate. In standard solid-state synthesis involving the direction reaction of two or more solids, extended annealing times and high temperatures are used to drive the reaction through all of the binary intermediates, finally resulting in the ternary or higher-order compound desired. This will only occur, however, if the ternary compound is more thermodynamically stable than any of the binary intermediates that form.[13] So, to improve the chances of forming new ternary and higher-order products,

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especially metastable products, finding methods of avoiding the nucleation of binary compounds is necessary. Removing the heterogeneous interfaces (and thereby removing the concentration gradients) by creating a homogeneous amorphous reactant mixture is one such method.

Various methods of creating homogeneous reactant mixtures (including solutions, fluxes, hydrothermal conditions, vacuum deposition, and modulated elemental reactants) have been developed, and many new compounds have been successfully prepared.[14,15] However, study of the fundamental aspects of the reaction, such as composition dependence, mechanism, or nucleation-related parameters, is typically hampered by the extremely complicated nature of the reaction, the lack of information about the structure and the composition of the species in solution, and what role they play in the reaction process.

Recently, Desre[10] published a theoretical paper demonstrating the potential for suppressing nucleation in multicomponent alloys by adding components in order to frustrate the nucleation process. He showed that, with each component added to the mixture, the probability of nucleating a binary compound is reduced by a factor of 10. The essence of his argument is that, at low temperatures, the extremely slow diffusion rates in most solids will prevent the reorganization and long-range diffusion necessary to establish a large enough area of correct stoichiometry for a critical nucleus of a binary phase to form. This situation can be directly compared to the organic chemistry frustration of impurities suppressing nucleation of the desired compound.

In a previous study, we measured the effect of composition on the nucleation energy of both the metastable compound $FeSb_3$ as well as the thermodynamically stable $FeSb_2$ phase to understand why $FeSb_3$ forms instead of the thermodynamically more stable mixture of $FeSb_2$ and Sb.[16] The amorphous reactants were prepared by depositing alternating ultrathin elemental layers sequentially onto a substrate from vapor deposition sources to form a modulated elemental reactant. If the diffusion distance is made small enough (i.e., the elemental layers are thin enough), then upon low-temperature annealing, the thin layers interdiffuse completely and produce a homogeneous amorphous intermediate.[15,17] Nucleation then controls what forms. A pronounced composition dependence to the nucleation energy was observed, with the metastable compound $FeSb_3$ nucleating only for amorphous compositions above 75% antimony.

In the present study, we have measured the nucleation energy of the skutterudite compound $La_xFe_4Sb_{12}$ from a series of homogeneous amorphous reactants, varying the Fe/Sb ratio. The binary skutterudite compound $FeSb_3$ is able to accommodate the added lanthanum as a loosely bound atom in a void in the crystal structure to form the "filled skutterudite" phase

$La_xFe_4Sb_{12}$. The binary compound competing with $FeSb_3$ to nucleate is $FeSb_2$, which cannot accommodate the added lanthanum within its crystal structure. This crystal chemistry permits us to test the theoretical predictions of Desre by adding lanthanum to the initial modulated elemental reactant. Desre's theory predicts that the addition of lanthanum would inhibit the nucleation of the diantimonide phase (for which it effectively acts as an impurity). Since La can be crystallographically incorporated into the skutterudite structure, its nucleation should not be inhibited. As a result, Desre's theory predicts that the addition of La would expand the Fe/Sb composition range over which the skutterudite compound can be synthesized.

Experimental Section

Layer deposition was performed in a custom-built high-vacuum deposition chamber with multiple sources and targets. A personal computer and custom automation software are used to control the deposition. Lanthanum and iron were evaporated from Thermionics electron-beam guns at a rate of ~0.5 Å/s. Antimony was evaporated from an effusion cell at a rate of ~0.8 Å/s. Each deposition source was independently monitored using Leybold Inficon XTC quartz crystal thickness monitors. The films were deposited onto polished silicon wafer pieces (for X-ray reflectivity), miscut quartz pieces (for X-ray diffraction), and silicon wafers coated with poly(methyl methacrylate) (PMMA). The coated wafers were then soaked in acetone to dissolve the PMMA and allow the multilayer films to lift off of the wafer surface. The pieces of film were then collected by vacuum filtration using Teflon filter papers. These film pieces were used for differential scanning calorimetry investigations.

Sample composition was measured using electron probe microanalysis (EPMA) using a Cameca S-50 instrument, a 10 keV accelerating voltage, a 10 nA beam current, and a 1 μm spot size. X-ray diffraction data on the powder after differential scanning calorimetry were obtained on a Scintag SDS-2000 $\theta - 2\theta$ diffractometer using a piece of miscut quartz as the sample holder. Diffraction data on the film-coated miscut quartz pieces, as well as all low-angle diffraction data, were obtained using a Philips X'Pert MRD diffractometer.

A TA Instruments DSC 2920 Modulated DSC was used to collect all DSC data. The heat flow in and out of the sample is monitored as the sample temperature is elevated at a specific rate to determine at what temperature phase changes and nucleation events occur. Approximately 0.5 mg of sample is placed and crimp sealed inside an Al sample pan. Several small pieces of each sample were heated under flowing nitrogen at a series of different heating rates up to either 250 °C or 550 °C to provide nucleation temperature information for calculation of the nucleation activation energy.

Results and Discussion

A table of samples is shown in Table 1. Samples were made over a range of Fe/Sb compositions to determine the effect of composition on nucleation energy in this system. The lanthanum composition for all samples is ~3 atom %, which corresponds to a formula of $La_{\sim0.5}Fe_4Sb_{12}$. For all samples, the Sb intended thickness was held constant, while the Fe intended layer thickness was varied to achieve the desired composition. The repeat layer thickness was determined either from the Bragg diffraction maxima resulting from the modulated nature of the deposited film or from the higher frequency maxima resulting from the interference of radiation reflected from the top and bottom surfaces of the film using Bragg's law. The agreement between the actual and intended repeat layer thicknesses was within 1 Å. All samples in this study were prepared with intended repeat layer thicknesses well below the critical thick-

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Table 1. A Table Listing Key Data for All Samples Prepared for This Study

	percent compostition (A%) ±1%			nucleation energy (eV) ±0.03 eV	exotherm (°C) ±1°C	thickness (Å) ±0.1 Å		
sample	Fe	Sb	La			actual	intended	phase
1	23.7	73.6	2.8	1.75	182	7.1	7.3	$La_xFe_4Sb_{12}$
2	24.9	72.4	2.6	1.70	196	6.6	7.4	$La_xFe_4Sb_{12}$
3	27.9	69.7	2.4	1.77	200	6.6	7.5	$La_xFe_4Sb_{12}$
4	25.9	71.7	2.4	1.63	170		7.4	$La_xFe_4Sb_{12}$
5	25.7	72.0	2.3	1.67	193	6.9	7.4	$La_xFe_4Sb_{12}$
6	23.9	73.9	2.2	1.63	183		7.4	$La_xFe_4Sb_{12}$
7	22.1	75.2	2.7	1.61	166	6.5	7.2	$La_xFe_4Sb_{12}$
8	22.7	74.4	2.9	1.65	165	6.6	7.2	$La_xFe_4Sb_{12}$
9	19.4	77.9	2.7	1.62	166	7.3	7.1	$La_xFe_4Sb_{12}$
10	15.2	82.0	2.7	1.77	167	7.2	7.1	$La_xFe_4Sb_{12}$
11	13.6	83.7	2.7	1.84	168	6.7	7.0	$La_xFe_4Sb_{12}$
12	11.9	85.0	3.1	1.84	170	6.9	7.0	$La_xFe_4Sb_{12}$
13	26.9	70.9	2.2	1.75	170		7.5	$La_xFe_4Sb_{12}$
14	32.0	64.9	3.0	1.96	209	7.8	7.6	$FeSb_2$
15	28.8	68.2	3.0	1.71	197	8.3	7.6	$FeSb_2$
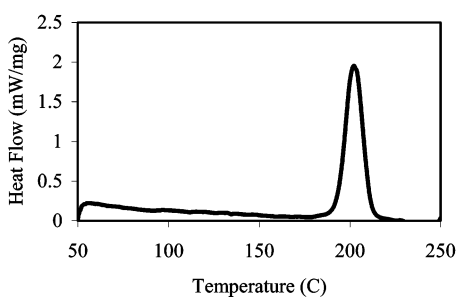
Figure 1. A DSC trace representative of those observed in this study. Note the large exothermic signal at 203 °C from the nucleation of the ternary skutterudite phase.
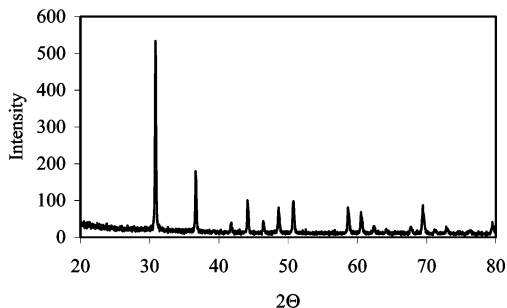
Figure 2. X-ray diffraction data showing the characteristic skutterudite pattern, which was indexed to a cubic unit cell with a lattice parameter of 9.16 Å.

ness value of ~35 Å previously observed to avoid interfacial nucleation in the Fe−Sb binary system.[16]

A combination of DSC and X-ray diffraction experiments was used to determine the reaction pathway. A representative DSC trace, shown in Figure 1, contains a prominent exothermic signal at 203 °C. Diffraction data collected before this exotherm show no diffraction maxima at high angles, indicating the sample is still amorphous with respect to X-ray diffraction. Data collected after this exotherm, shown in Figure 2, contained many sharp diffraction maxima that were easily indexed to the skutterudite structure. These data confirm that the reaction pathway progressed from a layered reactant through an amorphous intermediate state before nucleation.

All of the samples in Table 1 that formed the skutterudite phase had a lattice parameter of ~9.16 ± 0.03 Å. This consistency in the measured lattice parameters indicates that
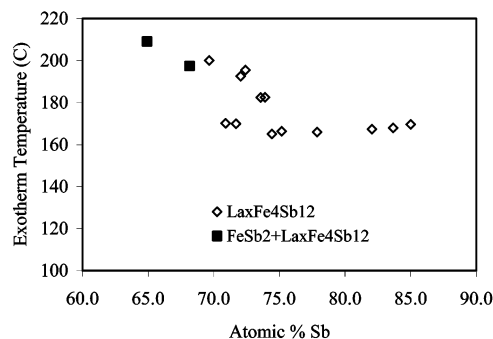
***Figure 3.*** A plot showing the nucleation exotherm temperature composition dependence.

the composition of the crystallites remains relatively constant despite changes in the reactant composition. For samples with excess Sb, diffraction maxima corresponding to crystalline antimony were observed. No diffraction from iron-containing phases was observed for any sample nucleating the skutterudite phase with an iron-rich composition. This suggests that any excess iron-containing phase was nanocrystalline or amorphous and probably segregated between the skutterudite grains.

A plot of nucleation exotherm temperature as a function of composition, shown in Figure 3, shows that the nucleation exotherm temperature depends on composition and is lowered with increasing Sb content. An examination of simple nucleation theory reveals there are two possible reasons for this composition dependence of the nucleation temperature. One possibility is that the nucleation energy itself changes with composition, decreasing with increasing Sb content. The other possibility is that the composition affects the diffusion rate in the mixture, increasing the rate with increasing Sb content. (An increase in the diffusion rate in the mixture would effectively allow the system to explore more possible states in a given time, therefore increasing the likelihood of assembling a suitable site for nucleation.) In an attempt to separate these two effects, we were able to estimate the nucleation energy by collecting DSC data at different heating rates. Such isothermal DSC data are typically analyzed using the method developed by Kissinger[16] in which the activation energy is obtained from the shift in exotherm temperature (T_p) as a function of scan rate, Q:

$$dLn[Q/(T_p)^2]/d[1/(T_p)] = -E_{crystallization}/R$$

Graphing $Ln[Q/(T_p)^2]$ versus $1/(T_p)$ gave straight lines with slopes $-E_{crystallization}/R$, yielding nucleation energies from 1.6 to 2 eV for the samples in Table 1. While these nucleation energies are associated with the nucleation and growth of the crystalline phase, the derivation of this relationship by Kissinger is based on several assumptions. It is assumed that the nucleation and growth can be described by the Johnson−Mehl−Avrami equation, that the nucleation and growth rates are constant at a constant temperature and that both the nucleation and growth rates may be described by Arrhenius expressions over the range of temperatures in which the peak temperature varies with scan rate. A plot of measured nucleation energy as a function of composition is shown in Figure 4. The minimum in nucleation energy for $La_xFe_4Sb_{12}$ is centered over the stoichiometric 1Fe/3Sb ratio and rises rapidly away from this value. For the two most iron-rich samples, $FeSb_2$ is observed to nucleate.
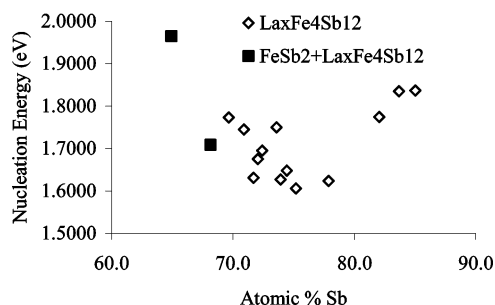
Figure 4. A plot of nucleation energy vs composition. The minimum in nucleation energy is at the stoichiometric 1Fe/3Sb ratio.
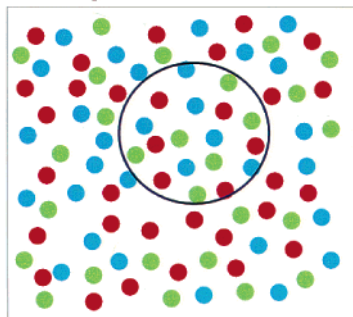
Figure 5. A schematic representation of one possible explanation for the composition dependence of the nucleation energy.

Figure 5 depicts the explanation for this composition dependence predicted by Desre. In this schematic, we consider the nucleation of a ternary phase with 1:1:1 composition ratio from a homogeneous amorphous mixture also with a 1:1:1 composition. Since the atoms in the amorphous mixture are homogeneously distributed, the composition anywhere in the mixture is very close to the stoichiometric composition for this theoretical crystalline phase. No long-range diffusion is necessary to produce a critical nucleus of the ternary crystalline phase. If we consider the nucleation of any binary compound from this same mixture, the third "impurity" element must diffuse out of a large enough area of the mixture for a critical nucleus of the binary phase to form. The net result is that the nucleation energy of the ternary phase should be lower than that of the binary phase.

In the system presented here, the binary phase $FeSb_2$ is unable to accommodate the added lanthanum into its structure. This effectively suppresses the nucleation of the $FeSb_2$ phase over a broad range of Fe/Sb composition. The binary skutterudite phase

$FeSb_3$, on the other hand, has an empty crystallographic site in the unit cell, which can accommodate the lanthanum atom. This result can be seen in the plot of nucleation energy as a function of composition in Figure 4. The composition range over which the skutterudite phase can be formed is much larger than was previously reported for the binary case.[16]

The ability to suppress the nucleation of a binary phase, thereby enhancing the nucleation of a higher-order phase by using multicomponent amorphous alloys as reaction intermediates, presents opportunities to selectively prepare ternary and higher-order compounds. Since binary compounds are not formed as reaction intermediates, phases that are metastable with respect to disproportionation into more thermodynamically stable binary phases are also accessible via this pathway. Examples of such metastable ternary compounds prepared using this pathway include several "filled" skutterudites MFe_4Sb_{12}, where $M = Lu, ...,$ and $Sn^{18,19}$ where the ternary atom is significantly smaller than the size of the vacancy site. The results presented herein suggest that the theory presented by Desre provides an explanation for why these metastable compounds preferentially nucleate relative to the thermodynamically expected phases from amorphous intermediates.

Summary

This study of the composition dependence of the nucleation activation energy of the ternary skutterudite compound $La_xFe_4Sb_{12}$ has shown a strong dependence on the Fe/Sb composition ratio. The nucleation energy is minimized near the stoichiometric ratio for the skutterudite phase and rises away from this ideal composition. The addition of lanthanum has been shown to suppress the formation of the competing binary phase. This results in an expansion of the composition range over which the skutterudite compound will nucleate, as predicted by the theory of Desre.

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