Controlling Solid-State Reaction Pathways: Composition Dependence in the Nucleation Energy of InSe

Oyinda Oyelaran, Thomas Novet, Christopher D. Johnson, and David C. Johnson*

Contribution from the Department of Chemistry and Materials Science Institute,
University of Oregon, Eugene, Oregon 97403

Received October 24, 1995⊗

Abstract: The crystallization of InSe from bulk amorphous indium−selenium alloys was studied as a function of composition. The composition dependence of the nucleation energy of InSe from amorphous alloys was determined using a Kissinger analysis of differential scanning calorimetry data. A minimum in the nucleation energy was found for the one-to-one composition. This minimum reflects the maximum driving force per unit volume found for this composition as well as the lack of short-range composition fluctuations required to nucleate stoichiometric InSe from nonstoichiometric amorphous alloys.

Introduction

Crystallization processes have always played an important role in synthetic molecular chemistry as an effective means of purifying substances, especially for the separation of enantiomers. With the advent of various chromatographic techniques which effectively separate mixtures, crystal growth is now often regarded only as a necessary precursor to a single crystal structure determination. Recently, however, there has been renewed interest in using the crystallization process to control the assembly of supramolecular structures using molecular self-organization.[1,2] Topochemical control resulting from control of the crystallization process has also enabled the targeted construction of solid-state structures and molecular syntheses impossible by classical routes as summarized in a recent review by Ozin.[3]

The same aspects of crystallization which made it useful for purification of molecular solids also make it an ideal kinetically rate limiting step in the synthesis of complex extended solids. This useful aspect of crystallization has not been applied in solid-state synthesis, however, as the rate of most solid-state reactions is limited by the slow rate of mass transfer, within or between reacting particles. Indeed, most solid-state reaction rates decrease with continued annealing time as product layers separate the reactants. Consequently, most solid-state reactions have appreciable rates only at high temperatures. This leaves preparation of single-phase, homogeneous products at the mercy of these highly variable but intrinsically slow interdiffusion processes. Extended annealing at high temperatures used to homogenize the products of solid-state reactions yields thermodynamically stable products.[4,5] Therefore, solid-state chemists have given the mechanisms of reactions in solids relatively little attention beyond breaking the reaction into the fundamental steps of interdiffusion of reactants, nucleation of the crystalline compounds, and subsequent growth of these crystallites.[6]

In the past 20 years, however, the importance of nucleation kinetics in the early stages of solid-state reactions has been increasingly recognized. The behavior of thin film diffusion couples, consisting of several hundred angstroms thick elemental layers, provide a striking illustration of the importance of kinetics in the early stages of solid-state reactions. It is well established experimentally that the evolution of thin-film, planar binary diffusion couples proceeds through a sequence of binary compounds. In some systems, for example transition metal silicides, it is common to have only a single compound grow between the reactants until either the metal or the silicon reactant is exhausted.[7] Several empirical rules have been formulated to predict the phase which will form using information in equilibrium phase diagrams. The first-phase rule of Walser and Bené, which states "The first compound nucleated in planer reaction couples is the most stable congruently melting compound adjacent to the lowest temperature eutectic on the bulk equilibrium phase diagram," is prototypical. The rule is based on the idea of an amorphous material initially forming between the reactants with a composition near that of the lowest temperature eutectic—the most stable liquid in the equilibrium-phase diagram. It is then assumed that the easiest compound to nucleate will be that most stable compound closest in composition to the glassy, interfacial phase.[8]

Exact theoretical treatments predicting the sequence of phase formation are not available as real systems are very complex, involving both interdiffusion and nucleation, both of which depend upon composition and the changing composition profiles at the reaction interface. Several proposals have been suggested to qualitatively explain the observed lack of some equilibrium phases in thin-film diffusion couples. It has been argued that nucleation barriers prevent phase formation,[9] that the formation of the missing phases is thermodynamically unlikely because of the low diffusion temperatures used in the experiments,[10] and that interfacial reaction barriers result in a growth instability which leads to the absence of phases.[11]

Experimentally, the problem can be simplified by separating interdiffusion from nucleation which is accomplished by starting with a superlattice of the elements as an initial reactant. If the component layer thicknesses are below a critical thickness, it is possible to anneal the modulated composite at a temperature

---

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Fagan, P. J.; Ward, M. D. *Sci. Am.* **1992**, *267*, 28−34.

(2) Fagan, P. J.; Ward, M. D. *Spektrum Wiss.* **1992**, *12*, 56−62.

(3) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612−648.

(4) Corbett, J. D. In *Solid State Chemistry Techniques*; Cheetham, A. K., Day, P., Ed.; Clarendon Press: Oxford, 1987; pp 1−38.

(5) DiSalvo, F. J. *Science* **1990**, *247*, 649−655.

(6) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558−1564.

(7) Clemens, B. M.; Sinclair, R. *MRS Bull.* **1990**, 19−28.

(8) Walser, R. M.; Bené, R. W. *Appl. Phys. Lett.* **1976**, *28*, 624−625.

(9) Meng, W. J.; Nieh, C. W.; Johnson, W. L. *Appl. Phys. Lett.* **1987**, *51*, 1693−1695.

(10) d'Heurle, F. M.; Gas, P. *J. Mater. Res.* **1986**, *1*, 205−221.

(11) Gösele, U.; Tu, K. N. *J. Appl. Phys.* **1989**, *66*, 2619−2626.

0002-7863/96/1518-2422$12.00/0

high enough to interdiffuse the layers while still being low enough in temperature to prevent nucleation thus forming an amorphous intermediate.[11,12] If amorphous intermediates are prepared at various compositions across a binary system, such as iron−silicon, it is possible to select the crystalline product which will nucleate from the intermediates using the overall composition.[13] Since nucleation is the rate-limiting step in forming a crystalline product from the amorphous intermediate, a kinetic route to new solids is provided where relative nucleation energies of various crystalline products determine which compound will preferentially form.[14] As suggested by Spaepen for nucleation of solid solution from liquid solution, the compound most likely to form is that with the largest driving force for nucleation.[15] While many references referring to nucleation rates and amount of undercooling observed for liquid metals and alloys exist, reports on the effect of amorphous solid composition on solid-state nucleation energies are scarce presumably because of the difficulty in controlling the interplay between nucleation, growth, and diffusion.

In an attempt to unravel the interplay between the steps in a solid-state reaction, we measure the nucleation energy of InSe as a function of the composition of the amorphous intermediate. The indium selenium system was chosen for the facile interdiffusion between indium and selenium layers resulting in a metastable amorphous rection intermediate which forms on standing at room temperature. The rate-limiting step in crystalline product formation is clearly nucleation, providing the opportunity to observe the composition dependence of nucleation with limited concerns regarding either diffusion or growth.

Experimental Section

Sample Preparation. A custom-built ultrahigh vacuum chamber[16] with independently-controlled deposition sources was used to prepare the multilayer films used in this study. Indium was deposited at a rate of 0.5 Å/s using a Thermionics e-beam Gun source independently controlled by a Leybold-Inficon XTC quartz crystal monitor. A Knudsen source controlled by an Omega 9000 temperature controller maintained selenium at a temperature of 235 °C. This resulted in a deposition rate of approximately 0.5 Å/s for selenium as monitored by a separate quartz crystal monitor. The intended thickness of the repeating unit containing an indium and selenium layer varied between 29 and 36 Å in all of the samples prepared. The thickness of the indium layers in the superlattice was either 9, 10, or 11 Å and the selenium layer thickness was varied to obtain the desired composition. To obtain sufficient sample mass for the DSC and TGA experiments, typically 75 layers were deposited resulting in a total film thickness of approximately 2000 Å.

Determination of Stoichiometry. The thermal-gravimetric mass change of the samples on oxidation, resulting in the formation of In_2O_3 and loss of selenium, was used to determine stoichiometry. A calibration curve was constructed which allowed determination of target layer thicknesses required to obtain a given stoichiometry. Subsequent samples were prepared using this calibration curve, and stoichiometry was checked for each sample by thermal-gravimetric analysis.

Thermal Analysis. The evolution of the samples subjected to elevated temperatures was monitored by DSC utilizing a TA Instruments TA9000 calorimeter fitted with a 910DSC cell.[12,13,17,18] The temperature difference detected in this experiment was greatly enhanced by examining the sample free of the substrate. This was accomplished by depositing the multilayer composite on a PMMA-coated wafer. The wafer was then immersed in acetone, which dissolved the PMMA and floated the multilayer film free of the substrate. The resulting pieces were collected by filtration through a Teflon filter and placed into an aluminum DSC crucible. The sample was then dried under reduced pressure to remove any residual acetone.

Table 1. The Intended Layer Thicknesses, Intended Compositions, and Experimentally Determined Compositions Using TGA Analysis for Samples Prepared as Part of This Study

sample	intended thickness (Å) In	 Se	measured Se/In ratio
IS130B	11	20	.92
IS123A	10	21	.94
IS130E	11	24	.96
IS123C	10	22	.97
OYE015	9	21	.97
OYE007	10	24	.99
IS130F	11	25	1.02
IS124A	10	23	1.03
IS124B	10	24	1.06
OYE010	10	21	1.09
OYE011	9	20	1.12

Three different calorimetry experiments were completed on each sample. A portion of each sample was heated at a constant temperature ramp from 40 to 550 °C at 10 °C/min, immediately followed by a subsequent run using the same sample and temperature ramp. Typically, a third such run was also collected. The difference between the first and second run records the irreversible changes in the superlattice as a function of temperature. The difference between the second and third runs is used to obtain a measure of the repeatability of the experiment.

In the second experiment, a portion of each sample was ramped at 10 °C/min to the temperature of interest. After they had cooled to room temperature, the samples were examined using high-angle X-ray diffraction. The samples were then returned to the DSC module and heated to the next higher temperature of interest. In this fashion, a series of "snapshots" are obtained of the sample's thermal and structural evolution.

The third experiment involved running portions of each sample at different scan rates from 2 to 20 °C/min and measuring the shift in the position of the crystallization exotherm as a function of scan rate. This information was used to determine the activation energy for nucleation as described further in the results section.

X-ray Diffraction. High-angle diffraction data were used to determine whether the as-deposited, floated, and annealed samples contained crystalline elements or compounds. Low-angle diffraction data were collected to determine if the samples contained a periodic layered structure and to determine the total film thickness and smoothness by observing the interference between X-rays scattered from the front and the back of the film. These data were collected on a Scintag XDS 2000 $\theta-\theta$ diffractometer with a sample stage modified to allow rapid and precise alignment.[18,19] X-ray flux was adjusted to optimize the low-angle diffraction data for each sample as they varied in thickness of the repeat unit and the total number of repeat units.

Results and Discussion

Nine indium−selenium samples of varying composition surrounding the equimolar composition were prepared as part of this investigation. The intended layer thicknesses and experimentally determined compositions using TGA analysis for these samples are summarized in Table 1. As expected, a linear relationship was found between the ratio of the intended In and Se thicknesses and the experimentally determined

---

(12) Cotts, E. J.; Meng, W. J.; Johnson, W. L. *Phys. Rev. Lett.* **1986**, *57*, 2295−2298.

(13) Novet, T.; Johnson, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 3398−3403.

(14) Fukuto, M.; Hornbostel, M. D.; Johsnon, D. C. *J. Am. Chem. Soc.* **1994**, *116*, 9136−9140.

(15) Thompson, C. V.; Spaepen, F. *Acta Metall.* **1983**, *31*, 2021−2027.

(16) Fister, L.; Li, X. M.; Novet, T.; McConnell, J.; Johnson, D. C. *J. Vac. Sci. Technol. A* **1993**, *11*, 3014−3019.

(17) Fister, L.; Johnson, D. C. *J. Am. Chem. Soc.* **1992**, *114*, 4639−4644.

(18) Novet, T.; McConnell, J. M.; Johnson, D. C. *Chem. Mater.* **1992**, *4*, 473−478.

(19) Novet, T.; Fister, L.; Grant, C. A.; Johnson, D. C. In *Supramolecular Architecture: Synthetic Control in Thin Films and Solids*; Bein, T., Ed.; American Chemical Society: Washington, DC, 1992; Vol. 499, pp 355−368.

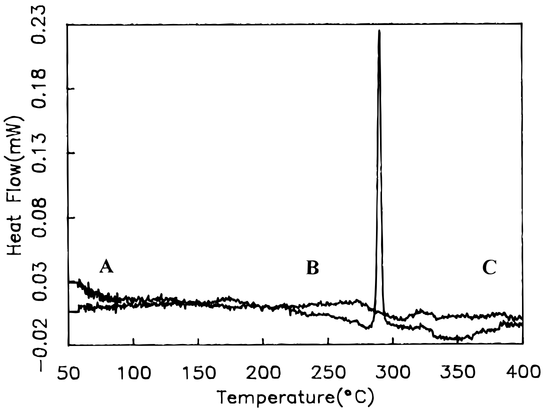

Figure 1. Differential scanning calorimetry data collected on sample IS130E with a temperature ramp of 10 °C/min. The sharp exotherm between 275 and 300 °C was observed in all samples. The letters indicate temperatures at which diffraction data were collected.

compositions within each set of samples made. Shifts in the exact positions of the crystal monitors relative to the sources and samples produced systematic discrepancies between the ratio of the intended In and Se thicknesses and the experimentally determined compositions between samples made in different sets.

The low-angle diffraction pattern of the as-deposited samples contained maxima resulting from interference between the front and back surface of the films which increased the intensity upon room temperature annealing suggesting that the films became smoother with time. No Bragg diffraction maxima resulting from the elemental layering were observed, suggesting that the samples interdiffused during deposition or at room temperature while waiting for X-ray analysis. The high-angle diffraction scans also contained no diffraction maxima, indicating that the samples were amorphous with respect to X-rays upon deposition.

The sample's crystallization behavior was explored using differential scanning calorimetry. All of the thermograms contained a large, sharp exotherm between 275 and 300 °C as can be seen in the representative thermogram shown in Figure 1. X-ray diffraction scans taken after annealing below the exotherm contained no diffraction maxima indicating that the samples were amorphous while diffraction data taken after the exotherm confirm that InSe has crystallized as shown in Figure 2. The facile interdiffusion of the indium and selenium at room temperature and the large, sharp exotherm found in the calorimetry data made this an ideal system in which to measure the composition dependence of nucleation. A linear relationship between composition and the temperature of maximum heat flow in the exotherm is shown in Figure 3. A similar linear relationship between composition and nucleation temperature was observed previously resulting from the addition of ternary components to amorphous nickel−zirconium alloys[20] while several researchers have observed that the maximum undercooling observed in metallic melts is related to the melt's composition.[15,21] Nucleation may involve the assembly of the correct ratios of atomic species through diffusive motion, structural change into one or more unstable intermediate structures, and formation of nuclei of the new compound. Possible underlying causes for this shift in the nucleation temperature with composition include a change in the interdiffusion rate, a change in the nucleation energy, or a change in the prefactor for nucleation with composition.

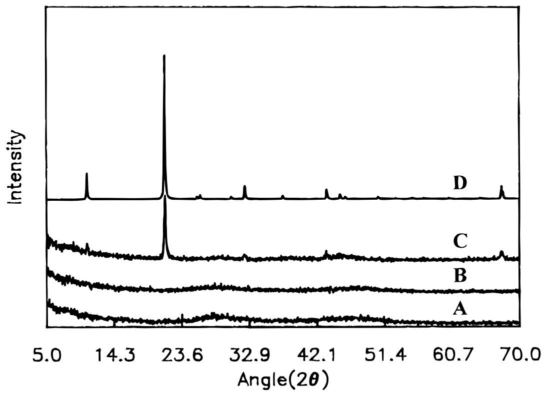

Figure 2. Evolution of the high-angle diffraction pattern of sample IS130F as a function of annealing temperature. As schematically shown in Figure 1, the diffraction data labeled A was collected on the as-deposited sample, the diffraction data labeled B were collected after heating the sample to 250 °C, and the diffraction data labeled C were collected after heating the sample to 400 °C. The diffraction pattern labeled D is the JCPDS file for crystalline InSe, confirming the nucleation and growth of InSe.

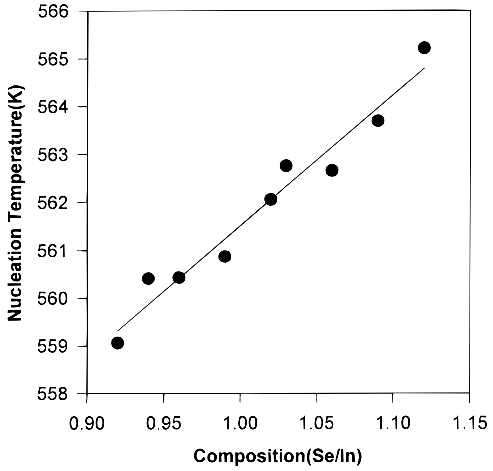

Figure 3. The composition dependence of the temperature corresponding to the maximum heat flow of the crystallization exotherm for the samples investigated in this study.

To determine the underlying cause of the observed composition dependence and quantify the stability of the amorphous reaction intermediate, differential scanning calorimetry data were collected as a function of scan rate to estimate the activation energy of the nucleation and growth process. Such non-isothermal DSC data are typically analyzed using a Kissinger analysis in which the activation energy can be obtained from the peak temperature, T_p, as a function of scan rate, Q:[22]

$$\frac{\mathrm{d}\ln[Q/T_p^2]}{\mathrm{d}[1/T_p]} = \frac{-E_{\mathrm{crystallization}}}{R}$$

Graphing $\ln[Q/T_p^2]$ versus $1/T$ gives a straight line with slope $-E/R$ yielding the activation energy for the nucleation and growth process. While this activation energy is associated with the nucleation and growth of InSe, its extraction from the non-isothermal DSC data is based upon many assumptions. The above equation is derived by assuming that the nucleation and growth can be described by the Johnson−Mehl−Avrami equation, that the amorphous and the crystalline states have the same

---

(20) Bhatnagar, A. K.; Rhie, K. W.; Naugle, D. G.; Wolfenden, A.; Zhang, B. H.; Callaway, T. O.; Bruton, W. D.; Hu, C. R. *J. Phys.: Condens. Matter* **1990**, *2*, 2625−2636.

(21) Perepezko, J. H. In *Proceedings of the 2nd International Conference on Solidification Processing*; Mehrabian, R., Kear, B. H., Cohen, M., Eds.; Reston, VA, 1980; Claitor's: Baton Rouge, LA, 1980; p 56.

(22) Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702−1706.

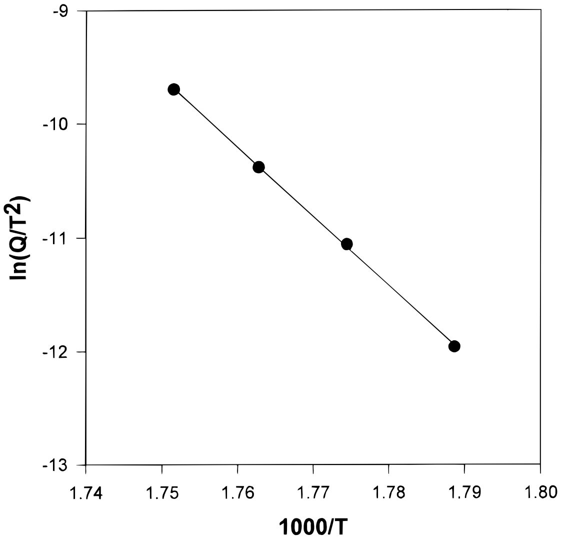

Figure 4. A representative Kissinger plot used to derive the activation energy for nucleation of InSe. The data are from sample IS130B. The arguments of the logarithm were made unitless by dividing by a constant T_0^2/Q_0 where T_0 is 1000 K and Q_0 is 1 deg/min.

composition, and that the nucleation and growth rates are constant at constant temperature. A further approximation is made that both the nucleation rate and growth rates may be described by Arrhenius expressions over the range of temperature in which the peak temperature varies with scan rate. Even though the samples examined as part of this study varied in composition about the nucleating compound InSe, graphing $\ln[Q/T_p^2]$ versus $1/T_p$ yielded straight lines for all of the samples studied as shown in Figure 4 for a representative sample.

The activation energies derived using the Kissinger expression reflect the barriers to nucleation and growth of the more stable crystalline InSe from the metastable amorphous intermediate. In classical nucleation theory as originally developed by Gibbs, such a metastable intermediate phase is always stable with respect to the formation of an infinitesimal droplet of a material with properties approaching those of a more stable phase provided it has a positive surface tension. Since the ratio of the surface area to volume of a droplet decreases rapidly with increasing size, there is a critical size droplet which is in unstable equilibrium with the metastable phase. The activation energy for a spherical particle in this classical picture is proportional to the ratio of the cube of the surface energy of a critical size droplet divided by the square of the Gibbs free energy difference between the metastable intermediate and the more stable phase for the volume of material in the critical droplet.[23] In contrast to this macroscopic approach, a second method considers the process of formation of a new phase from a metastable intermediate from a kinetic viewpoint, considering the stepwise addition of atoms to a cluster until a critical size cluster droplet is reached. In these microscopically based theories, the incorporation and dissolution of atoms to the clusters are assumed to proceed by thermally activated processes. A recent paper by Strey gives a useful overview of theoretical treatments of homogeneous nucleation.[24]

The variation of the activation energy determined using the Kissinger expression with composition of the amorphous intermediate is shown in Figure 5. There is a pronounced minimum in the activation energy for the nucleation and growth of InSe around the one-to-one stoichiometry. This minimum activation energy can be explained by considering the energy decrease during nucleation per unit volume transformed. In the In−Se binary system, the driving force for nucleation is a maximum at the stoichiometric composition, decreasing symmetrically as one moves off stoichiometry. While this variation in energy released during nucleation will lead to the observed composition dependence, it is worthwhile to also consider the atomic rearrangements which must occur in the amorphous alloy during the formation of a critical nucleus. If the overall composition is that of the line phase InSe, then only local rearrangements in bond angles and lengths need occur to form the critical nucleus. If the amorphous intermediate has a different composition from the compound being nucleated, longer range diffusion must occur to form a critical nucleus. Keeping the size of the critical nucleus constant as a function of composition, this composition fluctuation becomes more unlikely the farther in composition the amorphous alloy is from that of the nucleating compound again leading to the observed composition dependence.

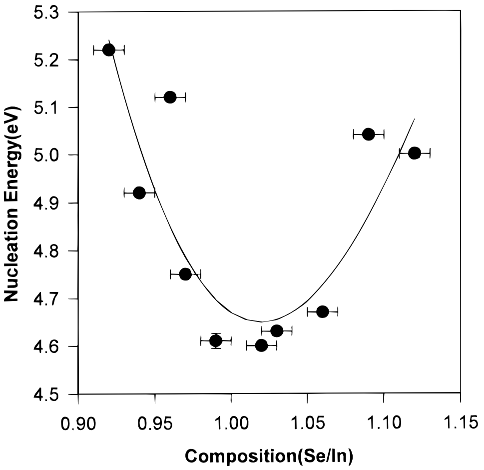

Figure 5. The variation of the activation energy determined using the Kissinger expression with composition of the amorphous intermediate.

The rapid increase in the activation energy for nucleation of InSe as the composition of the amorphous intermediate is increasingly varied from the stoichiometric ratio implies that the nucleation energy of adjacent compounds in the phase diagram will eventually become comparable to that of InSe. Indeed, samples prepared either more selenium rich or more indium rich than those used to prepare Figure 5 have two exotherms in the DSC data between room temperature at 400 °C. Samples more indium rich in composition than Se/In = 0.9 formed a mixture of InSe and In_4Se_3 as expected from the phase diagram.[25] Samples more selenium rich than Se/In = 1.12 formed a mixture of InSe and In_2Se_3, skipping the intermediate phase In_6Se_7 expected from the published phase diagram. Since the original modulation of In and Se diffuses out on standing at room temperature, In_2Se_3 must have a lower nucleation energy than In_6Se_7. Curiously, the first-phase rule of Walser and Bené predicts that In_2Se_3 should be the first phase formed at an In−Se interface, as In_2Se_3 melts congruently at 885 °C, while In_6Se_7 peritectically decomposes at 630 °C into In_2Se_3 and a molten In−Se alloy and InSe peritectically decomposes at 600 °C into a mixture of molten In−Se alloy and In_6Se_7.

These results have several implications for any synthetic technique attempting to use nucleation to provide phase

---

[23] Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1959**, *31*, 688−699.

[24] Strey, R.; Wagner, P. E.; Viisanen, Y. *J. Phys. Chem.* **1994**, *98*, 7748−7758.

[25] *Binary Alloy Phase Diagrams*, 2nd ed.; Massalski, T. B., Okamoto, H., Subramanian, P. R., Kacprzak, L., Eds.; ASM International: Materials Park, 1990; Vol. 3, pp 2664−2665.

selectivity. For example, several years ago we found that we could control and selectively nucleate the binary iron silicides using the composition of the amorphous intermediates.[13] The observed composition dependence of the nucleation energy for InSe provides a possible rationale for this selectivity. Similarly, from ternary amorphous intermediates we have observed the preferred crystallization of ternary compounds rather than binary compounds.[26] Again the composition dependence of the nucleation temperature provides a rationale for the ability to avoid thermodynamically stable binary compounds as reaction intermediates. The compound which nucleates from both binary and ternary amorphous intermediates, however, is that with the lowest nucleation energy.[14] The data presented in this paper show that it is possible to use the composition of an amorphous intermediate to change nucleation energies. Thus, for example, one can experimentally use composition to lower the nucleation of a ternary compound while raising the nucleation energy of a binary compound by adjusting the concentration of the ternary component. Whether this results in ternary phase formation, however, depends upon the relative nucleation energies of the two compounds. When a binary compound has been found to preferentially nucleate from the ternary amorphous intermediate, the nucleation temperature of the binary component was observed to increase with increasing concentration of the ternary element in the amorphous intermediate as expected from the results presented herein.[27] The ability to use composition of the amorphous intermediate to control nucleation energies and thus help direct crystallization of desired compounds represents a crucial step forward in the ability to design the synthesis of solid-state compounds.

Summary

The composition dependence of the nucleation energy of InSe from the amorphous alloys, determined using a Kissinger analysis of differential scanning calorimetry data, was found to have a pronounced minimum for the one-to-one composition. This minimum reflects the maximum driving force per unit volume found for nucleation and growth of InSe at this composition as well as the lack of short-range composition fluctuations required to nucleate stoichiometric InSe from nonstoichiometric amorphous alloys. The observed composition dependence provides rationale for the phase selectivity observed in nucleation-controlled synthesis of solid-state compounds using the composition of the amorphous intermediate.

Acknowledgment. This work was supported by the National Science Foundation (DMR-9213352 and DMR-9308854). Additional support by the Office of Naval Research (N0014-93-1-0205), the U.S. Department of Energy, Pacific Northwest Laboratories through the Energy Research Fellowship Program (C.D.J.), National Science Foundation-REU (CHE-9225069) (for O.O.), the University of Oregon, and the U.S. Department of Education Graduate Assistance in Areas of Need Program (T.N.) is gratefully acknowledged.

JA953560K

---

(26) Fister, L.; Novet, T.; Grant, C. A.; Johnson, D. C. In *Advances in the Synthesis and Reactivity of Solids*; Mallouk, T. E., Ed.; JAI Press Inc.: Greenwich CT, 1994; Vol. 2, pp 155−234.

(27) Hornbostel, M. D.; Fukuto, M.; Johnson, D. C. *J. Solid State Chem.* **1995**, *117*, 290−293.