Synthesis of $Cu_xMo_6Se_8$ without Binary Compounds as Intermediates: A Study Using Superlattices to Kinetically Control a Solid-State Reaction

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Abstract: The formation of $Cu_xMo_6Se_8$ by reaction of superlattice composites is explored as a function of elemental layer thicknesses making up the repeat unit while maintaining stoichiometry near the $Cu_xMo_6Se_8$ phase field. Layer thickness was found to control the reaction pathway of the ternary composites. The critical layer thicknesses below which one avoids interfacial nucleation of binary compounds obtained previously for binary systems were useful guides for predicting ternary system behavior. For elemental layers thicker than the binary critical layer thicknesses, the ternary composites were found to initially form $MoSe_2$. The $MoSe_2$ subsequently reacted with the rest of the composite to form the desired ternary compound on further heating. For elemental layers thinner than the critical layer thicknesses for the binary systems, the ternary composites reacted to form the desired ternary compound without forming $MoSe_2$.

Introduction

Synthetic molecular chemistry is based on techniques, reagents, and approaches which have high kinetic selectivity to prepare desired products in high yield. While this research targets particular compounds and develops new synthetic reagents, the details of the reaction mechanism are regarded as being as important as the product itself. The reaction mechanism provides an important conceptual framework for the synthetic chemist, promoting an understanding of cause and effect relationships between synthetic parameters and product distributions. Furthermore, the understanding of reaction pathways permits the extrapolation of results from one system to another and has led to the great richness of small molecule chemistry. The success of this approach is highlighted by the isolation of molecules with exceedingly strained structures, as well as structural and geometric isomers of compounds with the same composition.

In contrast to synthesis of molecular products, the preparation of extended solid-state compounds has been dominated by the high-temperature reaction of either elements or binary compounds. Such a reaction conceptually involves two steps, the interdiffusion of the reactants and the nucleation of crystalline intermediates and products. The rate-limiting step in these reactions is diffusion as a result of the high activation energy for solid-state diffusion and the macroscopic diffusion lengths. Neither interdiffusion nor nucleation are well understood in "real" reacting systems as the reaction mixture is heterogeneous with interfacial diffusion dominating the evolution of the system.[1,2] The complexity of this system, as shown schematically in Figure 1, has prevented the development of solid-state reaction mechanisms or methods to kinetically control the products. Consequently, the synthesis of new solid-state phases by conventional synthesis routes has been largely an empirical science.[3]

The focus of our research efforts has been to develop a synthetic approach to extended solids based on superlattice reagents. Superlattice reactants provide several important advantages compared to other synthetic approaches. They are prepared layer by layer allowing control of individual layer thicknesses on an angstrom length scale. Any element which is solid at room temperature can be incorporated in the superlattice.[4–6] The very high density of interfaces in these modulated composites permits the thermodynamics of the interfacial reactions to be explored using differential scanning calorimetry.[7–9] Finally, the time scale of the interfacial reactions in a multilayer permits in-situ studies of interfacial evolution using both low- and high-angle X-ray diffraction.[7,10–13]

Synthetically, the sequence of reaction intermediates between two solid elements can be controlled by adjusting the layer thicknesses within the repeating unit. If the thicknesses of the elemental layers are above a critical thickness, a crystalline binary compound will nucleate at the reacting interfaces. If the superlattice reactant is prepared with layer thicknesses below this critical thickness, the superlattice reactant evolves into an amorphous solid. The critical thickness varies considerably for different binary systems. In nickel–zirconium the critical thickness of the elemental layers required to avoid forming Ni_2Zr at the interface is on the order of hundreds of angstroms,[8] while for molybdenum–selenium the molybdenum layers must be less than 9 Å thick to avoid interfacial nucleation of $MoSe_2$.[14]

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

(2) Schmalzried, H. *Solid State Reactions*; Verlag Chemie: Deerfield Beach, FL, 1981; Vol. 12, pp 254.

(3) DiSalvo, F. J. *Science* **1990**, *247*, 649–655.

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

(5) Webb, R. J.; Goldman, A. M. *J. Vac. Sci. Technol. A* **1985**, *3*, 1907–1912.

(6) Nastasi, M.; Hung, L. S.; Johnson, H. H.; Mayer, J. W.; Williams, J. M. *J. Appl. Phys.* **1985**, *57*, 1050–1054.

(7) 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.

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

(9) Novet, T.; Xu, Z.; Kevan, S. D.; Johnson, D. C. *Mater. Sci. Eng. A* **1992**, *A162*, 115.

(10) Murakami, M.; Segmüller, A.; Tu, K. N. In *Analytical Techniques for Thin Films*; Tu, K. N., Rosenberg, R., Eds.; Academic Press, Inc.: New York, 1988; Vol. 27, pp 201–248.

(11) Fleming, R. M.; McWhan, D. B.; Gossard, A. C.; Wiegmann, W.; Logan, R. A. *J. Appl. Phys.* **1980**, *51*, 357–363.

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

(13) Greer, A. L.; Spaepen, F. In *Synthetic Modulated Structures*; Chang, L. C., Giessen, B. C., Eds.; Academic Press: New York, 1985; pp 419–486.

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

0002-7863/94/1516-0629$04.50/0

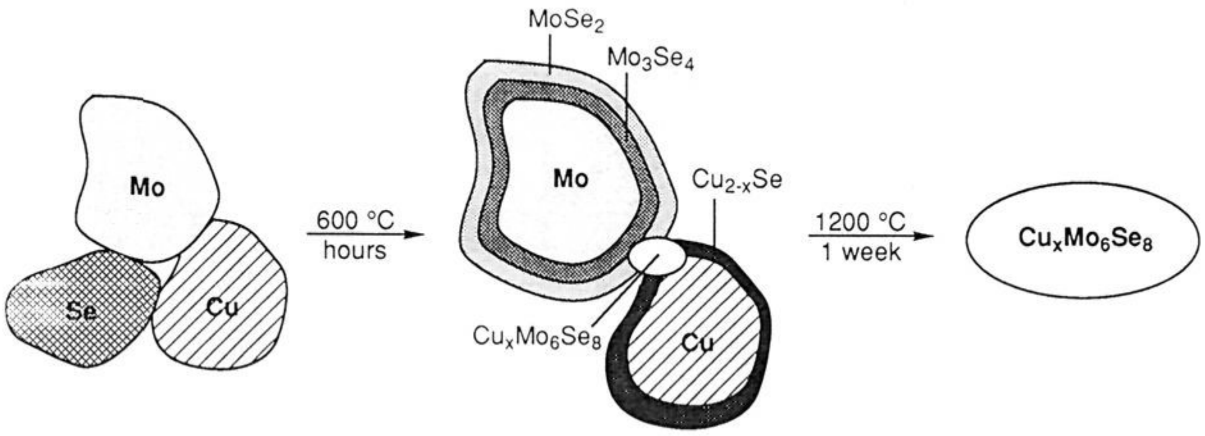

Figure 1. A typical solid-state reaction is heterogeneous with solid-state diffusion being the slowest step in the reaction as product layers become thicker, isolating the reacting species.

The critical thickness of a binary diffusion couple depends on many factors, including the driving force for crystallization, the diffusion rates of both atomic species, the complexity of the crystal structure, and the stoichiometric stability range of the compound being formed.[15]

The ability to avoid interfacial nucleation while interdiffusing a system to a homogeneous, amorphous intermediate allows nucleation, a kinetic phenomenon, to control product formation. Previous work on binary systems has demonstrated that nucleation of products can be controlled by the stoichiometry of the amorphous intermediate, permitting the kinetic trapping of compounds under conditions where they are thermodynamically unstable.[12]

In this paper we present data on ternary superlattice reactants of approximate composition $Cu_2Mo_6Se_8$ prepared over a range of layer thicknesses above and below the critical thicknesses found for the binary allows while maintaining overall stoichiometry. The goal of this study was to determine whether it was possible to avoid the nucleation of binary compounds in the evolution of a ternary superlattice reactant to a ternary compound by tailoring the structure of the initial superlattice.

Experimental Procedures

Sample Preparation. A custom-built ultra-high-vacuum chamber[4] with independently-controlled deposition sources was used to prepare the multilayer films used in this study. Copper and molybdenum were deposited at a rate of 0.5 Å/s using Thermionics e-beam Gun sources independently controlled by Leybold-Inficon XTC quartz crystal monitors. 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 1 Å/s for selenium as monitored by a separate quartz crystal monitor.

Thickness calibration of the deposition sources was done by preparing a progression of samples with increasing thickness of one of the elemental components. This calibration was done for layer thicknesses between 6 and 20 Å for molybdenum, 20 and 35 Å for selenium, and 2 and 10 Å for copper. Target layer thicknesses which give stoichiometries close to that desired (to the nearest angstrom) were calculated assuming crystalline densities for copper and molybdenum and a density for amorphous selenium which is 5% less than the bulk density. The large deviations from the intended thicknesses for samples with thicker layers, summarized in Table 1, result from the smaller percentage of interfacial volume in these samples when compared with samples containing thinner elemental layer thicknesses where the calibration was done. All samples were found to be molybdenum rich relative to $Cu_xMo_6Se_8$ as a result of the unknown density and stoichiometry of the interfacial regions due to interdiffusion during deposition.

Two different substrates were used for the multilayer composites produced for this study. Silicon wafers polished to ±3Å rms were used as X-ray suitable substrates for initial characterization of the as-deposited films. Silicon wafers were also coated with poly(methyl methacrylate) (PMMA)[14] for DTA studies as described below.

X-ray Diffraction. The low-angle diffraction resulting from the periodic layered structure of the as-deposited multilayer films was used to confirm the layered nature of the starting composites and to determine modulation thicknesses and interfacial widths.[16-20] These data were collected on a Scintag XDS 2000 θ–θ diffractometer with a sample stage modified to allow rapid and precise alignment.[7,21] The 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.

Table 1. A Summary of the Intended Layer Thicknesses and Measured Repeat Unit for the Superlattice Reactants Prepared in This Investigation[a]

sample no.	target layer thicknesses (Å) Cu	 Mo	 Se	target total repeat thickness (Å)	measured repeat thickness (Å)	target stoichiometry
1	7.5	45	123	183	255	$Cu_{1.3}Mo_{6.0}Se_{8.4}$
2	7.5	22.5	45	75	88	$Cu_{2.7}Mo_{6.0}Se_{6.1}$
3	7.5	22.5	61.5	91.5	110	$Cu_{2.7}Mo_{6.0}Se_{8.4}$
4	4.5	16.5	43.5	64.5	73	$Cu_{2.2}Mo_{6.0}Se_{8.1}$
5	3	12	29	44	48.5	$Cu_{2.0}Mo_{6.0}Se_{7.4}$
6	2	7	19	28	32	$Cu_{2.3}Mo_{6.0}Se_{8.3}$
7	2	7	19	28	38	$Cu_{2.3}Mo_{6.0}Se_{8.3}$
8	2	7	18	27	28	$Cu_{2.3}Mo_{6.0}Se_{7.9}$

[a] Sample 1 has a sequence of Cu–Mo–Cu–Se layers for the repeat unit while the remaining films have a Cu–Mo–Se sequence of layers.

High-angle diffraction data were used to determine whether the as-deposited, floated, and annealed samples contained crystalline elements or compounds.

Thermal Analysis. Differential thermal analysis (DTA) was used to assess the reaction between the elemental layers.[8,12,14,21] The temperature difference detected in this experiment is greatly enhanced if the layered sample is free of the substrate. This was accomplished by depositing the multilayer composite on a PMMA-coated wafer. This wafer is then immersed in acetone, which dissolved the PMMA and floated the multilayer film free of the substrate. The resulting pieces were collected by sedimentation into an alumina or platinum DTA crucible. The sample was then dried under reduced pressure to remove any residual acetone.

Two different calorimetry experiments were done on these samples. The first experiment was a temperature ramp from 40 °C to either 1000 or 1200 °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. The second experiment was a quenching experiment in which the samples were heated at 10 °C/min from 40 °C 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 DTA module and heated to the next higher temperature of interest. In this

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(15) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1959**, *31*, 688–699.

(16) Xu, Z.; Tang, Z.; Kevan, S. D.; Novet, T.; Johnson, D. C. *J. Appl. Phys.* **1993**, *74*, 905–912.

(17) Barbee, T. W., Jr. *MRS Bull.* **1990**, *15*, 17.

(18) McWhan, D. B. In *Synthetic Modulated Structures*; Chang, L. C., Giessen, B. C., Eds.; Academic Press: New York, 1985; pp 43–74.

(19) Névot, L.; Pardo, B.; Corno, J. *Rev. Phys. Appl.* **1988**, *23*, 1675–1686.

(20) Spiller, E. In *Physics, Fabrication, and Applications of Multilayered Structures*; Dhez, P., Weisbuch, C., Eds.; Plenum Press: New York, 1988; Vol. 182, pp 271–309.

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

annealed to 600 °C, the diffraction pattern consists of the 00*l* diffraction peaks of crystalline $MoSe_2$. After the sample is annealed to 1200 °C, the diffraction pattern is a superposition of peaks for $Cu_xMo_6Se_8$ and excess molybdenum.

To further explore the details of the sequence of phase formation, sample 3 was annealed at the following temperatures: 172, 227, 449, 727, 925, and 991 °C and quenched. These data show that by 172 °C the superlattice has partially interdiffused and $MoSe_2$ has heterogeneously nucleated at the evolving interfaces. The exotherm at 460 °C corresponds to crystal growth of the already formed $MoSe_2$. These diffraction data from the low-temperature anneals are similar to data collected on molybdenum–selenium superlattices which contain exotherms at approximately the same temperatures for films with similar molybdenum thicknesses.[14] In the molybdenum–selenium system, the first exotherm at 110 °C results from interdiffusion of the elements. Heterogeneous nucleation of $MoSe_2$ at the evolving interfaces results in the second exotherm at 170 °C. After annealing at 727 °C, diffraction peaks for $Cu_xMo_6Se_8$ are observed which have much smaller peak widths than those of the $MoSe_2$ formed at lower temperatures. As diffraction peaks for $Cu_xMo_6Se_8$ increase in intensity with further annealing, the intensity of the $MoSe_2$ diffraction features decrease. $Cu_xMo_6Se_8$ becomes more crystalline, with peak widths decreasing and more peaks becoming resolvable, with further annealing at higher temperatures.

These diffraction data suggest that the first three exotherms are associated with the formation of $MoSe_2$ while the high-temperature endotherm is associated with the reaction of $MoSe_2$ with the remaining components of the initial composite to form the ternary compound. Additional support for this sequence of reaction intermediates is found in the subsequent background calorimetry scans collected. The main feature in the two background calorimetry scans of samples heated to 1200 °C (shown in Figure 2) is an endotherm with an onset temperature of ~125 °C (peak at 139.6 °C). We suspect that this endotherm results from the reversible order–disorder phase transition resulting from the mobility of the copper atoms in the M_{12} sites of the Chevrel phase as previously observed in the analogous sulfide system.[23] This endotherm was not observed in calorimetry scans when this set of samples was heated below 600 °C, confirming that the ternary phase is not formed at low temperatures.

Cases with Mo Less than 12 Å. Three of the eight samples prepared had molybdenum layer thicknesses less than 12 Å. The low-angle X-ray patterns of the as-deposited samples all contain superlattice diffraction peaks. The high-angle X-ray pattern of the as-deposited samples 7 and 8 contained no diffraction peaks. Sample 6 as-deposited has a weak and broad (almost 4.5° wide) diffraction maxima corresponding to the 101 peak of molybdenum.

A representative high-temperature DTA data set for these samples is shown in Figure 4 which contains distinctly different thermal features than those of the thicker superlattice films. Compared to the second run, the initial DTA scan contains a small and broad exotherm between 40 and 650 °C as well as two small exotherms with onset temperatures at about 730 and 795 °C. High-angle X-ray data after annealing and the reversible endotherm at ~110 °C (peak at 126.6 °C) in the background DTA data set are consistent with the formation of the ternary product, $Cu_xMo_6Se_8$, during the first heating of the sample to 1200 °C.

To obtain more details of the reaction pathway, sample 6 was annealed to various temperatures (169, 231, 427, 727, and 912 °C), quenched to room temperature, and then probed with X-ray diffraction. The evolution of the diffraction scans with annealing temperature is shown in Figure 5. The diffraction pattern after annealing at the two lowest temperatures contains a broad diffraction peak at approximately 40° as well as a weak diffraction maxima at 45°, indicating that nucleation of a compound may have already occurred forming very small crystallites. On further annealing, this diffraction pattern evolves smoothly with gradual sharpening of the diffraction peaks into the ternary product and molybdenum as shown in Figure 5. For all of the ultrathin superlattices studied, the distinct and prominent 00*l* diffraction pattern of $MoSe_2$ found for the thicker superlattices was never observed.

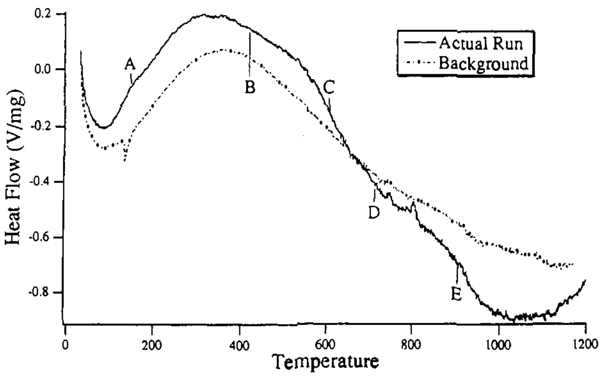

Figure 4. The high-temperature DTA data for sample 7. The letters indicate temperatures to which samples were annealed before being quenched for X-ray analysis. The diffraction data are presented in Figure 5.

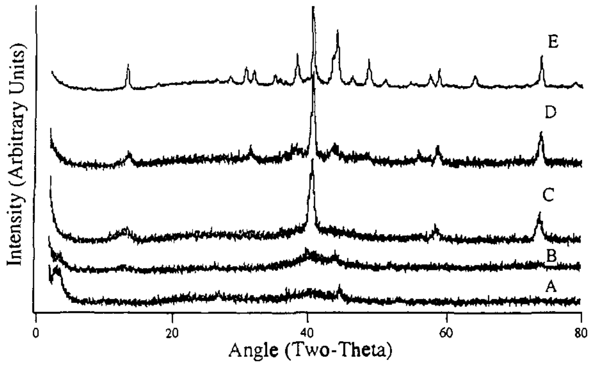

Figure 5. The high-angle X-ray diffraction patterns of sample 6 taken after the sample was annealed and then quenched to (A) 169 °C, (B) 231 °C, (C) 427 °C, (D) 727 °C, and (E) 912 °C.

Discussion

These results demonstrate the ability of a superlattice's initial elemental layer thicknesses to control the subsequent reaction sequence of the composite. A distinct difference between the evolution of composites containing molybdenum layers at or above and below 12 Å was observed. The thicker samples reacted to form $MoSe_2$ after the layers initially began to interdiffuse, presumably at the interfaces due to heterogeneous nucleation. The ultrathin films reacted to form the ternary compound without the formation of crystalline, binary intermediates. By analogy with previous studies on the reaction of binary multilayer composites,[4] we suspect that this is due to the disappearance of a distinct molybdenum–selenium interface before interfacial nucleation of $MoSe_2$ can occur.

The nucleation-limited behavior found for the ultrathin films results in a kinetically-controlled synthesis of $Cu_xMo_6Se_8$. If interdiffusion can be completed before any heterogeneous nucleation can occur, the system is trapped in a metastable, amorphous intermediate state. The compound which forms from this state will be the one with the smallest nucleation barrier, not necessarily the most thermodynamically stable as illustrated in Figure 6. By preparing such a metastable, amorphous reaction

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[23] Baillif, R.; Yvon, K.; Flukiger, R.; Muller, J. *J. Low Temp. Phys.* **1979**, *37*, 231–237.

Table 2. A Summary of Lattice Parameters Obtained for the Ternary Phase $Cu_xMo_6Se_8$ Along with the Secondary Phases Observed for Samples Annealed to 1200 °C[a]

sample no.	rhombohedral lattice parameters *a*	rhombohedral lattice parameters *α*	secondary phases obsd
2	6.81(1)	95.03(1)	Mo
3	6.82(1)	95.14(1)	Mo
6	6.81(1)	95.13(1)	Mo + larger cell
7	6.79(2)	94.11(1)	Mo + larger cell

[a] Samples 1, 4, and 5 were annealed at 600 °C and the diffraction pattern after annealing revealed that these samples formed $MoSe_2$ as a reaction intermediate. Sample 8 was also annealed to 600 °C and the diffraction pattern obtained after the anneal showed that $Cu_xMo_6Se_8$ formed. The diffraction peaks were very broad, preventing refinement of lattice parameters.

fashion, a series of "snapshots" are obtained of the sample's thermal and structural evolution.

The first experiment was carried out with either a Netzsch STA409 simultaneous DTA/TGA (thermogravimetric analysis) instrument on a TA Systems 910 module with a 1600 °C DTA cell. Alumina sample and reference crucibles were used in the Netzsch instrument and sample mass was not observed to change during anneals. The sample area was evacuated for 30 min before argon was allowed to flow through the sample space at a rate of 100 cm^3/min. The TA Systems DTA module was contained within a nitrogen atmosphere drylab maintained at less than 0.5 ppm of oxygen. Platinum sample and reference crucibles were used in this instrument.

Results

A series of eight ternary superlattice composites were made over a range of layer thicknesses with approximate stoichiometry $Cu_2Mo_6Se_8$. The intended stoichiometries, individual elemental layer thicknesses, and total repeat unit thickness for these samples are found in Table 1. For these samples, the low-angle diffraction patterns contained Bragg maxima resulting from the repeat unit of the superlattice. The positions of these maxima were used to determine the actual total repeat thickness as reported in Table 1. The rapid decrease in intensity of the superlattice Bragg maxima with increasing diffraction angle indicates that there is significant interfacial interdiffusion of the elements during deposition. Due to the high diffusion rate of copper in selenium, the actual structure of the multilayers soon after deposition consists of alternating amorphous copper–selenium layers and molybdenum layers with a significant interdiffused region between them. The difference between the intended and actual thicknesses in part results from the unknown density of this interdiffused region as discussed in the Experimental Section.

An independent estimate of the deviations from stoichiometry can be obtained from the lattice parameters of the crystalline ternary products obtained after annealing at 1200 °C in the Netsch simultaneous DSC/TGA along with diffraction evidence for additional products. The lattice parameters of the ternary products formed from samples 2, 3, 6, and 7 are summarized in Table 2. The lattice parameters obtained for the ternary products are consistent with previously reported lattice parameters for $Cu_xMo_6Se_8$. Although no binary compounds were observed as impurity phases, crystalline molybdenum was observed in all samples, thus confirming the molybdenum-rich composition of the initial superlattice reactants. In addition, samples prepared with molybdenum layers thinner than 12 Å contained an impurity phase with a large unit cell. Although there are only a few diffraction maxima clearly assignable to this impurity, their positions are consistent with the formation of a condensed cluster compound containing either Mo_9Se_{11} or $Mo_{12}Se_{14}$ clusters.[22] Further efforts are underway attempting to prepare this impurity compound in higher yield by varying the stoichiometry of the initial superlattice composite.

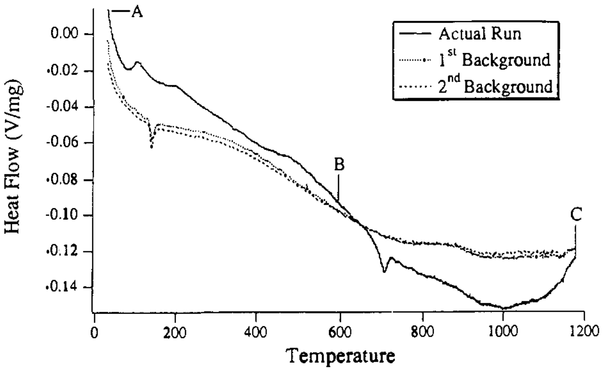

Figure 2. High-temperature DTA data obtained for sample 2. High-angle X-ray diffraction data were taken at (A) room temperature, (B) after a portion of the sample was taken to 600 °C at 10 °C/min three times, and (C) after a second portion of sample was taken to 1200 °C at 10 °C/min three times. All thermal features in the 600 °C experiment coincide with the 1200 °C experiment.

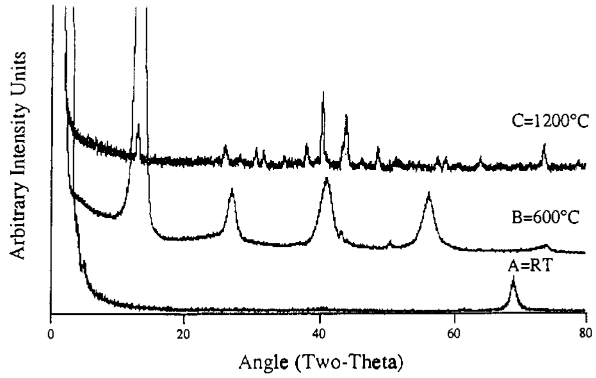

Figure 3. The high-angle X-ray diffraction patterns of sample 2: (A) as-deposited and on a silicon substrate; (B) after three runs to 600 °C at 10 °C/min; and (C) after three runs to 1200 °C at 10 °C/min on a second portion of sample.

To explore the sequence of reactions which occur in these superlattice films as they are heated, low-temperature differential scanning calorimetry and/or high-temperature DTA experiments were conducted. The structural changes in these composites were monitored using X-ray diffraction. The reaction pathways of these samples fall into two categories. The first is those samples in which the Mo layer thickness is 12 Å or greater and the second is those with a Mo thickness less than 12 Å.

Cases with Mo Thickness 12 Å or Greater. Five of the eight samples prepared had molybdenum layer thicknesses of 12 Å or greater. The high-angle diffraction pattern of the three as-deposited samples with the thickest elemental layers contained diffraction peaks for crystalline Mo. Only the diffraction pattern of the thickest sample (sample 1) contained Bragg peaks for crystalline Se. The two thinnest samples in this set (samples 4 and 5) had no diffraction peaks in the high-angle diffraction patterns.

A representative high-temperature DTA data set for this group of samples is shown in Figure 2. The scan obtained during the initial heating of the sample contains three exotherms with onset temperatures at ~110, 170, and 460 °C and an endotherm with an onset temperature of ~680 °C. Figure 3 contains the high-angle X-ray diffraction data obtained from the sample used in Figure 2 at room temperature, after thermal analysis to 600 °C, and after thermal analysis to 1200 °C. The initial diffraction scan contains the low-angle diffraction peaks resulting from the modulation of the superlattice and a diffraction signal between 60 and 80° due to the silicon substrate. There is also a very broad and weak diffraction maximum at approximately 40° probably due to very small molybdenum crystallites. After the sample is

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(22) Chevrel, R.; Gougeon, P.; Potel, M.; Sergent, M. *J. Solid State Chem.* **1985**, *57*, 25–33.

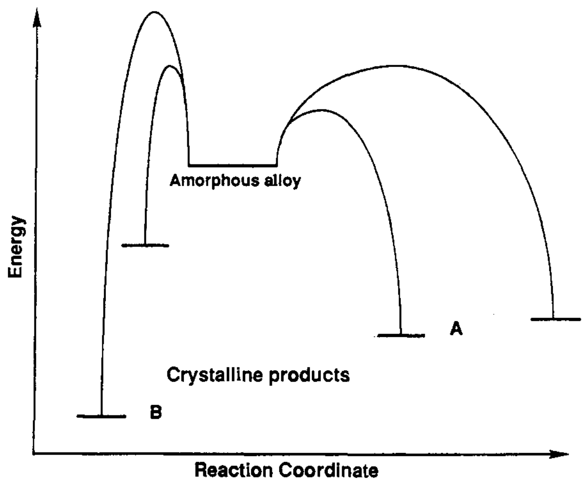

Figure 6. An energy versus reaction coordinate diagram for the nucleation of various compounds from an amorphous intermediate. The compound which forms at low temperatures will be the one with the lowest nucleation barrier (compound A), not necessarily the compound with the lowest free energy (compound B).

intermediate it should be possible to prepare ternary compounds which are unstable with respect to a mixture of binary compounds under the reaction conditions since nucleating a ternary compound involves only local rearrangement of the atoms. Nucleating a binary compound, conversely, involves disproportionation of the ternary amorphous intermediate, a more difficult process since it requires longer diffusion distances. If this is found to be generally true, then superlattice reagents will provide a long-sought synthetic route to extended solids which permits kinetic control of reaction intermediates and products.

A second important result from this investigation is the potential transferability of the critical layer thicknesses of the binary components as design guides for the preparation of ternary superlattices which evolve to form amorphous intermediates. For the ternary copper–molybdenum–selenium system, the relevant binary systems are Mo–Se, Cu–Se, and Cu–Mo. Previous investigations in the Mo–Se system[14] found that the Mo elemental thickness determines whether $MoSe_2$ or an amorphous alloy forms on interdiffusion. Only for molybdenum–selenium superlattices containing Mo layers less than 9 Å was a homogeneous, amorphous intermediate formed. Preliminary work done in the copper–selenium system found facile interdiffusion of copper and selenium at room temperature forming an amorphous intermediate for individual elemental layer thicknesses of at least 20 Å. The other relevant binary system, copper–molybdenum, was not observed to intermix for layer thicknesses greater than approximately 20 Å, and thinner samples resulted in the formation of a metastable copper–molybdenum alloy.[24]

For the targeted stoichiometry, $Cu_2Mo_6Se_8$, the expected limiting critical thickness based on the binary studies should be the molybdenum layers. Consistent with this, molybdenum layer thicknesses 12 Å or greater resulted in the formation of interfacial $MoSe_2$ while samples with molybdenum thickness less than 12 Å avoided the formation of interfacial $MoSe_2$. This result suggests that by determining the critical layer thicknesses in binary systems it will be possible to rationally prepare amorphous, ternary reaction intermediates.

While superlattices offer significant advantages as precursors to extended compounds, preparing the initial superlattices is challenging. A major difficulty is the lack of technology capable of controlling layer thicknesses on a single angstrom scale. In this paper, the targeted copper thickness were as thin as 2 Å, so a 1-Å error in layer thicknesses results in a 50% stoichiometry error. In our thin samples, we have found weak diffraction signals due to a second phase with large d-spacings. Our samples may contain larger condensed cluster units as were found in the previously studied indium and alkali metal–molybdenum–selenium systems.[22] This impurity phase was never observed in thick samples and no literature reports were found of copper–molybdenum–selenium compounds containing larger condensed clusters. This suggests that avoiding stable binary compounds is necessary in order to access these phases in the copper–molybdenum–selenium system. Attempts to prepare these secondary phases as the major product by systematically varying the stoichiometry of the initial ternary superlattice are underway.

Conclusion

Superlattices are unique solid-state reactants permitting control of composition on an angstrom length scale. Due to the short diffusion distances, the initial composites can interdiffuse at relatively low temperatures (several hundred degrees Centrigrade) in relatively short times (hours). These reaction conditions can avoid interfacial nucleation of binary compounds in the reacting superlattice. The results presented here demonstrate that layer thicknesses within a superlattice can be used to control intermediates in a solid-state reaction. This suggests that superlattices could be used to kinetically trap ternary compounds which are thermodynamically unstable with respect to binary compounds. This work also suggests a rational design strategy, based on previously determined critical thicknesses from binary systems, can be used to prepare ternary composites which evolve into amorphous reaction intermediates. The development of such a synthetic methodology would result in a dramatic change in how solid-state chemists approach synthetic problems. Kinetic control would permit a strategic approach to the synthesis of complex extended compounds in much the same way as molecular chemists approach complex molecular compounds, targeting both stoichiometry and structure.

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(24) Fister, L. Unpublished results.