

Extension of Multilayer Precursor Synthesis to the Ternary $\text{In}_x\text{Nb}_3\text{Se}_4$ System

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A series of elemental multilayer films was prepared with an overall composition of $\text{In}_x\text{Nb}_3\text{Se}_4$ with $x = 0-5$. The indium-containing samples were found to undergo a solid-state amorphization reaction before crystallization while the Nb_3Se_4 crystallized heterogeneously at the reacting niobium-selenium interfaces. The crystallization of Nb_3Se_4 from the amorphous samples is studied as a function of indium composition. © 1995 Academic Press, Inc.

INTRODUCTION

The multilayer precursor technique promises to be the first general technique in solid state synthesis which provides kinetic control of products (1). In this method, thin elemental multilayers are annealed at low temperatures to allow the elements to interdiffuse. If the layers are thin enough, it is possible to completely mix the elements before any crystalline compounds can nucleate or grow (2). It has been demonstrated in at least one system that this amorphous intermediate is kinetically stable (3); the nucleation of crystalline compounds at higher temperatures determines the final product and control of the nucleation is the source of kinetic control in this method. This allows the synthesis of metastable compounds because other, more stable compounds are never crystallized (4).

This method depends on the ability to prepare a kinetically stable amorphous alloy of the desired elements at a specific composition. It is therefore necessary to understand this solid-state amorphization reaction. On a simple level, it can be understood as a competition between interdiffusion of the elements and nucleation of compounds in the interfacial regions. The large stress, high defect density, and compositional variations in the interfacial regions cause nucleation barriers to be lower than in the uniform material. If the interfaces can be annealed away before nucleation can occur, then the nucleation will become less likely and a stable amorphous phase can be formed. Therefore, if interfacial nucleation can be inhibited and diffusion enhanced, the amorphization reaction will be favored. From this it is clear that the initial layer

thickness of the multilayer will play an important role. As the layer thickness is decreased, diffusion distances become smaller, favoring amorphization over crystallization.

Both interfacial nucleation and diffusion become complicated processes in ternary systems. It is not possible to predict the critical layer thickness where the amorphization will occur. An experimental approach to this problem is to study the component binary systems in the hope that conditions can be found where each of the binary systems forms a stable amorphous phase (5). Then one might expect that the amorphization reaction will also occur in the ternary systems.

In this paper, we report on experiments in which we compare results from the binary niobium-selenium system to the ternary indium-niobium-selenium system. This system was chosen in the hope of producing a niobium analog to the Chevrel phases. The Chevrel phases contain octahedra of molybdenum with face-capping chalcogens to form a Mo_6X_8 cluster. The third element (indium in this case) sits between clusters and supplies electrons to stabilize the cluster bonding. This unusual bonding, with strong bonding within each cluster and weak interaction between clusters, gives these compounds a number of interesting properties (6). In the process of studying this system, we discovered some surprising reactivity in a series of samples with compositions of $\text{In}_x\text{Nb}_3\text{Se}_4$, where $x = 0-5$.

EXPERIMENTAL

Sample Preparation

A custom-built ultrahigh vacuum chamber with independently controlled deposition sources was used to prepare multilayer films (7). Niobium and indium were deposited at a rate of $0.5 \text{ \AA}/\text{sec}$ from independent electron beam evaporators. The deposition rate was controlled by a quartz crystal thickness monitor. Selenium was deposited from a Knudsen source at a rate of $0.3-0.7 \text{ \AA}/\text{sec}$ as monitored by a separate thickness monitor. Accumulation

of an elemental layer was allowed to proceed until the desired thickness had been achieved (to the nearest angstrom). A shutter was then closed over the source and the substrate was repositioned over the next source for deposition of the next layer. The multilayer repeat distance for all samples was on the order of 20 Å. A series of samples was prepared where the niobium:selenium molar ratio was held at 3:4 and the indium concentration was varied.

Films were deposited on poly(methylmethacrylate) (PMMA) coated silicon wafers. A piece of each wafer was broken off and used for low angle X-ray diffraction studies. The remainder of the sample was removed from the wafer by dissolving the PMMA in acetone and filtering the sample out of the resulting suspension. Typical samples had a mass of approximately 2 mg.

Determination of Stoichiometry

A series of binary Nb–Se and In–Se samples was prepared with varying metal–selenium layer thickness ratios. The stoichiometry of each of these samples was determined by thermal–gravimetric mass change on oxidation and loss of selenium. A calibration curve was constructed which allowed the determination of layer thickness values required to obtain a given stoichiometry (to within 5%). Ternary samples were prepared using this calibration curve.

Differential Scanning Calorimetry

The evolution of the samples as they were subjected to elevated temperatures was monitored by DSC using a TA Instruments TA9000 calorimeter fitted with a 910DSC cell. Approximately 1 mg of sample was used for each experiment. Samples were heated from ambient temperature to 600°C at a rate of 10°C/min under flowing nitrogen and then allowed to cool to room temperature. Without disturbing the sample, this cycle was repeated two more times. The heat flow associated with irreversible changes in the sample was found by subtracting the data for the third heating from those of the first. A measure of the repeatability of the experiment and the degree to which any irreversible changes had gone to completion during the first heating was found by subtracting the data for the third heating from those of the second.

X-Ray Diffraction

The low-angle diffraction resulting from the periodic layered structure of the as-deposited multilayer films was used to determine modulation thicknesses. These data were collected on a Scintag XDS 2000 theta–theta diffractometer with a sample stage modified to allow rapid and precise alignment (8). High-angle diffraction data were used to determine whether the as-deposited or subse-

quently annealed samples contained crystalline elements or compounds.

RESULTS

In the binary Nb_3Se_4 , the scanning calorimetry data show no sharp exotherms; only a broad, slow release of heat, as shown in Fig. 1a. This is typical of the interfacial growth of a crystalline phase rather than the formation of a kinetically stable amorphous phase and subsequent crystallization. High-angle X-ray diffraction confirms this conclusion. Figure 2 shows the high-angle diffraction from the same sample after the calorimetry experiment, and then after a 6-h annealing at 600°C. While the sample is nearly amorphous to X-rays after the first heating, the beginnings of Nb_3Se_4 crystallites can be seen. After the 6-h annealing, the Nb_3Se_4 diffraction pattern is clearer. A second crystalline phase is present. This second phase is probably an extremely niobium-rich $\text{Nb}_{1+x}\text{Se}_2$ but it cannot be conclusively identified.

In contrast, the ternary samples, despite having slightly larger layer thicknesses (20 Å as opposed to 16 Å), all

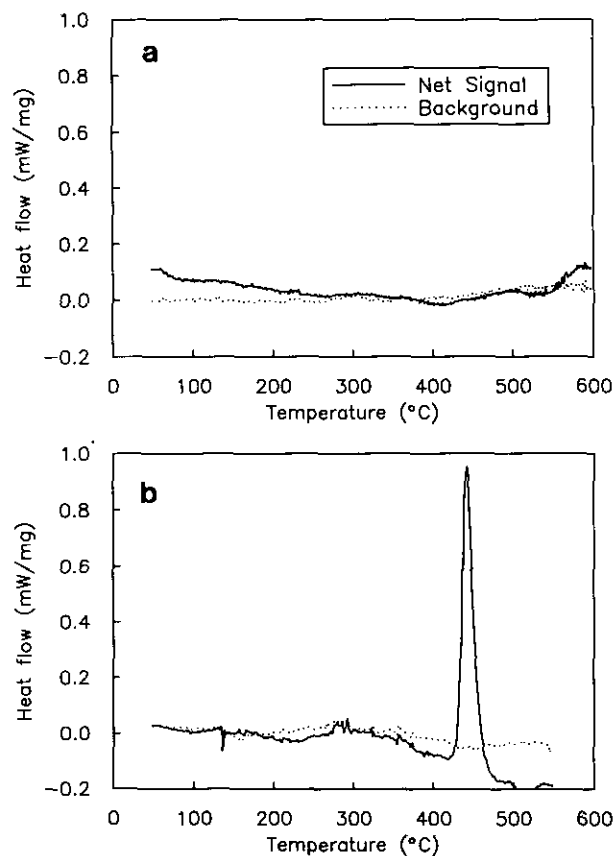


FIG. 1. Differential scanning calorimetry data from binary Nb_3Se_4 (a) and ternary InNb_3Se_4 (b) multilayers. The binary shows no sharp crystallization exotherm as in the ternary.

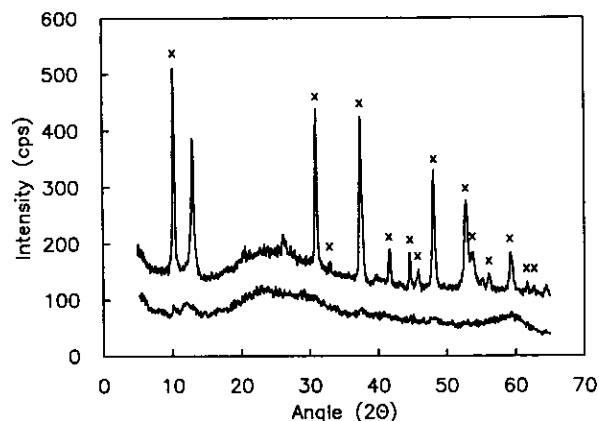


FIG. 2. X-ray diffraction of the binary sample after the calorimetry experiment shown in Fig. 1a (lower curve) and after 6-hr annealing at 600°C (upper curve). Nb_3Se_4 peaks are marked. Upper curve is offset for clarity.

show a sharp, exothermic crystallization between 400 and 450°C. This rapid crystallization is characteristic of crystallization from an amorphous intermediate as opposed to the slow, diffusion-limited crystallization after nucleation at multilayer interfaces (3). The calorimetry data for a sample with an average composition of InNb_3Se_4 are shown in Fig. 1b. After heating to temperatures below the exotherm, X-ray data indicate traces of elemental indium but no crystalline niobium- or selenium-containing compounds. After heating to 550°C, X-ray data, shown in Fig. 3, indicate that only the binary compound Nb_3Se_4 has crystallized. There were no indications of any ternary compounds or of the unidentified phase which formed in the binary samples.

The crystallization temperature for a series of five samples was found to depend on the amount of indium. The

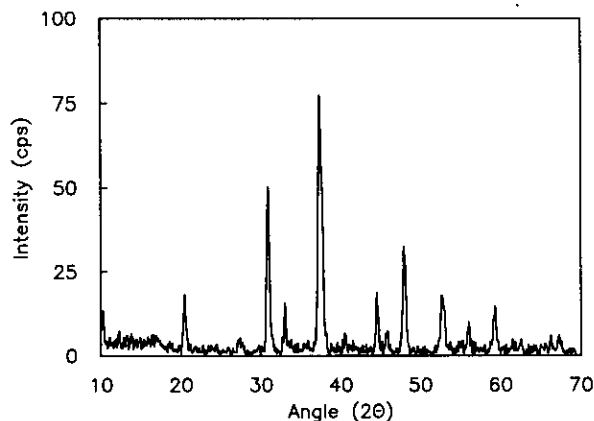


FIG. 3. X-ray diffraction of ternary sample after the calorimetry experiment shown in Fig. 1b. All peaks correspond to Nb_3Se_4 , with preferred orientation.

temperature of crystallization is an indicator of the kinetic barrier to crystallization. While the barrier height cannot be measured from these data, trends in the nucleation energetics can be determined from the variation of crystallization temperature with indium concentration. These data are shown in Fig. 4. There is a minimum in the crystallization temperature at a concentration of 2–3 mole of indium per mole of Nb_3Se_4 .

DISCUSSION

The binary Nb_3Se_4 did not form an amorphous intermediate despite reduction of the multilayer layer thickness to as small as 16 Å. This can be compared to multilayers with a composition of Nb_5Se_4 . These multilayers have a critical layer thickness of 60 Å, below which the amorphous intermediate forms (3). The indium-containing samples, which all have layer thicknesses near 20 Å, do become amorphous. This is a surprising but fortuitous result; the amorphization reaction is easier in the ternary system than in the component binaries. The indium diffuses rapidly through the adjacent selenium layer (indium–selenium binary multilayers interdiffuse at room temperature and lose their layering within a few days). Therefore, in the ternary samples, indium will have diffused to the niobium–selenium interface well before Nb_3Se_4 can nucleate at that interface.

There are a number of mechanisms by which the indium, once present, can inhibit interfacial Nb_3Se_4 nucleation. One is by simply diluting the selenium. This will change the composition profile at the niobium–selenium interface, which will change the nucleation energetics. It is also possible that the indium increases the diffusion rates of either niobium or selenium. Increased diffusion rates facilitate formation of the alloy. It can also inhibit

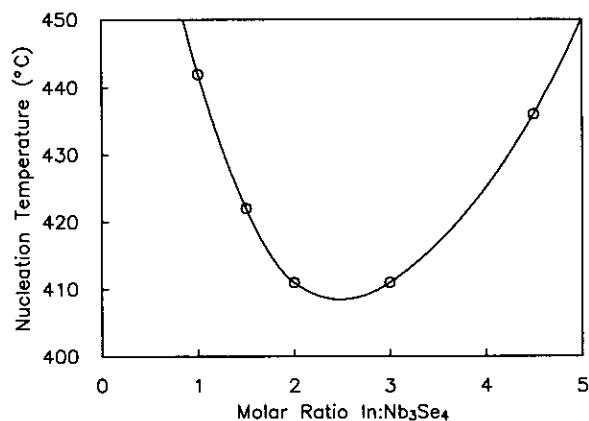


FIG. 4. Crystallization temperature as a function of indium concentration. The line is smooth curve through the data to provide a visual guide.

interfacial nucleation by reducing internal stress and lowering the defect density at the interface.

The composition dependence of the Nb_3Se_4 nucleation from the ternary alloy shows a minimum at an indium concentration of 2–3 mole per mole of Nb_3Se_4 . The increase in the nucleation temperature at high indium concentrations is readily understood as a statistical effect. In order for nucleation to occur, thermal composition fluctuations must produce a critical nucleus of pure Nb_3Se_4 . As niobium and selenium become more dilute, this becomes less probable, therefore increasing the activation energy for nucleation.

The enhancement of nucleation by indium at low indium concentrations is a more surprising result. The above arguments suggest that the activation energy for nucleation should be a monotonically increasing function of the indium concentration. The results suggest that the indium is increasing the diffusion rates of the niobium or selenium, and therefore increasing the attempt frequency for nucleation. The competition between these two effects produces the observed minimum in the nucleation temperature. In this system, indium acts as a solid-state flux, enhancing the diffusion of the niobium and selenium reactants. Note that while these reactions occur above the melting point of indium, small amounts of selenium in indium raise the melting point of indium to well above 500°C, so these reactions occur in the solid state. No melting endotherms were observed in the calorimetry experiments.

CONCLUSION

In conventional high-temperature synthesis the reaction occurs at the interfaces of bulk pieces of the elements. As the reaction proceeds, all of the possible compounds in the phase diagram will form. After extended heating, the thermodynamic products will be produced. The reaction of the binary Nb_3Se_4 follows a similar pathway: the

reaction occurs at the layer interfaces and multiple phases are formed (in this case, at least two). In contrast, the ternary $\text{In}_x\text{Nb}_3\text{Se}_4$ first forms an amorphous intermediate phase and the nucleation determines which crystalline phase forms.

We have shown that the composition can be used to adjust the nucleation kinetics but were not able to form compounds other than Nb_3Se_4 . However, since the amorphization reaction was successful, other methods of controlling nucleation can still be attempted. One approach could be to deposit the multilayer directly on a crystalline substrate which has specific lattice constants. This would favor formation of phases with similar lattice parameters in the same way as it does in heteroepitaxy. Another approach is to seed the multilayer with a few layers of elements which are known to form a compound which is isostructural to the desired compound. Since $\text{Cu}_x\text{Mo}_6\text{Se}_8$ can be synthesized from multilayers, we are currently attempting to perform such a seeding experiment.

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REFERENCES

1. T. Novet and D. C. Johnson, *J. Am. Chem. Soc.* **113**, 3398 (1991).
2. R. B. Schwarz and W. L. Johnson, *Phys. Rev. Lett.* **51**(5), 415 (1983).
3. M. Fukuto, M. D. Hornbostel, and D. C. Johnson, *J. Am. Chem. Soc.* **116**, 9136 (1994).
4. L. Fister and D. C. Johnson, *J. Am. Chem. Soc.* **114**, 4639 (1992).
5. L. Fister, D. C. Johnson, and R. Brown, *J. Am. Chem. Soc.* **116**, 629 (1994).
6. R. Chevrel, P. Gougeon, M. Potel, and M. Sergent, *J. Solid State Chem.* **57**, 25 (1985).
7. L. Fister, Xiao-Mei Li, J. McConnell, T. Novet, and D. C. Johnson, *J. Vacuum Sci. Technol. A* **11**(6), 3014 (1993).
8. T. Novet, J. M. McConnell, and D. C. Johnson, *Chem. Mater.* **4**, 473 (1992).