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On phase relations in the system As_2Se_3–Sb_2Se_3

Preliminary X-ray diffraction analysis of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 materials showed evidence of terminal solid solubility. However, results of an investigation on the phase relation in this system, subsequently published by Berkes and Myers [1], showed no solid solubility between As_2Se_3 and Sb_2Se_3. In view of the disparity between our findings and those of Berkes and Myers it seems necessary to further clarify the controversy. This investigation was performed by X-ray diffraction and liquid metal solution calorimetry with specimens of crystalline As_2Se_3–Sb_2Se_3, in the range of 0 to 0.5 g atomic fraction of Sb_2Se_3. The calorimetric results on the heats of formation of these alloys are also of interest. It was not our intention to prove or disprove Berkes and Myers' findings, but to assemble data needed for interpreting electrical, optical and crystallization characteristics of these materials [2–5].

Amorphous specimens of $(1-x)As_2Se_3$–xSb_2Se_3 ($x = 0.05$, 0.10, 0.20, 0.30, 0.40, 0.45, 0.50) were prepared from As_2Se_3 and Sb_2Se_3, which were initially prepared from high purity As, Sb and Se (99.999 + %). For each of the As_2Se_3 and Sb_2Se_3 compounds, nominally stoichiometric amounts were placed in a quartz ampoule which was repeatedly evacuated, flushed with argon, and finally evacuated to 10^{-6} Torr before sealing. Each sealed ampoule was heated for about 5 h at 623 K, whereupon the temperature was raised to 1023 K and maintained for about 5 h. The resulting As_2Se_3 and Sb_2Se_3 were in turn placed, in the desired proportions, in a quartz ampoule, which was again flushed, evacuated and sealed. To ensure vigorous mixing the ampoule with the molten material was rotated by a motor shaft while in the furnace (125 rpm). The ampoule was held at 1023 K for 1 h, then withdrawn from the furnace and quenched in air while still in rotation. This technique, described in more detail elsewhere [6], allows the preparation of homogeneous materials. Electron micro-probe analysis revealed no detectable variation in chemical composition and confirmed the stoichiometry of the prepared materials. The amorphous state of these alloys was confirmed by standard metallographic and X-ray diffraction techniques.

Crystalline samples were prepared by annealing amorphous materials in sealed, evacuated, vycor-capsules for 40 h at 400 K, followed by annealing for 80 h at 523 K. Under such conditions these amorphous materials are entirely crystallized within a few hours. However, to approach closer to thermodynamic equilibrium, a much longer annealing time was employed. During annealing, special precautions were taken to avoid any temperature gradient in the specimen tube. This eliminated the possibility of phase separation by vapour transport, due to the vapour pressure difference between As_2Se_3 and Sb_2Se_3. In addition, because the ampoules were small in size and were sealed, the specimens retained identical overall chemical composition before and after annealing. Standard metallographic and X-ray diffraction techniques did not reveal the existance of amorphous phase in the annealed materials.

The heats of formation of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 based on crystalline As_2Se_3 and Sb_2Se_3 were measured by liquid metal solution calorimetry with bismuth as solvent. The calorimetric procedure and the method of calculation have been described by Bever et al. [7] elsewhere. The specimens were added from 273 K to the bath at 623 K. Successive additions consisted of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 samples and corresponding mechanical

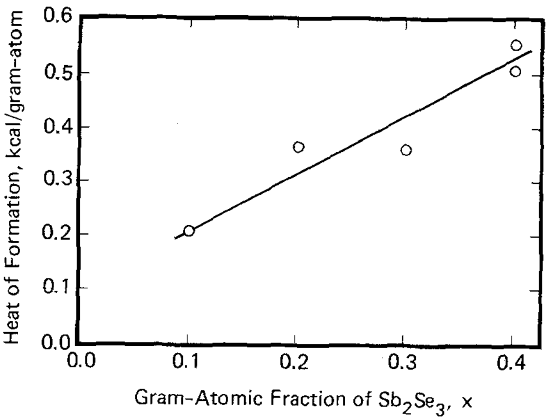

Figure 1 Composition dependence of the heat of formation of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 at 273 K, based on crystalline As_2Se_3 and Sb_2Se_3.

mixtures of crystalline As_2Se_3 and Sb_2Se_3. The calorimeter was calibrated with bismuth; a value of 4.96 kcal g-atom^{-1} was taken as the difference between the heat contents of bismuth at 273 and 623 K [8]. Heat effects associated with the additions of the specimens were determined and plotted against the atom fraction of Se in the bath before and after the respective addition.

The heat of formation of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 at 273 K was the difference between the heat effects of the additions of this material and the corresponding mechanical mixture of crystalline As_2Se_3 and Sb_2Se_3. Fig. 1 shows the heat of formation of crystalline $(1-x)As_2Se_3xSb_2Se_3$ materials, which had been annealed at 523° K, as a function of x. The heat of formation is positive in the range $x = 0$ to 0.4, and increases with increasing Sb_2Se_3 content.

For X-ray diffraction measurements, ground crystalline material was mixed with a 75% solution of collodion in alcohol, spread on a microscope slide and dried. The specimens were scanned from $2\theta = 70$ to 8° in an X-ray diffractometer with Cu$K\alpha$ radiation at 34 kV and 14 mA and at a speed of 0.2° min^{-1}. The crystallographic structures of the phases present in crystalline $(1-x)As_2Se_3$–xSb_2Se_3 materials were identified by comparison of their X-ray diffraction patterns with those of As_2Se_3 (monoclinic) and Sb_2Se_3 (orthorhombic). Although there was considerable overlap of prominent peaks of As_2Se_3 and Sb_2Se_3, a few peaks occurred at different positions and could be used for the identification of phases present in the crystalline $(1-x)As_2Se_3$–xSb_2Se_3. The characteristic peaks used were at $2\theta = 18.00°$ for As_2Se_3 and at $2\theta = 16.85°$ for Sb_2Se_3.

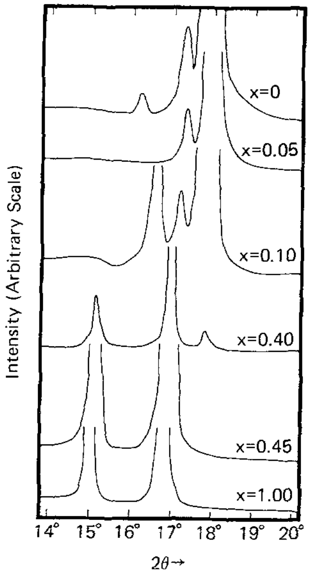

Figure 2 X-ray diffraction patterns for crystalline specimens of $(1-x)As_2Se_3$–xSb_2Se_3.

Fig. 2 shows the X-ray diffraction patterns of $(1-x)As_2Se_3$–xSb_2Se_3 for $x = 0.05$, 0.10, 0.40 and 0.45 as well as patterns for As_2Se_3 and Sb_2Se_3. At $x = 0.05$ the X-ray pattern shows only the peaks for As_2Se_3 with a slight shift in position. At $x = 0.1$ the material consists mostly of a phase with the As_2Se_3 structure, but a small amount of a second phase with the Sb_2Se_3 structure is also present. When x increases from 0.1 to 0.4, the fraction of the phase with the Sb_2Se_3 structure also increases. At $x = 0.45$ the peaks characteristic of As_2Se_3 are completely absent. This indicates that at 523 K the phase boundary on the As_2Se_3 side occurs at a composition between $x = 0.05$ and 0.1, and on the Sb_2Se_3 side between $x = 0.40$ and 0.45.

The phase diagram of the system As_2Se_3–Sb_2Se_3 published by Berkes and Myers [1] shows a eutectic composition at approximately 0.14 g-atomic fraction of Sb_2Se_3 ($x = 0.14$) and a temperature of 636 ± 5 K. Their diagram does not show any mutual solubility between solid As_2Se_3 and Sb_2Se_3. In contrast to this, the X-ray diffraction results of the present investigation indicate solid solubility between As_2Se_3 and

Sb_2Se_3. The solubility limit of Sb_2Se_3 in As_2Se_3 at 523 K lies between 0.05 and 0.10 g-atomic fraction of Sb_2Se_3. At the Sb_2Se_3-rich side of the phase diagram the solubility limit is 0.55 to 0.60 g-atomic fraction of As_2Se_3 in Sb_2Se_3.

The positive heat of formation of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 at 273 K suggests that the bonding in these alloys is weaker than the bonding in the individual compounds of As_2Se_3 and Sb_2Se_3. In such cases, the entropy-temperature product in the expression $\Delta G = \Delta H - T\Delta S$ must be large enough to yield a negative value for the free energy of formation and make the material stable with respect to its components at higher temperatures. For example, Jena *et al.* [9] obtained positive heats of formation for the compound In_3SbTe_2 from InSb and InTe. They investigated the effects of temperature on the free energy and heat of formation and concluded that a phase having weaker bonding may, in general, be expected to be unstable at lower temperature and stable at higher temperature. In the present investigation, the effect of temperature was not investigated explicitly. The specimens, however, were prepared by annealing at a high temperature and cooling rapidly to room temperature. Even if these materials were metastable at room temperature, it is not likely that they would decompose into their components at this temperature because of an insufficiently fast rate of diffusion. Positive heats of formation have been observed in other chalcogenide systems, for example, in Se–Te alloys near 20 at.% Te [10].

The presence of solid solubility in the As_2Se_3–Sb_2Se_3 phase diagram demonstrated by the X-ray results is further supported by the values of the heats of formation obtained by liquid metal solution calorimetry. If there were no solid solubility, the only difference in the enthalpy between crystalline $(1-x)As_2Se_3$–xSb_2Se_3 and the corresponding mechanical mixture of crystalline As_2Se_3 and Sb_2Se_3 would be due to morphological differences. The effect of such morphological differences on the enthalpy should be negligible; so the heats of formation of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 with reference to crystalline As_2Se_3 and Sb_2Se_3 would be close to zero. In this investigation, however, appreciable heats of formation were measured and they increased with Sb_2Se_3 content.

Since the disagreement between the results of this investigation and that of the phase diagram of As_2Se_3–Sb_2Se_3 [1], the details of the phase diagram below the eutectic temperature should be re-examined.

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