Critical Examination of Ga$_2$Se$_3$ Phase Equilibria

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The Ga$_2$Se$_3$ phase equilibria were examined by DTA, X-ray diffractometry, visual observation, and isothermal crystal growth to resolve discrepancies in the reported binary phase diagrams. The Se-rich solid solubility extends to less than 60.5 at.% Se. There is no peritectic transformation at 880°C, nor is there a liquid immiscibility from 75 to 85 at.% Se. The rate of crystal growth influences the incorporation of lattice defects and thus determines which polymorphic form of Ga$_2$Se$_3$ crystallizes from the melt. The preferred liquidus curve from 60 to 100 at.% Se is presented and compared to those reported in the literature.

Introduction

The Ga–Se binary phase has been reported by Rustamov *et al.* (RBL) (*1*), Suzuki and Mori (SM) (*2*), and most recently in this journal by Ollitrault-Fichet *et al.* (ORF) (*3*). All agree on several features: (1) the layered compound GaSe melts at ~930°C and has a narrow homogeneity range; (2) two-liquid immiscibility exists between Ga and GaSe (~5–18 at.% Se, although the range is somewhat disputed) and a monotectic temperature of ~920°C; (3) Ga$_2$Se$_3$ melts at ~1010°C; and (4) the liquidus curves from 0 to 65 at.% Se are comparable, including agreement on the GaSe–Ga$_2$Se$_3$ eutectic temperature of ~880°C. There are also some disagreements. Only RBL observed the compound Ga$_2$Se, whereas the other two investigations found this composition to be a mixture of Ga and GaSe. ORF reported a two-liquid immiscibility from 75–85 at.% Se and a monotectic temperature of 770°C; RBL reported a nearly isothermal liquidus "plateau" at nearly the same temperatures, but

SM reported liquidus temperatures as much as 100°C higher. ORF also reported the peritectic decomposition at 880°C of the Se-rich metastable phase of Ga$_2$Se$_3$(ss) (~65 at.% Se), a much wider homogeneity range than reported by Palatnik and Belova (PB) (*4*). This paper addresses the two controversial points raised by ORF: (1) the existence of the Se-rich liquid immiscibility, and (2) the confusing phase equilibria involving the Se-rich Ga$_2$Se$_3$ solid solution.

It should be stated from the outset that the phase diagram of ORF is incorrect in principle since the monotectic transition was not represented by an isotherm which *extended* to the Ga$_2$Se$_3$(ss) phase boundary. Since this L$_1$ − L$_2$ + Ga$_2$Se$_3$ transition would precipitate (dissolve) solid Ga$_2$Se$_3$ on cooling (heating) regardless of the initial starting compositions, there should have been observable DTA thermal arrests at the monotectic temperature for total compositions of 65–75 at.% Se. However, no DTA arrests would have been observed in this (*T, x*) region if the Ga$_2$Se$_3$(ss) boundary extended to the liquidus at the monotectic

temperature, a condition neither indicated by ORF nor observed in this study.

Sample Preparation and Characterization

Two- to five-gram samples were synthesized from the high-purity elements (Ga, 5 9's from Alusuisse; Se, 5 9's from Asarco) although this degree of purity is probably not essential to the phase equilibria. Safe reaction from the elements can be performed in a two-zone furnace, in which the Se is maintained at a lower "reservoir" temperature of ~550–600°C while it reacts with the Ga-rich melt, preferably held above all liquidus temperatures of ~1020°C. As indicated by ORF and PB, the thermal treatments, and especially their sequence, are very critical to the determination of Ga_2Se_3 phase equilibria. Therefore, we made most of our observations on solids isothermally prepared by distilling Se from homogeneous liquids, thereby avoiding the need for solid phase reactions during slow-cooled preparations. The distillation also used a two-zone furnace, one zone in which the solid would isothermally crystallize from the solution, and the other which was lowered to slightly below the condensation (dew point) temperature for the respective liquidus composition (5). Stoichiometric α- and γ-Ga_2Se_3 was dissolved and recrystallized, and the composition of the solid was gravimetrically compared to that of the starting material.

Visual observation in a transparent furnace allowed the detection of liquid + solid coexistence at known total composition (including the vapor phase). Liquidus points were also determined by solubility measurements, in which the liquid in equilibrium with a Ga_2Se_3 crystalline ingot was decanted and the weight loss of the solid was then used to calculate the liquidus composition. These compositions represent the Ga-rich limits since mass transport in the liquid would over-estimate the actual amount of solid dissolved. Differential thermal analysis (DTA) was performed in an apparatus described previously (6). In addition to taking the precaution expressed by ORF of minimizing the free volume in the DTA ampoule to maintain the Se-content of the condensed phase, it is also important to control the temperature gradient imposed on the condensed phase, especially when molten, to minimize induced composition gradients.

Polycrystalline samples were characterized by X-ray powder diffraction using a GE XRD-6 diffractometer with CuKα radiation, and the d spacings were compared to the reported X-ray characterization of the Ga_2Se_3 polymorphs found in Refs. (3) and (4), which can be summarized as follows. The two nominally stoichiometric polymorphs, designated β and γ, are monoclinic (space group Bb and $a = b = 6.66$ Å, $c = 11.65$ Å, $\gamma = 108.12°$) and cubic zincblende (space group $F\bar{4}3m$ and $a_0 = 5.462$ Å), respectively. Both structures contain vacancies on $\frac{1}{3}$ of the Ga sites; in γ they are randomly distributed, but in β they are ordered uniaxally along the pseudocubic (111) direction. The α form is related to γ except that crystal defects, proposed by PB to be stacking faults, produce the following X-ray pattern anomaly: the all-even integer diffraction peaks are sharp and correspond to $a_0 = 5.422$ Å, and the all-odd peaks are substantially broadened and correspond to $a_0 \sim 5.45$ Å. ($F\bar{4}3m$ does not allow mixed integer diffraction peaks.)

Phase Diagram Results

The DTA results will be discussed first, and, with solubility measurements, will be used to construct the liquidus curve. It will be argued that there is neither a peritectic reaction at 880°C nor a monotectic transition at 770°C. The Ga_2Se_3 polymorphic equilibria will then be characterized by X-

ray analysis of solid phases prepared under a variety of conditions.

Representative DTA heating and cooling scans for 60–90 at.% Se are shown in Fig. 1. There are several points to be considered from these data. In general, the last-to-melt temperature, defined as the beginning of rapid return of ΔT to the baseline, coincides with the first-to-freeze temperature, defined as the onset of the exothermic reaction in the cooling curve. These temperatures correspond to the liquidus curve; they are plotted in Fig. 2 with values from other sources. All the DTA liquidus results are generally consistent from 60–70 at.% Se; however, there is less agreement from 70–100 at.% Se. We noticed that repeated DTA melting and freezing resulted in progressively higher apparent liquidus temperatures. If the sample was removed from the DTA ampoule, powdered, and rerun, the initial results were repeated. Furthermore, if the samples were held overnight at
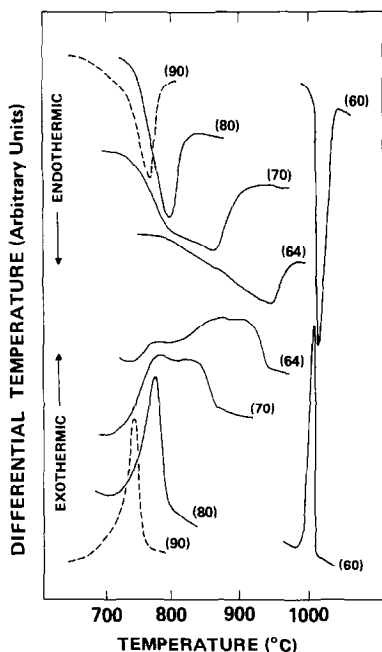

FIG. 2. Ga–Se phase diagram from 50 to 100 at.% Se. This study: (▲) DTA, (■) solubility; Other data: (●) Strauss (unpublished), (○) RBL (Ref. (1)), (▽) ORF (Ref. (3)), (□) PB (Ref. (4)).

least 100°C above the liquidus temperature, this effect was minimized, but not eliminated. We suggest that this behavior is due to composition gradients in the DTA melts resulting from the unavoidable thermal gradients in the DTA furnace, and that it may be responsible for the anomalously high liquidus temperatues reported by SM. Since the density–temperature–composition data are unavailable for this system, this hypothesis cannot be confirmed at present. We also noticed that faster cooling rates did produce more pronounced "second" peaks in some of the scans; this may have been a source of confusion to ORF. We have carefully selected our DTA results presented in Fig. 2. Furthermore, since there may have been some supercooling of 85–95 at.% Se samples during thermal analysis, we have drawn the liquidus curve through the solubility data at the Se-rich region of the diagram. We note

FIG. 1. Typical DTA curves for 60, 64, 70, 80, and 90 at.% Se alloys.

that the solubility of Ga in liquid Se is comparable to that of other metals, such as Zn (see Hansen or Elliot (7) for typical binary diagrams). The liquidus curve is also consistent with unpublished dew point vapor pressure measurements for 60–100 at.% Se (5).

The heating and cooling curves of samples with compositions 62–65 at.% Se exhibit broad arrests with no distinct peak at 880°C indicative of a peritectic reaction or other phase transition. Note that there is a "second peak" in the exotherm for the 64 and 70 at.% Se samples at approximately 800°C, which is the temperature of the arrests for the 80 at.% sample. This behavior is just that expected from the shape of the liquidus curve shown in Fig. 2. The rapid change in liquidus composition (~70–90 at.% Se) in the temperature interval 760–820°C requires a larger fraction of solid to be dissolved (precipitated) during heating (cooling) through this temperature interval than for similar adjacent intervals. However, this effect does not require a monotectic reaction. The smooth decrease in liquidus temperature from 70 to 90 at.% Se and the absence of a DTA arrest at 770°C for samples containing 65–75 at.% Se lead us to conclude that a monotectic does not occur in this region.

Since ORF reported metallographic analysis of a quenched 80 at.% Se liquid as evidence for liquid immiscibility, we repeated that experiment in a 1-mm diameter, 10-cm-long, capillary ampoule to minimize diffusion during the rapid cooling. Ga$_2$Se$_3$ crystals were uniformly distributed over the length of the ingot, having been nucleated at the circumference, which cooled first. A similar experiment performed on Cu–Se of a similar composition clearly produced two distinct vertical zones on quenching (8). In this latter case, the liquid immiscibility can also be easily visually observed since the two liquids have different thermal emissivities. Although ORF did not report details of their quenching, it was probably insufficiently fast to prevent segregated crystallization. Se condensation measurements of the Se vapor pressure over melts from 60 to 100 at.% Se (5) do not support a liquid immiscibility which would require a coincident set of pressure curves for temperatures and compositions inside the two-liquid field. In general, the occurrence of a two-liquid region depends on the melting point of the Se-rich binary compound and its tendency to form a Se-rich solution, i.e., a eutectic. If this portion of the liquidus curve is lowered sufficiently, it cannot join the liquidus arising from elemental Se, which will not contain enough metal in solution. For example, ZnSe has a high melting point (1515°C) and a slowly decreasing Se-rich liquidus, whereas TlSe has a low melting point (330°C) and a two-liquid immiscibility (7).

Consider next the question of the Se-rich boundary of Ga$_2$Se$_3$(ss). According to the phase diagram of ORF, a sample of 63 at.% Se, precipitated by cooling the liquid, would be in the Ga$_2$Se$_3$(ss) single phase field at ~875°C; i.e., completely solid. Visual observation indicated that such a sample is composed of two condensed phases, solid + liquid. Isothermal recrystallizations at 908, 850, 820, and 760°C confirmed that the Se-rich boundary is less than 60.5 at.% Se, in agreement with the metallographic results of PB, and the X-ray patterns indicated all solids were the α phase. These results are consistent with our DTA results, and they further disprove the existence of a peritectic decomposition of a Se-rich solid solution near 880°C.

Many of the data presented by ORF were determined on quenched samples, whereas the present results were obtained on isothermally grown samples. In order to directly compare the two sets of data, some quenching experiments were performed. Liquid compositions were chosen to produce saturation at temperatures compara-

ble to those of the isothermal growths. Above 750°C, where the α phase was obtained by isothermal crystal growth, the γ phase was obtained by quenching to room temperature. This behavior suggests that only during slow growth are the lattice defects, which characterize the α phase, able to develop. Furthermore, if an ingot of γ is partially melted and slowly frozen in contact with a γ "seed," the newly frozen material is α. We thus believe that the preference for α is not related to a lack of γ nucleation. On the contrary, the quenched samples seem to indicate that γ is the nucleating phase. Below 680°C the β phase is obtained by either fast or slow-cooled crystal growth from a Se-rich solution. However, at ~730°C the isothermal growth produces neither α nor β, but rather a cubic form with $a_0 = 5.422$ Å, which is very similar to that of α, but the all-odd integer peaks are *sharp*. Gravimetric analysis indicated the composition was close to 60 at.% Se. The liquidus composition in equilibrium with this solid is approximately 95 at.% Se and the temperature is close to the $\gamma–\beta$ transition temperature of 730°C. Under these conditions the crystal defects are either not thermodynamically stable, or are inhibited in the crystal growth process. We postulate that the X-ray results of ORF for 62 and 64 at.% Se samples, which showed pairs of all-even peaks, arose from the growth of two phases: one which formed during the initial cooling to the 750°C annealing temperature, and the other which recrystallized from a Se-rich liquid during annealing. However, they did not give sufficient detail of their processing conditions for us to successfully reproduce the experiment.

The interpolymorphic equilibria were not clearly summarized by ORF. In agreement with PB, but contrary to ORF, we found that ingots of γ can be cooled to room temperature, after transformation from β at ~800°C, without transformation to the α phase. The β to γ transition can be observed in DTA although it is somewhat sluggish, beginning at ~760°C with heating rates of 2°C/min; but β can be obtained from the same sample after melting *only* if a slight excess Se (~0.1 at.%) is distilled from the solid prior to the low-temperature annealing. This may have occurred naturally in the study of PB if the sample were placed in a new evacuated ampoule for the low-temperature annealing. Stoichiometry certainly plays an important role in the vacancy ordering, and the growth defects normally obtained from slowly solidifying a melt inhibit this ordering. Ga-rich samples will not transform to β under any conditions. It was also observed that β could be irreproducibly obtained from γ or α without *melting* in excess Se. The similarity of the X-ray patterns for the slow-cooled Ga- and Se-rich compositions suggests a similarity in the "defect" structures. If they are related to a high density of stacking faults, the homogeneity range has little influence on their stability. The difference arises in the ease of achieving nominal stoichiometry at low temperature: it is more readily achieved by Se-rich α. This explains the reason why PB observed that β could be obtained only from α which originated from a Se-rich melt. Our results indicate that the Se-rich material must be brought closer to nominal stoichiometry before β will form. The behavior of the cubic polymorphs of Ga_2Se_3 is interesting with regard to the stability of the crystal defects characteristic of the α phase. At this point the exact nature of the defects producing the broad diffraction peaks is unknown, but ORF and Khan and Ali (9) have indicated that X-ray diffraction studies are currently underway to elucidate their nature.

A comment about phase diagrams is in order here. Their accepted usage is to summarize phase equilibria in a convenient form. Thermodynamically speaking, it is unimportant whether or not the phases con-

tain crystallographic defects or deviations from stoichiometry. Our results show that the α phase is in equilibrium with Se-rich liquids above 730°C, and that β is the equilibrium phase below that temperature. Although the β to γ transformation is reversible and γ is the high-temperature phase formed by chemical vapor transport, γ does not slowly crystallize from either a stoichiometric or nonstoichiometric melt. This phenomenon is not a matter of nucleation. Rapidly quenching produces a γ-phase, even from Se-rich solutions, but further homogenization produces α. In the binary phase diagram, the solidus curve must be for α phase above 730°C, and γ must then be represented inside the solid solution field. Below 730°C the solidus curve pertains to the β phase. In chemical vapor transport experiments, the Se pressure is generally below that for the three-phase equilibrium: $Ga_2Se_3(s) + Ga\text{-}Se_{liquid}$ (>60 at.% Se) + Se vapor. Again, these conditions represent points inside the solid solution phase field, not at the Se-rich boundary. Although ORF were correct in pointing out that the γ phase, free from the crystallographic defects of α, has a simpler structure, it is not necessarily the more stable phase. In fact, unpublished DTA measurements of the relative heats of fusion of α and γ indicated that, compared to the same melt, α is more stable by about 0.2 kcal mole^{-1} (10). The α phase is metastable only in the sense that is does not transform into β when cooled below 730°C and does not transform into γ with the removal of a slight excess of Se.

Summary

The homogeneity range for Ga₂Se₃ extends to less than 60.5 at.% Se. There is neither a two-liquid region from 75 to 85 at.% Se nor a peritectic reaction involving Se-rich solution of Ga₂Se₃. However, the Se-rich liquidus curve does exhibit an unusually flat region, signifying an abrupt change in the Ga solubility and probably a change in the liquid structure as well.

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