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## Section 12. Solid state amorphization

Crystal-to-amorphous phase transformation of the Ga–Sb  
high-pressure phaseV.E. Antonov<sup>\*</sup>, O.I. Barkalov, E.G. Ponyatovsky*Institute of Solid State Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow district, Russian Federation***Abstract**

The solid-state amorphization and subsequent crystallization of the quenched 'white tin' high-pressure phase of Ga–Sb alloys containing 20–80 at.% Sb were studied at ambient pressure by differential scanning calorimetry and dilatometry. Within the experimental uncertainty, the heat of both amorphization and crystallization did not change over the homogeneity region for the 'white tin' phase (47.5–52.5 at.% Sb); the heats were exothermic and equal to  $3.5 \pm 0.5$  and  $8.3 \pm 1.0$  kJ/mol, respectively. The amorphization was accompanied by a sample volume expansion of about 25%. The processes of amorphization and crystallization involved a multistage process.

**1. Introduction**

The thermal and volume effects accompanying the solid-state amorphization of metastable high-pressure phases (HPP), heated at atmospheric pressure, have been studied for four systems, Cd–Sb [1], Zn–Sb [1], Al–Ge [2] and Ga–Sb [3]. The temperature interval for this transformation in every system was broad (a few ten Kelvin) and the shape of the calorimetric and volumetric curves was rather complicated. The latter was most surprising in the case of the Ga–Sb system where the composition, GaSb, of the metallic HPP coincided with that of the semiconducting low-pressure phase (LPP), so no problems could be expected with chemical bonding in the formation of a semiconducting amorphous phase. (The compositions of the HPP in the other systems were not stoichiometric and differed from the compositions of the stoichiometric LPP.)

One of the possible explanations for the complex character of the GaSb HPP amorphization is that the short-range order in the amorphous phase varies with temperature. If so, different stages of the amorphization process should depend on the composition of the HPP in a different manner. Recent X-ray and superconductivity measurements [4] have shown the HPP in the Ga–Sb system to have a homogeneity composition range in the vicinity of 50 at.% Sb. This paper reports the effect of the alloy composition on the heat release and volume expansion accompanying amorphization and the subsequent crystallization of the HPP in the course of heating at ambient pressure.

**2. Experiment**

Ga–Sb samples containing 20, 30, 40, 45, 47.5, 50, 52.5, 55, 60, 65, 70 and 80 at.% Sb were prepared by alloying appropriate amounts of Ga and Sb (both 99.999 wt% pure) in evacuated quartz tubes and subsequent quenching into a cold water bath. Along with the polycrystalline GaSb alloy thus ob-

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tained, a GaSb single crystal was also used. No difference between their behaviour was revealed in the subsequent experiments.

The Ga–Sb samples in the form of discs 5 mm in diameter and 1–3 mm in height were treated at 7 GPa and 520 K for 24 h in a ‘Toroid’ quasihydrostatic high-pressure chamber and cooled to liquid nitrogen temperature before the pressure was released. An X-ray analysis of the samples was performed using a DRON-2.0 diffractometer ( $\text{CuK}\alpha$  radiation) at 100 K and ambient pressure. The thermal and dilatometric analyses were carried out with a PE DSC 7 differential scanning calorimeter and PE TMA 7 thermomechanical analyzer, with a heating rate of 20 K/min. The samples were loaded into both instruments without warming above 100 K.

### 3. Results

The homogeneity region for the HPP phase in the Ga–Sb system was studied in Ref. [4] on samples produced at a pressure of 7 GPa at temperatures from 370 to 620 K for up to 72 h. It was shown that the lattice parameters of the HPP varied noticeably over the composition range from 40–45 to 55–60 at.% Sb and remained nearly constant outside this interval. At the same time, only the samples containing from 47.5 to 52.5 at.% Sb exhibited no reflections due to excess Ga or Sb in their X-ray patterns. The results from the X-ray examination of the samples in the present work were similar.

The above is indicative of the fact that either the process of HPP formation was incomplete or the cooling rate was not high enough to prevent the possible precipitation of Ga and Sb from the HPP (The  $T$ – $P$ – $c$  phase diagram for the Ga–Sb system has not been studied in detail; see Ref. [5]). Thus, the homogeneity range of the Ga–Sb HPP can only be established as being no more than 40–60 at.% Sb and no less than 47.5–52.5 at.% Sb.

With the heating rate used, the HPP was considered to transform completely into the amorphous state below 350 K, since its lines were not observed in the X-ray patterns of the samples heated to this temperature. In the case of the samples containing 47.5, 50 and 52.5 at.% Sb, no crystalline lines were present at all while the intensities of the Ga or Sb

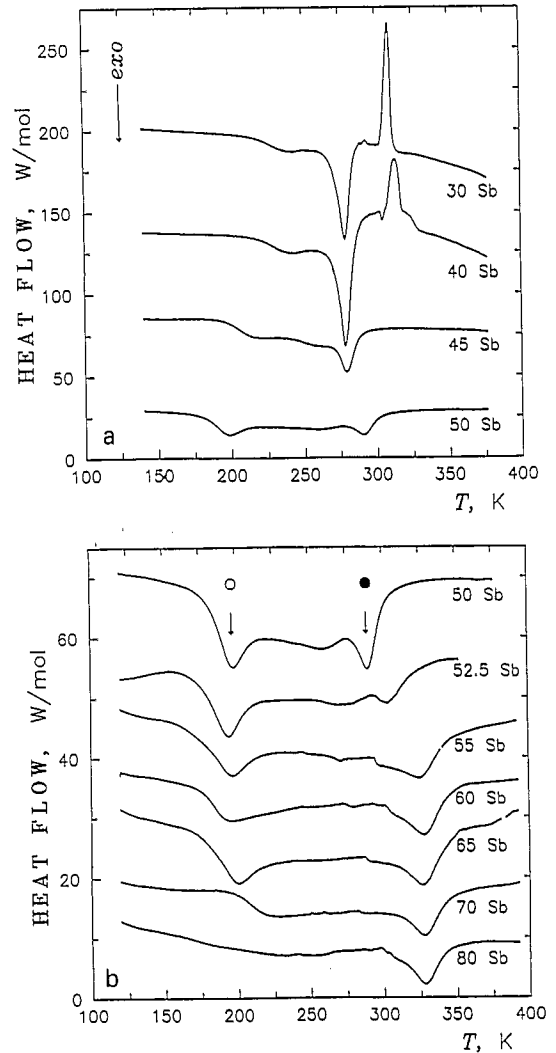


Fig. 1. Heat flow versus temperature on heating the quenched Ga–Sb high-pressure phase at 20 K/min. The arrows in Fig. 1(b) indicate the positions of the peaks shown with corresponding symbols in Fig. 5(a).

lines in the patterns of the other samples were approximately the same as those before heating.

Representative DSC traces are shown in Figs. 1(a) and (b). (The endothermic peaks positioned at approximately 310 K in the curves for the samples with 30 and 40 at.% Sb are due to the melting of the excess gallium.) The values of the integrated exothermic heat of amorphization are given in Fig. 2 and the changes in the sample volume accompanying amorphization are illustrated in Fig. 3. The corre-

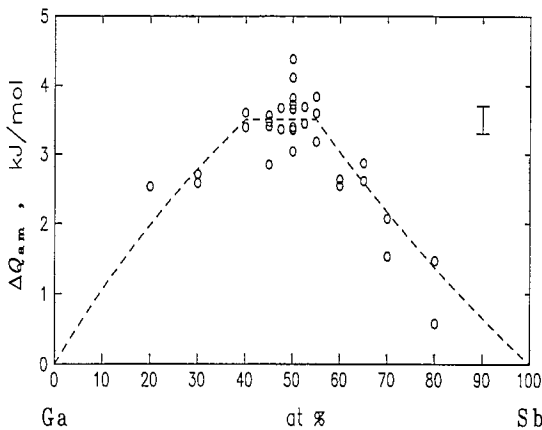


Fig. 2. Integral exothermic heat of amorphization for the Ga–Sb high-pressure phase versus the sample composition. The dashed lines are plotted under the assumption that the samples were mixtures Ga + Ga<sub>40</sub>Sb<sub>60</sub> and Ga<sub>55</sub>Sb<sub>45</sub> + Sb in the left and right two-phase regions, respectively. The bar in the upper right corner shows the uncertainty in the heat evaluation due to a large temperature interval of the transformation.

sponding temperature dependence of the first temperature derivative of the sample volume are depicted in Fig. 4 and the values of the total increase in volume caused by amorphization are presented in Fig. 5(b).

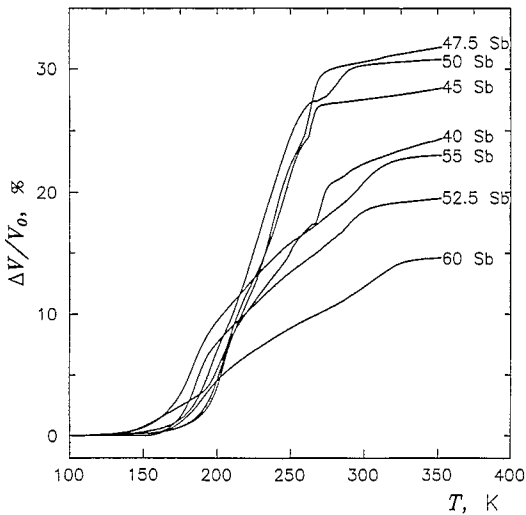


Fig. 3. Relative change in the sample volume versus temperature during the heating of the quenched Ga–Sb high-pressure phase at 20 K/min. (The volume was calculated in the isotropic approximation from the experimental temperature dependence of the sample length.)

#### 4. Discussion

As is seen from Figs. 1 and 4, the shape and positions of the peaks in the DSC and dilatometric curves are similar. For the sample of equiatomic composition, as was first shown in Ref. [3], they are nearly identical, i.e., the heat release is proportional to the volume expansion. This suggests that both effects originate from one and the same process throughout the temperature interval of amorphization.

In the case of the samples with compositions noticeably deviating from equiatomic, the curves are very different. For example, the intensity ratio of the leftmost to rightmost peak in the DSC and dilatometric curves are quite different for the sample with 40 at.% Sb. If it is assumed that the short-range order in the amorphous phase varies with temperature, this can easily be explained, since the effect of changing the alloy composition upon the heat of formation of this phase should be temperature dependent. A noticeable shift of the leftmost and rightmost peaks in the opposite directions with increasing antimony content, within the homogeneity range of the HPP (Fig. 5(a)), can also be explained in the same way.

The last phenomenon that should be mentioned is the crystallization of the amorphous Ga–Sb phase

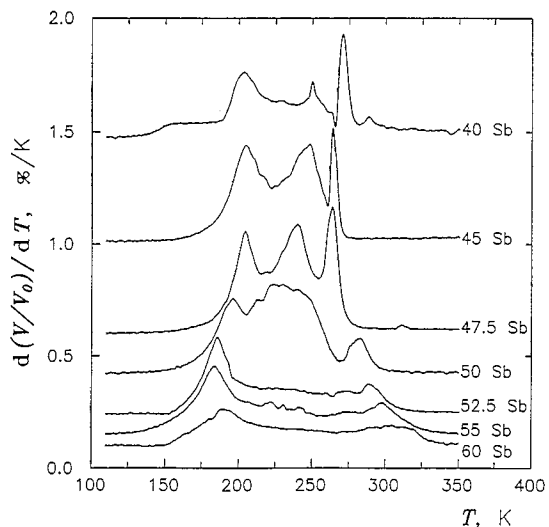


Fig. 4. First derivative with respect to the temperature of the dependence depicted in Fig. 3.

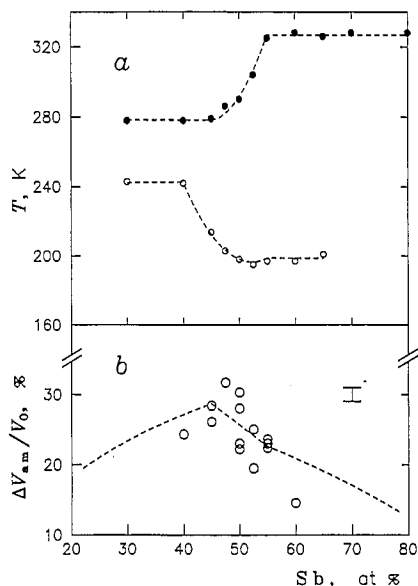


Fig. 5. (a) Positions of the leftmost (○) and rightmost (●) exothermic peaks in the DSC curves depicted in Fig. 1 as a function of the sample composition; (b) relative values for the total volume expansion of the Ga-Sb samples due to amorphization of the high-pressure phase. The dashed line is plotted under the assumption that the homogeneity range of the high-pressure phase was from 45 to 55 at.% Sb. The bar in the upper right corner shows the uncertainty in the volume evaluation due to a large temperature interval of the transformation.

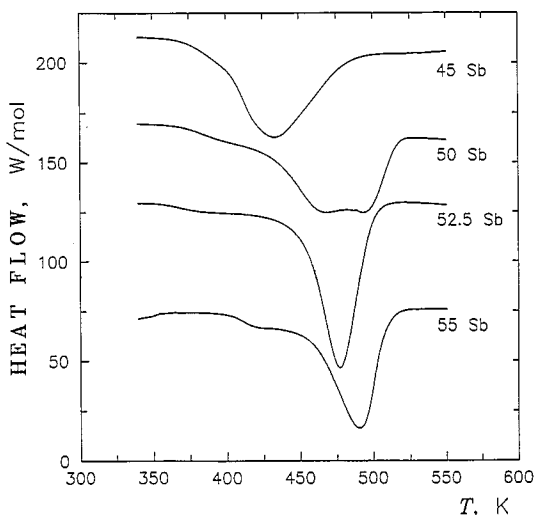


Fig. 6. Heat flow versus temperature on heating the amorphized Ga-Sb samples at 20 K/min.

which, according to the X-ray data, occurs within the temperature interval 360–550 K. As is seen from Fig. 6, this is again a multi-step process and its complex character manifests itself most clearly exactly for the sample of equiatomic composition. This effect is currently under investigation.

## 5. Conclusions

When heated to 350 K at ambient pressure, the quenched Ga-Sb high-pressure phase, containing from 47.5 to 52.5 at.% Sb, transforms completely into the amorphous state. Both the amorphization and the subsequent crystallization of the phase are multi-step processes. The effect of the variation of the phase composition on the shape of the DSC and dilatometric curves and the temperature interval for amorphization is consistent with the supposition that the short-range order in the amorphous phase is dependent on the temperature of amorphization.

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