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Solid state amorphization of the GaSb high pressure phase

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The process of solid state amorphization of the quenched high pressure GaSb 'white tin'-phase was studied at normal pressure by means of differential scanning calorimetry (DSC) and dilatometry. The value of the exothermal heat of amorphization was 4 ± 1 kJ/mol and expansion of the sample volume varied in 20–28% range. The amorphization process was found to follow a multistep course well reproduced by DSC and dilatometry curves

1. Introduction

In 1965, McDonald et al. [1] reported that solid state amorphization (SSA) occurs on heating at atmospheric pressure the metastable high pressure phase (HPP) of GaSb retained by cooling to low temperatures before releasing the pressure. This seems to be the first observation of SSA. Later, this phenomenon was observed for some other alloys (Zn–Sb, Cd–Sb, Al–Ge), for ice and quartz [2].

Thermal and volume effects of SSA have been studied for the three systems, Cd–Sb, Zn–Sb and Al–Ge [2,3]. A characteristic feature of these systems is that the compositions of their HPP are essentially different from those of the stoichiometric low pressure phases (LPP). It might be one of the reasons why the shape of the DSC and volumetric curves, especially in the case of the Zn–Sb system, was rather complicated [4].

In the present work, we have studied amorphization of HPP in the Ga–Sb system where the compositions of the HPP and LPP coincide.

2. Experiment

The samples of GaSb single crystals (5 mm in diameter and 1–3 mm in height) were exposed to 7 GPa and 520 K for 24 h in a quasihydrostatic high pressure chamber of 'Toroid' type, cooled to liquid nitrogen temperature, and then the pressure was released. X-ray analysis of the samples was performed on a DRON-2.0 diffractometer at 100 K and normal pressure using Cu K_α radiation. Thermal and dilatometric analyses were carried out on PE DSC 7 differential scanning calorimeter and PE TMA 7 thermomechanical analyzer. The samples were loaded into these apparatuses without heating above 100 K.

3. Results

The general set of diffraction lines of the GaSb HPP was well indexed in a 'white tin' bct cell with parameters $a = 5.449$ Å, $c = 3.087$ Å, $c/z = 0.567$ and specific volume $V_a = 22.91$ Å^3/atom at 100 K and 1 atm, which were somewhat different from those reported in refs. [1,5]. Besides, few additional weak lines were observed that allow one to speculate that the structure of the HPP is more complicated.

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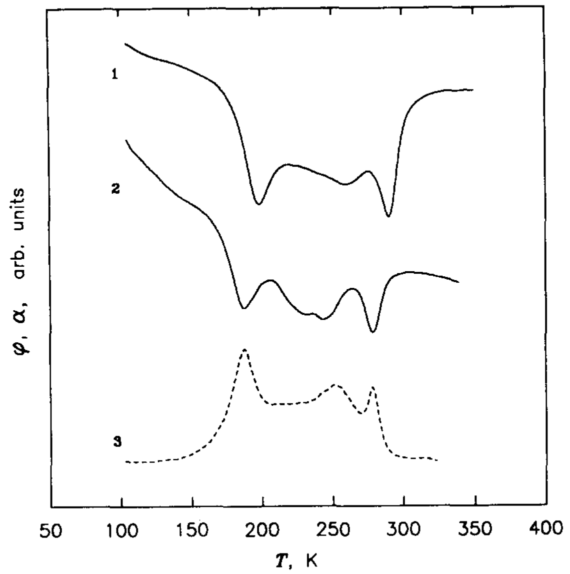

Fig. 1. Exothermal heat flow (φ; curves 1 and 2) and the first derivative of the GaSb sample volume with respect to the temperature (α; curve 3) plotted against the temperature. The heating rate was 20 K/min for curve 1 and 5 K/min for curves 2 and 3.

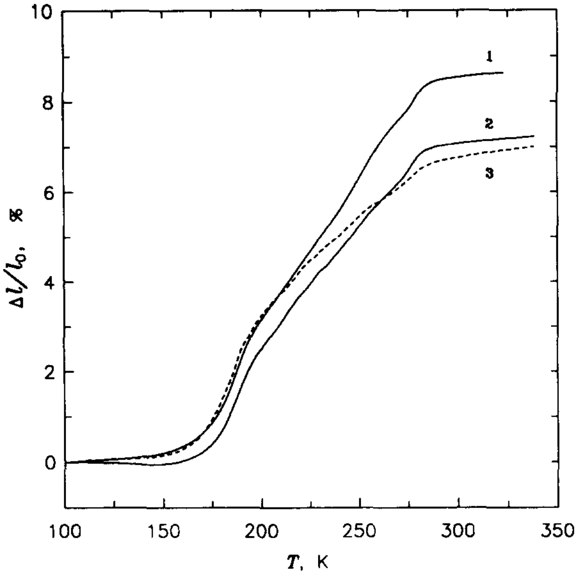

Fig. 2. Relative elongation of the GaSb sample as a function of temperature during heating (5 K/min). Curves 1–3 stand for three different samples subjected to the same thermobaric treatment at 7 GPa and 520 K for 24 h.

With the heating rates used, the crystal-to-amorphous phase transformation in the HPP was found to proceed completely below room temperature, since no distinct lines were observed in the X-ray patterns of the samples heated to this temperature.

Figure 1 shows representative DSC traces recorded at two different heating rates, 20 and 5 K/min (curves 1 and 2, respectively). One can see that an increase in the heating rate resulted only in a shift of the curve as a whole towards higher temperatures. The value of the integral exothermal heat effect of amorphization was 4 ± 1 kJ/mol. By contrast with the SSA of HPP in the Zn–Sb and Cd–Sb systems [2,4], three distinct peaks were observed on the DSC traces.

As is seen from fig. 2, the amorphization was accompanied by a large expansion of the samples. The scatter in the expansion effects for the different samples treated in the same way exceeded the experimental error and might be due to an additional relaxation process in the amorphous state.

The relative change of the sample volume with temperature is presented in fig. 3 by a solid curve. The dashed curve in this figure shows a corresponding dependence of the heat release. These two curves are seen to coincide within the

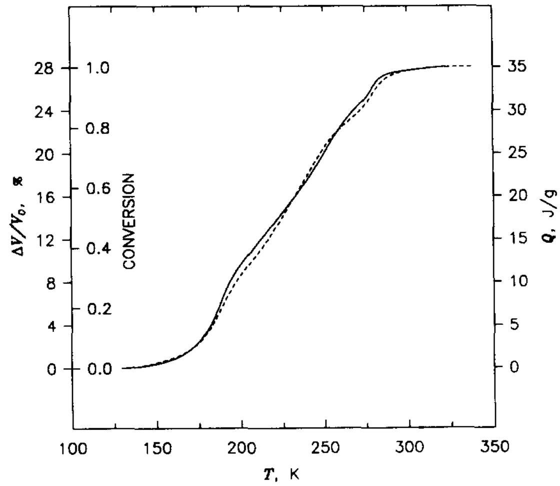

Fig. 3. Relative change in the sample volume ($\Delta V/V_0$, ——) and the integral heat effect (Q, - - - - - -) vs. temperature during the heating (5 K/min) of GaSb high pressure phase. (The volume of the sample was calculated in an isotropic approximation using curve 1, fig. 2; temperature dependence of heat release was obtained from curve 2, fig. 1.)

error limits. Besides, positions of the peaks of the dilatometric curve and those of the DSC traces are nearly the same (compare curves 2 and 3, fig. 1). Such a similarity of the DSC and dilatometric curves was earlier observed for solid state amorphization in the Cd–Sb and Zn–Sb systems [2,4].

In the two experiments (calorimetric and dilatometric), the heating was stopped at $T_q = 225$ K and samples were quenched down to the liquid nitrogen temperature. X-ray analysis has shown that the quenched samples still contained the crystalline phase with the slightly changed lattice parameters $a = 5.441$ Å, $c = 3.095$ Å, $c/a = 0.569$ but the same atomic volume $V_a = 22.91$ Å^3/atom.

4. Discussion

Taking into account a steep dependence of V_a against composition due to a large difference between the atomic radii of Ga and Sb, one can suppose that the composition of the 'intermediate' crystalline phase was not changed. The observed changes in the lattice parameters may be caused by a phase transformation(s) in the crystalline phase occurring with increasing temperature. Note, that a transformation in the crystalline phase may be the reason why the SSA process in GaSb was, as is seen from the shape of the DSC and volumetric curves, divided into separate stages.

Since the volume effect of this possible transition is close to zero anyway, the expansion of the sample observed during heating should be primarily due to the SSA process. Taking into account the coincidence of the heat release and volumetric curves, the same could be said about the heat effects.

5. Conclusions

To our surprise, amorphization phenomena in the Ga–Sb system with coinciding compositions of HPP and LPP appeared to be even more complicated than in the Cd–Sb and Zn–Sb systems where these compositions are different. The observed multi-step amorphization process in GaSb might be due to a phase transformation in the metastable crystalline HPP in the course of its heating.

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References

[1] T.R.R. McDonald, R. Sard and E. Gregory, J. Appl. Phys. 36 (1965) 1498.
[2] E.G. Ponyatovsky and O.I. Barkalov, Mater. Sci. Rep. 8 (1992) 147.
[3] O.I. Barkalov, V.M. Teplinsky and A.F. Gurov, High Press. Res. 9 (1992) 173.
[4] V.E. Antonov, E.A. Arakelyan, O.I. Barkalov, A.F. Guzov, E.G. Ponyatovsky and V.M. Teplinsky, to be published in J. Alloys Comp.
[5] V.F. Degtyareva, I.T. Belash, E.G. Ponyatovsky and V.I. Rashupkin, Fiz. Tverd. Tela (Leningrad) 32 (1990) 1429 (in Russian).