INVESTIGATION OF $\alpha \rightleftharpoons \beta$ TRANSITION IN GeTe–SnTe ALLOYS AT HIGH PRESSURES

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An $\alpha \rightleftharpoons \beta$ transition of the first kind, with a volume discontinuity of about 2%, was detected by x-ray diffraction in GeTe–SnTe alloys at high pressures: at p = 27 kbar for the 94 mol.% GeTe–6mol.% SnTe composition and at p = 12 kbar for the 74 mol.% GeTe–26mol.% SnTe material. The pressure dependences (up to 100 kbar) of the parameters and volumes of unit cells of both alloys were investigated. It was found that the composition of the alloy affected the pressure of the $\alpha \rightleftharpoons \beta$ transition. Phase diagrams for "pure" GeTe and for both alloys were obtained.

It is known [1] that GeTe and SnTe form a continuous series of solid solutions which, depending on the composition, have either the rhombohedral (A7 type) or cubic (NaCl type) structure. At room temperature and at atmospheric pressure the alloys containing less than ≈65% SnTe have the rhombohedral structure; other alloys (containing more than ≈65% SnTe) crystallize out in the cubic structure. It was found subsequently [2] that heating alters the rhombohedral GeTe–SnTe alloys to the cubic modification and the transition temperature depends on the composition.

At atmospheric pressure pure GeTe undergoes, at T = 400°C [2, 3], a phase transition from A7 to NaCl.[1]

We have reported [4] that a similar $\alpha \rightleftharpoons \beta$ transition takes place also in GeTe at a high pressure (p = 35 kbar) and room temperature. On the basis of the observations reported in [3, 4], the phase diagram of GeTe should have the form shown in Fig. 1.

Until recently, the transformation of GeTe at high temperatures has been assumed to be continuous since no sudden change of volume has been found [2, 3]. Having observed that the same transition in GeTe at p = 35 kbar is accompanied by a volume discontinuity of ≈3% and is thus a transition of the first kind, we have suggested that the (P, T) diagram of GeTe may have a critical point at which the curve representing a transition of the first kind changes to a curve of the second kind [5]. It was reported thereafter [6] that the $\alpha \rightleftharpoons \beta$ in GeTe at 400°C is a transition of the first kind (accompanied by a 1.4% change in volume) and therefore it does not seem necessary to assume a critical point at p > 0. However, a change in the symmetry during the $\alpha \rightleftharpoons \beta$ transition in GeTe ($C_{3v} \rightleftharpoons O_h$) satisfies the requirements of the Landau theory [5] of phase transitions of the second kind, which take place without any change in volume [7].

By analogy with pure GeTe, we may assume that at room temperature but at high pressures, GeTe–SnTe alloys also undergo an $\alpha \rightleftharpoons \beta$ transition [4] and the transition pressure depends on the alloy composition: The value of this pressure should decrease when the concentration of SnTe is increased.

The present paper reports an investigation of the influence of high pressures on the structure of two GeTe–SnTe alloys[2] of the following compositions:

1) 94 mol.% GeTe + 6 mol.% SnTe,

2) 74 mol.% GeTe + 26 mol.% SnTe.

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[1]The following notation is used: α-GeTe is the rhombohedral modification; β-GeTe is the cubic phase. The same notation (α = rhombohedral, β = cubic) is employed for GeTe–SnTe alloys.

[2]The authors thank L. E. Shelimova and S. I. Novikova for supplying the samples.

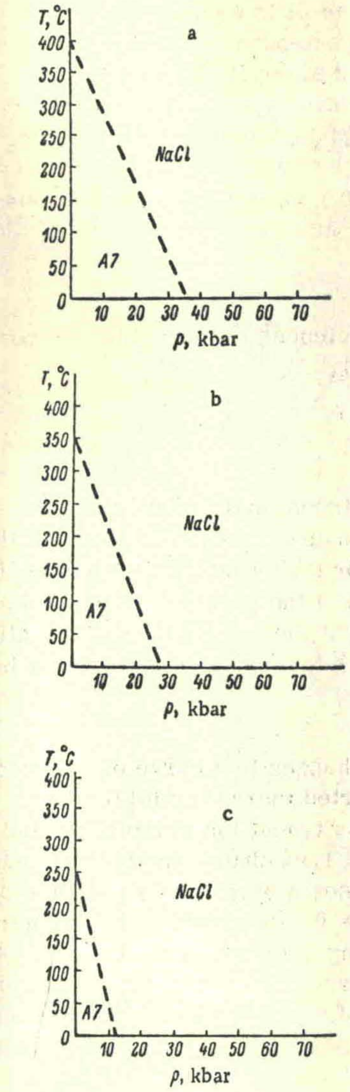

Fig. 1. Phase diagrams of GeTe and of GeTe–SnTe alloys. a) GeTe; b) alloy No. 1; c) alloy No. 2

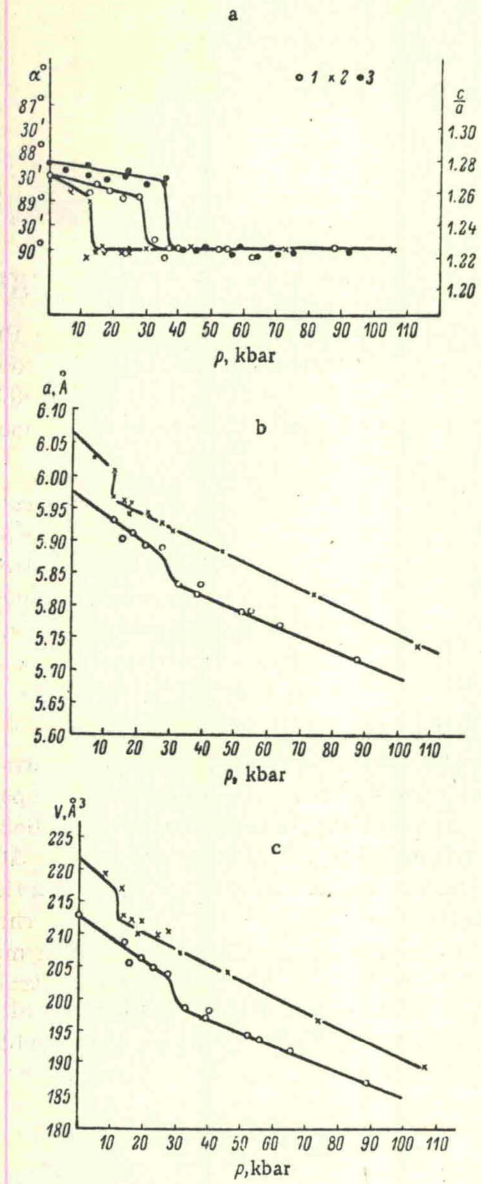

Fig. 2. Pressure dependence of the unit-cell parameters and volumes of alloys Nos. 1 and 2 and of GeTe. 1) Alloy No. 1; 2) alloy No. 2; 3) GeTe. a) Rhombohedral angle α; b) parameter *a*; c) unit-cell volume.

The initial unit cell parameters (Table 1) for alloys 1 and 2 at atmospheric pressure and room temperature were obtained from Debye diffraction patterns, recorded using copper radiation in an RKU-114 camera; sodium chloride was used as an internal standard.

Under normal conditions the investigated alloys (1 and 2) have the same structure as α-GeTe, whose space group, according to the latest data [6], is C^5_{3V}(R3m).[3]

An x-ray diffraction investigation of the alloys was carried out at pressures up to 100 kbar at room temperature using a high-pressure x-ray camera [8] which had an amorphous boron pellet with a channel to take a sample. Molybdenum radiation was used in this investigation. The samples were in the form of a mixture of a GeTe–SnTe alloy with amorphous boron and with sodium chloride, taken in the 30 : 20 : 25 proportions by weight; boron was added in order to reduce absorption and sodium chloride was used to estimate the pressure from the compressibility using the x-ray diffraction data [9].

[3]The D^5_{3d}(R$\bar{3}$m) space group attribution to α-GeTe, given in [4], is incorrect.

TABLE 1. Initial Parameters of Unit Cells

Alloy composition	Hexagonal phase		Rhombohedral phase	
	a, Å	c, Å	a, Å	α
94 mol. % GeTe+6 mol. % SnTe	8.34±0.01	10.63±0.04	5.977±0.004	88°26′
74 mol. % GeTe+26 mol. % SnTe	8.45±0.02	10.73±0.03	6.061±0.004	88 30

TABLE 2. Cubic-Cell Parameters of High-Pressure Phase

Alloy	p, kbar	a, Å
94 mol. % GeTe+6 mol. % SnTe .	32	5.84±0.01
74 mol. % GeTe+26 mol. % SnTe .	17	5.95±0.01

It was found that at high pressures both alloys underwent an $\alpha \rightleftharpoons \beta$ phase transition of the first kind. X-ray diffraction patterns of the β-phases of both alloys and of pure GeTe were identical; there were no additional lines which would indicate ordering in the distribution of Ge and Sn atoms in the alloys. The results of an x-ray diffraction investigation at high pressures (Fig. 2) indicated a sudden change in the lattice parameters and in the unit cell volume at certain pressures. The angle α of alloy 1 changed suddenly at p = 27 kbar from 88°50' to 90° and the unit cell volume changed suddenly (at the same pressure) by ΔV = 1.9%. At p = 12 kbar the angle α of alloy 2 changed from 88°50' to 90°, with a corresponding volume change ΔV = 2.0%. The pressure dependences of the unit cell parameters and volumes of both alloys were linear (they were calculated by the least-squares method). The unit cell parameters of the high-pressure cubic phases of the investigated alloys are given in Table 2.

Figure 3 shows the dependence of the $\alpha \rightleftharpoons \beta$ transition pressure on the composition of the alloys at room temperature. It is evident from that figure that the transition pressure decreases when the concentration of SnTe is increased. Obviously, the replacement of some of the germanium atoms with larger tin atoms increases the packing density in the NaCl-type structure.

From the results obtained on the $\alpha \rightleftharpoons \beta$ transition temperature at atmospheric pressure and at high pressures, we could plot the phase diagrams of the investigated alloys (Fig. 1).

In conclusion, we must mention that an investigation of the phonon dispersion in SnTe has indicated [10] that the phase transition in GeTe and in GeTe–SnTe alloys is similar to the transition in perovskite-type ferroelectrics and that therefore these materials are diatomic ferroelectrics. Obviously, the rhombohedral α-phase [space group C_{3v}^5(R3m)] should have ferroelectric properties but the β-phase [space group O_h^5(Fm3m)] should be paraelectric. If this conclusion [10] is correct, then the results obtained by us indicate that the ferroelectric-paraelectric transition temperature of diatomic ferroelectrics GeTe and GeTe–SnTe decreases with increase of pressure (Fig. 1) in a manner similar to perovskite-type ferroelectrics $BaTiO_3$ and $PbTiO_3$ [11].

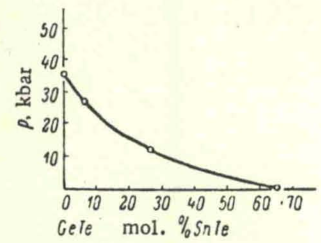

Fig. 3. Dependence of the $\alpha \rightleftharpoons \beta$ transition pressure on the alloy composition at room temperature.

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