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Structural study of $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ solid solutions

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Abstract. The reversible cubic \leftrightarrow rhombohedral ($O_h^5 \leftrightarrow C_{3v}^1$) phase transition of GeTe-rich $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ solid solutions is studied by means of high-temperature x-ray analysis. The temperature and composition changes of the rhombohedral lattice parameters are found. They prove the displacive nature of the solid solution phase transition. With an increasing amount of heterovalent Ag and Bi atoms replacing Ge cations, the phase transition temperature T_c decreases.

1. Introduction

The IV–VI compound GeTe and solid solutions (sss) based on it are narrow-band-gap semiconductors with a wide range of homogeneity. Some of them, called TAGS, are successfully applied in the direct conversion of heat energy in electricity by radioisotopic thermoelectric generators for the space system for nuclear auxiliary power SNAP-19 [1–4]. This determines the practical interest in GeTe-rich sss.

According to the T - x projection of the Ge–Te phase diagram, GeTe possesses three polymorphic forms at normal atmospheric pressure: a low-temperature rhombohedral α form (space group symmetry, $R\bar{3}m \equiv C_{3v}^1$; point group symmetry, $3m$) which is the binary analogue of the grey arsenic structure; a low-temperature orthorhombic γ form (space group symmetry, $Pnma \equiv D_{2h}^{16}$; point group symmetry, mmm) which is the black phosphorus type for less than 50.4 at. % Te and $p_c > 1.1 \times 10^{27} \text{ m}^{-3}$ (below T_c); a cubic β form (space group symmetry, $Fm\bar{3}m \equiv O_h^5$; point group symmetry, $m\bar{3}m$) which is NaCl type (above T_c). The phase transition (PT) temperature T_c depends on composition and varies from about 700 K on the Ge-rich side to about 630 K on the Te-rich side of the phase diagram [5].

The lattice constants of the rhombohedral and orthorhombic phases are related to those of cubic phase by [6]

$$a^\alpha = a^\beta \quad a^\gamma = b^\gamma = a^\beta \sqrt{2} \quad c^\gamma = 2a^\beta.$$

The point or space group symmetries of the α - and γ -phases are subgroups of the β -phase group symmetry:

$$\begin{array}{llll} 3m \in m\bar{3}m & mmm \in m\bar{3}m & mmm \bar{\in} 3m & R\bar{3}m \in Fm\bar{3}m \\ Pnma \bar{\in} Fm\bar{3}m & Pnma \bar{\in} R\bar{3}m & & \end{array}$$

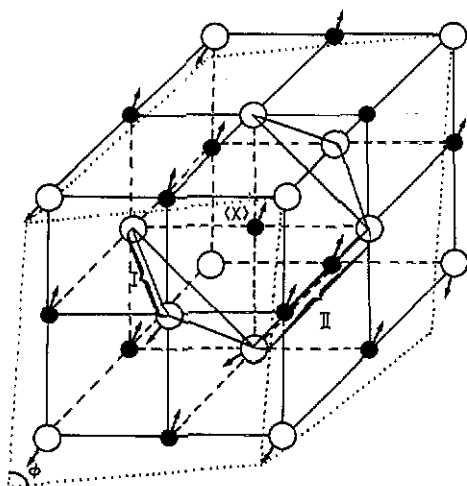


Figure 1. High-temperature rock-salt structure (—, - - -) and its rhombohedral distortion (· · ·) at the reversible cubic \leftrightarrow rhombohedral phase transition of GeTe and GeTe-rich $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ sss: ●, Ge, Ag or Bi cations; ○, Te anions. I and II, respectively, show the distances between the Te atoms ($d_{\text{Te-Te}}$) in the layer (intralayer Te-Te distances) and between the layer (interlayer Te-Te distances) in the layered rhombohedral structure.

where \in is inclusion but $\bar{\in}$ is non-inclusion of one group as subgroup of another [7].

According to these relations the crystal structure of the α - and γ -phases can be viewed as a distorted cubic structure. The $\beta \leftrightarrow \alpha$ PT may be discontinuous (first order) or continuous (second order) but the $\alpha \leftrightarrow \gamma$ and the $\beta \leftrightarrow \gamma$ PTs may be of only first order [7].

The crystal structure of GeTe may be viewed as compacted cubic packing of Te atoms with octahedral interstices filled with Ge atoms (coordination number, 6) [8–10]. The structure of α - and γ -phases could be obtained from the structure of the β -phase by means of ferroelectric (coordination number, 3:3) or antiferroelectric (coordination number, 2:2:2) distortions. The GeTe cubic \leftrightarrow rhombohedral and cubic \leftrightarrow orthorhombic PTs, respectively, are the simplest conceivable ferroelectric and antiferroelectric PTs [6].

The rhombohedral distortion of GeTe below T_c can be described in terms of three components.

(i) The optical distortion is a spontaneous static relative shift $\langle x \rangle$ (in parts of the lattice constant a) of the two cubic sublattices along the $\langle 111 \rangle$ direction which becomes the rhombohedral c axis. It is caused by the softening of the zone-centre transverse optical (τ_0) phonon mode. As a result the inversion symmetry is lost, double Ge-Te layers are formed and spontaneous polarization occurs, although this cannot be observed because it is screened by the free carriers.

(ii) The acoustic distortion is the homogeneous rhombohedral shear strain ϵ_s , which manifests itself as a change in the interaxial angle ($2\epsilon_s = \Delta\Phi = \pi/2 - \Phi$) in radians of the unit cell (in the rhombohedral shear strain the cubic lattice is stretched to the rhombohedral c axis and contracted in the perpendicular direction).

(iii) The dilational strain ϵ_d is due to a change in the lattice constant or a change δV in the specific volume (figure 1) [11, 12].

Similar structural PTs have been observed in SnTe [13–15], in isovalent ss, $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ [16, 17], $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ [18, 19] and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ [20] and in GeTe-rich heterovalent sss of the type $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{1-y}((\text{Sb}(\text{Bi}))_2\text{Te}_3)_y]_x$ [21–23].

The present study consists of an x-ray investigation of the PTs of GeTe-rich $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ sss ($0 < x < 0.20$) in a temperature interval from 300 to 700 K.

2. Experiment

The high-temperature diffraction studies of powder samples were carried out on a Philips diffractometer APD-15 with Cu $K\alpha$ radiation ($\lambda = 0.154051$ nm) in an argon atmosphere. The heating rate was less than 3 K min^{-1} . The temperature was maintained with a thermoregulator.

The PT was observed by measuring the temperature dependences of the ss lattice parameter. A low-temperature ss described by a rhombohedral lattice parameter can be visualized as a slight distortion of the high-temperature cubic phase. It is well known that the Bragg reflection intensities (neutron or x-ray) are very weak for odd index reflection (h, k, l all odd) in the undistorted cubic phase. The sublattice shift gives rise to a strong increase in the odd index reflection intensities whereas the even index reflections decrease slightly in intensity [14, 24]. This allowed us to determine the sublattice shift. The change in symmetry can also be observed by measuring the angular separation of appropriate pairs of reflections, e.g. $(hk0)$ and $(hk\bar{0})$ that merge in a single line at the cubic phase. The diffraction peaks are sufficiently sharp. So the value of 2θ and the angular separation of the above-mentioned reflection pairs was read to $\mp 0.020^\circ$ or better.

The lattice parameters were computed using the least-squares method. The error in the interaxial angle was -0.01° and the error in the lattice constant was less than 0.0002 nm.

3. Results and discussion

The C_{3v}^5 phase of GeTe is characterized by two layered packs Ge–Te in the direction perpendicular to the trigonal crystal axis [10]. The distances between the Te ions in the layer (intralayer) (I) are smaller than the Te–Te distances between layers (II) (see figure 1). They become equal in the cubic phase.

The observed temperature dependences of $\Delta\Phi$ and $d_{\text{Te-Te}}$ (I and II) (figures 2(a) and 2(b), respectively) show that with increasing $[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]$ content x the observed increase in the intralayer (I) and decrease in the interlayer (II) Te–Te distances and in $\Delta\Phi$ are accelerated. As a result the PT occurs at lower temperatures, i.e. T_c decreases:

$$2\varepsilon_{xy} = \Delta\Phi \quad \Delta\Phi/2 = \langle x \rangle^2.$$

The rapid increase in intralayer (I) Te–Te distances is in contrast with the slow decrease in the interlayer (II) Te–Te distances from 300 K to a higher temperature for all the examined sss. They become equal in the cubic phase. Obviously in these temperature intervals the magnitude of the thermal motions of the atoms is not sufficient to change the C_{3v}^5 phase into cubic. The interaction between the anions and cations influences strongly only the intralayer Te–Te distances. Near T_c the changes in both distances are accelerated. This may be connected with the strength of the cation–anion interaction and with gradual destruction of the double-layered Ge–Te packs of the

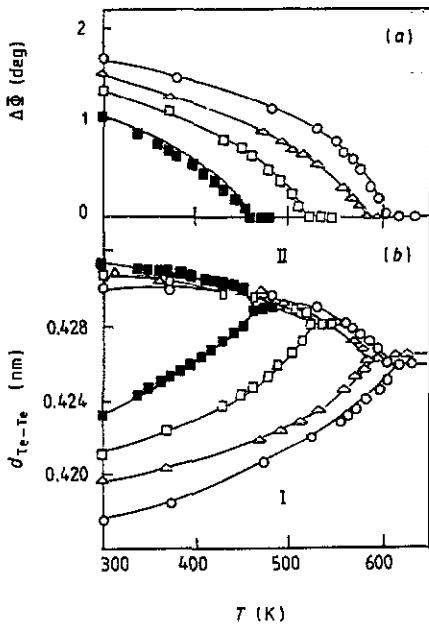


Figure 2. Temperature dependences of (a) the deviation of interaxial angle from 90° ($\Delta\Phi = 90 - \Phi$) and (b) intralayer (I) and interlayer (II) of GeTe-rich $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ sss: \circ , $x = 0.03$; \triangle , $x = 0.05$; \square , $x = 0.10$; \blacksquare , $x = 0.15$.

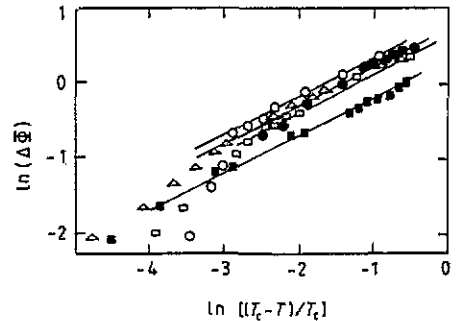


Figure 3. Estimation of the power in the deviation of the interaxial angle from 90° for GeTe [16] and GeTe-rich $(\text{GeTe})_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ sss. \bullet , GeTe, $x = 0$; for other symbols, see figure 2.

rhombohedral phase on increase in the thermal motion of the atoms. The Te-Te distances in the cubic phase are different for all compositions studied and increases with increasing content x of $[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ in the alloy. This is a result of the larger atomic radii of the Ag and Bi atoms ($R_{\text{Ag}^+} = 0.113$ nm; $R_{\text{Bi}^{3+}} = 0.12$ nm) introduced to replace Ge ($R_{\text{Ge}^{2+}} = 0.065$ nm) and the corresponding increase in the lattice constant.

The temperature behaviour of $\Delta\Phi$ may be characterized by similar regions. From 300 K to about 450 K, $\Delta\Phi$ decrease almost linearly but above this temperature up to T_c the changes in $\Delta\Phi$ are also accelerated.

The displacive nature of the ss PT is evident from the results presented. As the $\text{C}_{3v}^5 \leftrightarrow \text{O}_h^5$ PTs in GeTe and GeTe-rich sss take place without any changes in the number of atoms per unit cell (there are two atoms or one formula unit per primitive unit cell in these two phases), the translation group is the same in both phases. It has been shown theoretically [25] that according to the Landau-Lifshitz type of symmetry criterion the GeTe $\text{C}_{3v}^5 \leftrightarrow \text{O}_h^5$ PT can be of second order. The appropriate order parameters are the relative sublattice shift, which can be identified as the first-order parameter, and the change $\Delta\Phi$ in the interaxial angle which can be identified as the second-order parameter [26]. The temperature dependence of the homogeneous rhombohedral shear strain is given by [27]

$$2\varepsilon_s = \Delta\Phi \sim [(T_c - T)/T_c]^\beta$$

where β is the critical index of the second-order parameter. The values of β determined

from the experimental temperature dependences of GeTe [16] and GeTe-rich ss interaxial angle $\Delta\Phi$ ($\beta = 0.5$ (figure 3)) corresponds to the value found from the phenomenological Landau theory for a second-order transition ($\beta = 0.5$). However, as can be seen from figure 3, close to T_c ($(T_c - T)/T_c < 0.05$) the deviation of the experimental points from this dependence is observed. This may be connected with high degree of anharmonicity in the ss thermal motion at these temperatures. It is in good agreement with theoretical conclusions about the importance of anharmonicity in GeTe [28] and the influence of anharmonicity, especially close to T_c , found from a neutron diffraction study of GeTe [26].

4. Conclusions

(1) As a result of the x-ray study of the structural phase transition of GeTe-rich $\text{GeTe}_{1-x}[(\text{Ag}_2\text{Te})_{0.5333}(\text{Bi}_2\text{Te}_3)_{0.4667}]_x$ sss the temperature and composition changes of the rhombohedral lattice parameters (Φ , a , $d_{\text{Te-Te(I)}}$ and $d_{\text{Te-Te(II)}}$) and T_c were established. They prove the displacive nature of the ss $\text{C}_{3v}^5 \leftrightarrow \text{O}_h^3$ phase transition. The composition changes of these parameters have already been discussed [29].

(2) The temperature changes of intralayer and interlayer Te-Te distances and of the deviation of the uniaxial angle from $\pi/2$ are almost linear from 300 K to about 450 K. They are accelerated near T_c .

(3) The value of the critical index $\beta = 0.5$ of the second-order parameter corresponds to the value found from the phenomenological Landau theory for second-order structural phase transition ($\beta = 0.5$).

(4) The deviation of the experimental points from the dependence

$$\Delta\Phi \sim [(T_c - T)/T_c]^{0.5}$$

at $(T_c - T)/T_c < 0.5$ may result from the anharmonicity of ss thermal motion at these temperatures.

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