

THERMAL EXPANSION OF SEMICONDUCTOR MATERIALS

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The thermal expansion of tellurides of germanium, bismuth, and intermetallic compounds is investigated over the temperature range 293–973 K.

At present there is a very active search for and synthesis of new semiconductor materials. To introduce them into practice, one must study in detail their behavior under different technological conditions and determine the physicochemical characteristics, in particular, the thermophysical ones, which include the coefficient of thermal expansion (CTE).

The CTE of semiconductor compounds was measured using a DKV-5A automated quartz dilatometer [1].

One must often measure the CTE of specimens in a controlled gas medium, which is not provided for by the design of the DKV-5A dilatometer. In particular, this refers to the specimens investigated in the present work. Therefore, we somewhat modified the instrument somewhat by locating a protective quartz tube inside the heating device, in which a measuring cell is placed and to which an inert gas with a certain flow rate is supplied continuously. Thus, the necessary medium is created and, in our opinion, the field of application of the DKV-5A dilatometer is expanded substantially. This refers especially to investigating the CTE of new chemically active materials. To prevent distortion of the symmetry of the temperature field, the protective tube is fastened strictly centered inside a vertical tubular electric furnace. The permissible value of the flow rate (0.033–0.05) liter/sec of the gas is carefully maintained and measured using a rotameter. To decrease axial temperature gradients in the working zone of the furnace, the tube with the electric spiral is surrounded by heat insulation. Inside the tube there is a massive steel cylinder and the protective quartz tube. This permits a decrease in the axial temperature gradient in the specimen zone to 50 K/m.

Specimen temperatures as functions of time obtained experimentally with different heating rates show that in the initial stage of heating to 423 K the temperature increases very slowly (< 0.017 K/sec) in all regimes. This is important for obtaining a valid dilatogram and hence a reliable CTE value for the specimen. With the structural changes made by us to the instrument into whose space the protective quartz tube is placed, the rate of temperature rise is decreased somewhat further in all regimes. In our opinion, this improves the reliability of the obtained experimental data in the initial stage of heating.

To produce tellurides of germanium, bismuth, and intermetallic compounds, use was made of metals of semiconductor purity (Ge is GPZ-1, Bi is Bi-0000, and Te is 4DA). The GeTe (50.6 at. % Te), Bi₂Te₃, GeBi₂Te₄, and GeBi₄Te₇ specimens for dilatometric investigations were produced by melting in a double quartz test tube in an inert medium, namely, argon under a pressure of 1 atm. Prior to melting, small pieces of the indicated substances were placed in a quartz ampul 5 mm in diameter. The ampul was installed vertically in the quartz thick-walled test tube, which was connected to a vacuum system and placed in the vertical tubular resistance furnace. For purposes of decontamination and moisture removal the system was evacuated to a pressure of 10^{-2} – 10^{-3} mm Hg with simultaneous warm up at a temperature of the order of 423 K for about an hour. Then the test tube was filled with high-purity argon (with residual impurities of nitrogen of no more than 0.006%, and of oxygen of 0.0007%) having water vapor content of no more than 0.007 g/m³ under normal conditions.

Test tubes with the substance were slowly heated to the corresponding melting temperature and then the temperature was increased by approximately 50 K. The test tube was continuously shaken and the specimens were

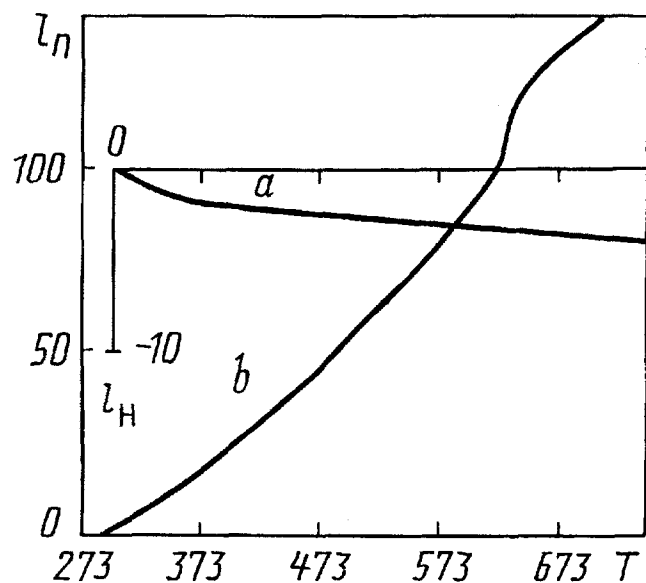


Fig. 1. Dilatograms of the zero drift of the instrument and of germanium telluride. l_n , l_H , μm ; T , K.

kept under these conditions for about 15–20 min. Then they were cooled slowly and annealed at temperatures of, respectively, 873, 673, and 473 K for no less than 10 h. Thereafter they cooled down slowly together with the furnace and were removed from the quartz ampul. The specimens were of cylindrical shape and followed completely the geometry of the ampul cavity. Their diameter was about 5 mm. The specimen ends were first worked using a needle file and then, fixed in a special mandrel, were ground by hand. This working of the specimens in the mandrel permitted a sufficiently high accuracy and parallelism of their ends to be achieved, which is important in measuring CTE using the above-described dilatometer. Nonparallelism of the ends and specimen length were determined to an accuracy of ± 0.001 mm using a UZA-2 comparator or to an accuracy of ± 0.01 mm using a micrometer. The length of the GeTe specimen is 18.05 mm, of GeBi_2Te_4 37.75 mm, of Bi_2Te_3 23.61 mm, and of GeBi_4Te_7 13.49 mm.

From the standpoint of the geometric dimensions of the existing measuring cell and achievement of an acceptable accuracy in measuring CTE of about 1–2%, which was provided by the given instrument and its measuring system, the optimum length of the specimen must be about 50 mm.

Because of the lack of a sufficient amount of the investigated substances one is sometimes unable to prepare specimens of the optimum length. Therefore, prior to installing specimens of shorter length in the measuring cell, we built them up to the indicated optimum size using quartz cylindrical inserts. The temperature region of our investigations is $\theta < T < 2\theta$ (θ is the Debye temperature). Over this range all the quantities in the Grüneisen relation depend only slightly on the temperature [2]. Therefore, the finite interval (ΔT) for our measurements can be sufficiently large – of the order of 50 K. Account was also taken of the fact that, other things being equal, the confidence interval in determining the CTE is inversely proportional to the temperature interval. Therefore, the error in determining the CTE will be larger, the larger the magnitude of ΔT .

With a decrease in the temperature interval one must improve the accuracy in measuring the temperature so that the error in determining ΔT does not exceed 1–2%. In the present work these conditions hold and the relative error is no more than 1.5–2% with an automated system of temperature recording using a potentiometer. A parallel measurement of the thermocouple emf using a V7-21 digital millivoltmeter permits more than a twofold decrease in the indicated error. The specimen investigated should not be excessively large since it is difficult to create the required uniform temperature field in it and attain temperature equilibrium in an acceptable time interval [1].

Figure 1 gives dilatograms for the zero drift of the instrument (a) and for the GeTe specimen (b).

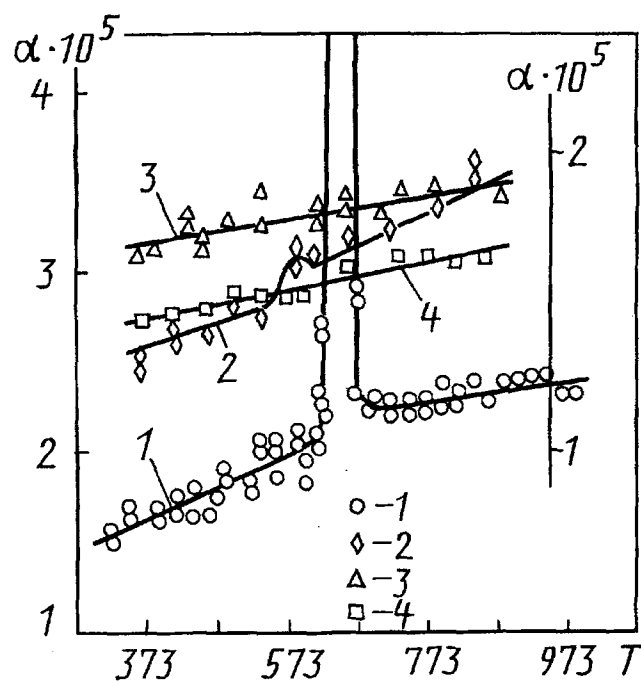


Fig. 2. Temperature dependences of the thermal expansion coefficients for tellurides of germanium, bismuth, and intermetallic compounds: 1) GeTe; 2) Bi₂Te₃; 3) GeBi₂Te₄; 4) GeBi₄Te₇. α , K⁻¹.

In calculating the limiting error of CTE values for germanium telluride and the other materials the remarks on choosing the optimum value of the finite temperature interval were taken into account. For GeTe it is appropriate to estimate the error for two temperature ranges: up to the phase transition temperature and beyond this temperature, namely, 293–573 K and 663–963 K, respectively.

The error in determining the CTE of GeTe over the temperature range 293–573 K, according to the procedure of [1], is 3%. For the temperature interval 663–963 K the value of the limiting relative error will be somewhat smaller and is 2.5%.

The limiting relative error for CTE values of the other specimens is calculated similarly to [1]. Its value can be estimated for the entire temperature range of the investigations since for these substances the CTE depends weakly on the temperature. The GeBi₂Te₄ specimen was approximately two times as long compared to GeTe and had a value of the CTE comparable to that of a low-temperature modification α -GeTe. Therefore, the limiting error of CTE values for GeBi₂Te₄ is of the order of 2.5% over the entire temperature range investigated. The experimental values of the other specimens have the same limiting error. The reliability index is 0.95. The most likely values of the errors [3] in the data on the CTE obtained experimentally will be somewhat smaller and for GeTe will be 2% (293–573 K) and 1.7% (663–963 K), for Bi₂Te₃ 1.7%, for GeBi₂Te₄ 1.7%, and for GeBi₄Te₇ 2%.

Figure 2 gives the temperature dependences of the CTE values for GeTe, GeBi₂Te₄, Bi₂Te₃, and GeBi₄Te₇ over the temperature ranges 293–973, 293–833, 293–813, and 293–793 K, respectively.

In the present work the CTE of GeTe is determined over a larger temperature range than in [4, 5], namely, almost to the melting temperature. Unlike the present work and [4, 5], in [6, 7] use was made of single-crystal GeTe specimens of close compositions in order to investigate the phase transition dilatometrically. The specimen of [6] contained 50.6 at.% Te, and the specimen of [7] somewhat less than 50.6 at.% Te. However, even this insignificant difference in the composition, unfortunately not given by the authors in a quantitative expression, had a substantial effect on the character of the temperature dependence and the value of the CTE. The change in the specimen volume was strongly dependent on its composition: in the specimen with 50.6 at.% Te the phase transition occurred with increasing volume, and in the specimen with < 50.6 at.% Te with decreasing volume. The authors of [7] showed experimentally and explained the inconsistency of the experimental data of [4] and [5] on the volume change in the phase transition by assuming that in [4] and [5] specimens of different (though insignificantly

so) compositions were investigated. The values of the phase transition temperature in heating these single-crystal specimens almost coincide: 627.5 K for [6] and 626 K for [7]. In cooling the specimens the phenomenon of hysteresis is observed for both, namely, the transition temperature shifts to the region of lower values. However, the magnitude of the hysteresis is different. In [7] it is almost two times smaller and is of the order of 7 K. Strong anisotropy of the CTE is observed for the single-crystal specimen of [7]. Here the values of α_{\perp} in [7] and [6] practically coincide up to 550 K, and α_{\parallel} in [7], unlike that in [6], has a negative value in the entire region investigated.

In our experiments on polycrystalline specimens with the composition 50.6 at.% Te we obtained a magnitude of hysteresis even larger than that in [6] although the data on the transition temperature practically coincide within the measurement error. The transition temperature is 626.5 ± 1 K and the magnitude of the hysteresis is of the order of 32 K. Unfortunately, in the earlier works [4, 5], where the authors investigated polycrystalline GeTe specimens, the issue of hysteresis is not discussed. Moreover, the information in all the current works on the value of the phase transition temperature is very inconsistent: 648 K [1], 638 [4], 669 [5], 627 [6], 626 [7], and 663 K [8]. Taking into account the experimental data (626.5 K) of the present work obtained by us, we can argue that the values of the phase transition temperatures for germanium telluride (50.6 at.% Te) of [6, 7] are likely to be the closest to the true values.

It is well known that a phase transition involves significant stresses in the crystal that can result in formation of microcracks. Evidently, this explains the phenomenon of hysteresis observed in the specimens. In our opinion, the magnitude of the hysteresis characterizes indirectly the perfection of the crystal. There are more dislocations in semicrystalline specimens than in single-crystal ones. Therefore the magnitude of the hysteresis for our polycrystalline specimens is likely to be much larger than for the single-crystal ones [6, 7].

From the temperature dependence (Fig. 2) of the CTE of germanium telluride it can be seen that the CTE depends weakly on the temperature up to the point of polymorphic transformation. This dependence is described by the linear function $\alpha_{av} = (1.35 + 9.091 \cdot 10^{-4} T) \cdot 10^{-5}$ over the temperature range 273–543 K. The rather distinct peak on the curve corresponds to the phase transition. However, the phase transition occurs, nevertheless, in some narrow temperature interval rather than entirely isothermally, as claimed in [4].

Following the phase transition, the CTE of the new β -GeTe phase also depends on the temperature very weakly. The CTE values of the high-temperature phase can be calculated by using the following linear dependence: $\alpha_{av} = (2.25 + 3.351 \cdot 10^{-4} T) \cdot 10^{-5} K^{-1}$ for $T = 673$ –973 K.

In [5, 9] it is shown that the abrupt phase transitions occurring in germanium telluride in a reverse temperature course involve a decrease in the symmetry of a cell and result in displacement of germanium atoms in octahedrons of the cubic package of tellurium atoms. At present a value of the displacement of Ge atoms from the ideal position along the solid diagonal is determined. In this case a continuity of the α -GeTe structure forms, the layers being corrugated. This causes anisotropy of the physical properties of α -GeTe, particularly of the thermal expansion ($\alpha_{\parallel} < \alpha_{\perp}$ by approximately 2 times at 300 K). For the high-temperature modification β -GeTe there is no thermal expansion anisotropy.

Our analysis of the experimental data [6] shows that the values of α_{\perp} at 300 K almost coincide in heating and cooling and differ little (of the order of 15%) from the values for β -GeTe at 700 K. By using recommendations [2] for a rhombohedral lattice and experimental data (α_{\parallel} and α_{\perp}) [7] we calculated the value of the average CTE at 300 K. It turned out to be much higher, than in our experiments and [4], of the order of 20–25%, which indicates the approximate character of the calculation formula [2] for the crystal system in question.

Thus, the temperature dependences of the CTE for the single-crystal specimens [6] differ substantially from the dependence obtained for polycrystalline ones (Fig. 2). The indicated factors demonstrate clearly the advisability of performing similar complementary investigations on both single-crystal and polycrystalline specimens.

For $GeBe_2Te_4$ the temperature dependence is expressed by a linear function over the entire temperature range (273–833 K) that corresponds to the equation

$$\alpha_{av} = (1.51 + 3.20 \cdot 10^{-4} T) \cdot 10^{-5} K^{-1} .$$

A linear dependence of α_{av} on the temperature is also observed for GeBi_4Te_7 in the temperature interval 273–793 K: $\alpha_{av} = (1.37 + 3.215 \cdot 10^{-4}T) \cdot 10^{-5} \text{ K}^{-1}$. For bismuth telluride the temperature dependence of the CTE has deviations from linearity at a temperature of 523 K. By the way, for single-crystal Bi_2Te_3 specimens [10] we observe a sudden change in the temperature dependence of the CTE at approximately the same temperature: α_{\perp} has a maximum and α_{\parallel} has a minimum. Evidently, in the polycrystalline specimens we encounter manifestations of the same effects of structure rearrangement that are observed in investigating single-crystals.

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