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09

Effect of heat treatment on optical and electrophysical properties of α-GeTe

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Comprehensive research aimed at studying the effect of structural changes caused by thermal treatment on the optical and electrophysical properties of GeTe in its rhombohedral structural modification have been performed using μ-Raman and μ-PL methods, together with measurements of the temperature dependences of electrical resistance and the Hall coefficient in a wide temperature range. Infrared PL in the range of 0.7−0.8 eV was detected for this compound for the first time. An analysis of the experimental dependences of the PL spectra on the concentration of charge carriers (holes) and temperature, using the results of calculations of the electronic structure in the electron density functional approximation, made it possible to establish its interband nature.

Keywords: germanium telluride, Raman scattering, photoluminescence, electrical and thermal conductivity, thermopower.

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Germanium telluride (GeTe) is the base of the most efficient materials for thermoelectric generators that convert heat into electricity. Recent studies have shown that the efficiency of these materials can be improved, which will significantly expand the scope of economically reasonable use of thermoelectric devices [1,2]. However, the stability and reproducibility of these new materials are still insufficient for their practical application. It is known that the electronic properties of GeTe are largely determined by the high concentration of structural defects — vacancies of germanium. This leads to the fact that in the pure stoichiometric GeTe, the concentration of charge carriers (holes) is of the order of $10^{21}\,\mathrm{cm}^{-3}$ [3]. A high concentration of defects affects both the electronic and thermal properties such as electrical and thermal conductivity, thermopower, as well as the structural stability of the material, which together determine the effectiveness and practical value of the material for thermoelectric applications. In this study, along with measurements of electronic and transport properties, we use optical spectroscopy methods (Raman scattering and photoluminescence), as well as calculations using the density functional theory to study the relationship between the structural state determined by thermal history, the concentration of charge carriers and the electronic and phonon structure of germanium telluride.

The samples were produced by direct melting of the components in evacuated sealed quartz ampoules, followed by homogenizing annealing at a temperature of 770 K for 170 hours. After annealing, the ingot in the ampoule cooled down together with the furnace to 320 K for 20 hours. At high temperatures, GeTe has a cubic structure ($Fm\bar{3}m$), however, a transition to a rhombohedral α-phase which is ferroelectric ($R3m$) occurs at 700−720 K (depending on the vacancy concentration). It should be noted that at all cooling rates that were used in the experiments, at temperatures below 700 K, the samples had a rhombohedral structure, i. e. the phase transition from cubic to rhombohedral structure and vice versa always occurs under the conditions of our experiments. After synthesis and annealing, samples were prepared for the study of transport and optical properties. Measurements of the temperature dependences of the Hall coefficient and electrical resistance at temperatures of 100−800 K were carried out using original experimental setups [4,5]. The error in determining the Hall constant did not exceed ±5 %, and the electrical resistance ±2 %. When measuring the temperature dependences, the heating and cooling rate of the sample was 5−10 K/min. The samples for measuring transport properties had the lamella shape with typical dimensions $15 \times 8 \times 1$ mm. The vibrational and electronic characteristics of crystals were measured using micro-Raman scattering of light (μ-Raman) and micro-photoluminescence (μ-PL) using a LabRam HREvo UV-VIS-NIR-Open spectrometer (Horiba, France) with a confocal microscope and closed-cycle cryostat system RC-102 (Cryo Inc., USA). To excite the μ-Raman and the μ-PL spectra in the temperature range of 5−300 K, the line $\lambda = 632.8$ nm (1.96 eV) He−Ne-laser was used. The excitation density varied in the range from 1 to 50 kW/cm^2.

Our earlier results of studying electron transport showed that prolonged annealing of α-GeTe samples of nominally stoichiometric composition at a temperature of 600−650 K (below the rhombohedral–to–cubic structural transforma-

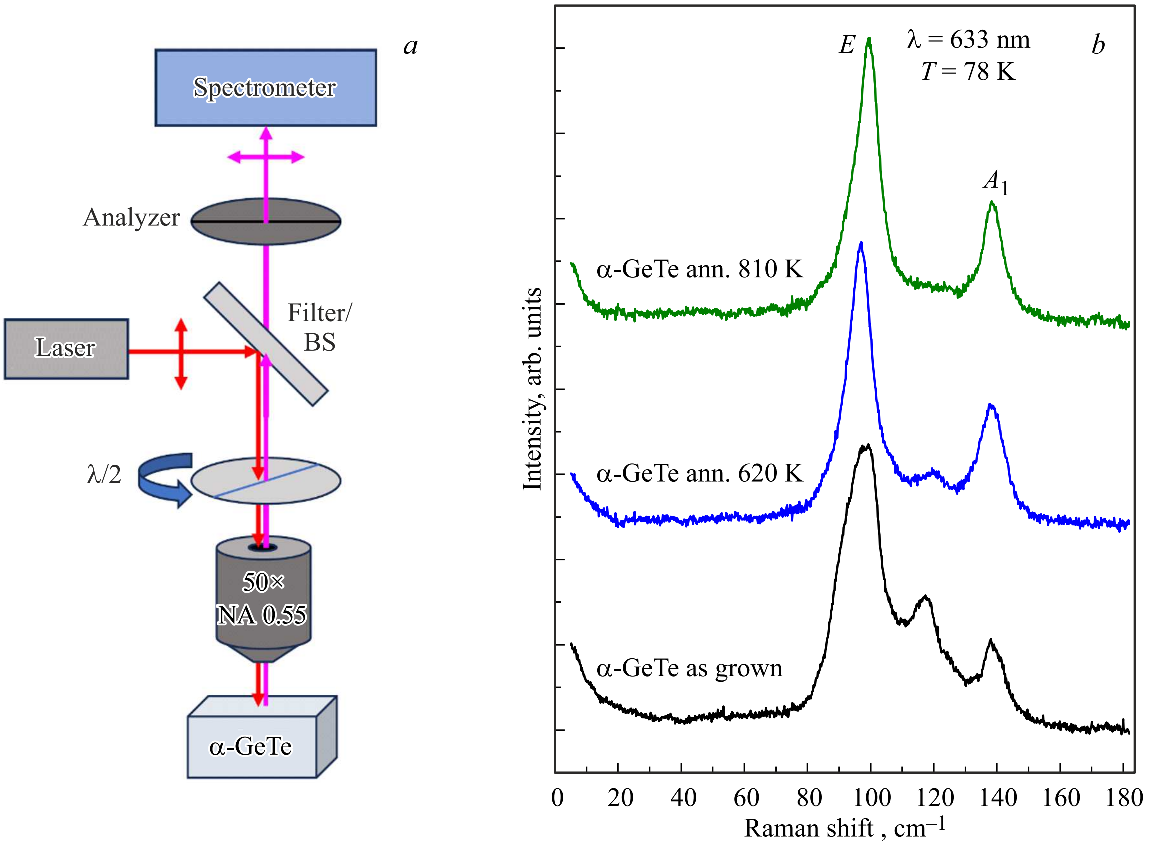

Figure 1. *a* — experimental scheme μ-Raman measurements with angular resolution. *b* — polarized μ-Raman spectra of the initial and annealed α-GeTe samples obtained at $T = 78$ K in the scattering geometry $x(yz)\bar{x}$, where z is the direction of the trigonal axis.

tion temperature) for about 100 hours leads to a decrease in charge carrier concentration, an increase in electrical resistance and an increase in mobility. In contrast, when the samples are heated to 800–820 K (above the temperature of structural transformation), the hole concentration increases, and their mobility decreases. This „high-temperature state“ with a higher concentration of charge carriers is metastable and persists during thermal cycling of samples in the range of 300–820 K at a rate greater than 1 K/min. „Low-temperature“ state can be restored by isothermal annealing at a temperature of 600–650 K for several tens of hours [6].

To shed light on the nature of the observed phenomena, comprehensive studies of the vibrational and electronic properties of α-GeTe samples of nominally stoichiometric composition annealed at temperatures of 620 K and 810–20 K were carried out.

The rhombohedral α-GeTe is a strongly anisotropic material. It was shown in Ref. [7] that the intensities of phonon modes of different symmetry in its Raman spectra depend differently on the angle between the direction of polarization of the incident radiation and the direction of the crystallographic axis of the crystal. Polarization measurements of the Raman spectra with angular resolution were performed to avoid possible errors when comparing the spectra of the polycrystalline α-GeTe samples we studied. The experimental scheme is shown in Figure 1, *a*. The linearly polarized exciting laser radiation first passed through a half-wave plate located in front of the focusing lens. Rotating the half-wave plate at a fixed angle made it possible to rotate the polarization of the incident radiation in the horizontal plane. In the „backscattering“ geometry used by us, the Raman radiation from the sample was collected by the same lens and passed through the same half-wave plate. As a result, the polarization vector of the radiation rotated by the same angle, but in the opposite direction. The rotation of the analyzer located in front of the entrance slit of the spectrometer made it possible to register either a parallel or a crossed component of the polarized Raman spectrum. This procedure made it possible to obtain the most reliable view of the Raman spectra of different samples, suitable for comparison. We plan to present the angular dependences of the Raman spectra obtained from various α-GeTe planes and their detailed analysis in an expanded publication.

In this paper, Figure 1, *b* shows the polarized Raman spectra obtained at $T = 78$ K for samples of bulk α-GeTe. Two main peaks are observed in these spectra, which are characteristic of the rhombohedral structural modification of GeTe. The first of them is attributed to the doubly degenerate transverse/longitudinal optical phonon mode of E ($\sim 99.8\,\mathrm{cm}^{-1}$), and the second is attributed to the

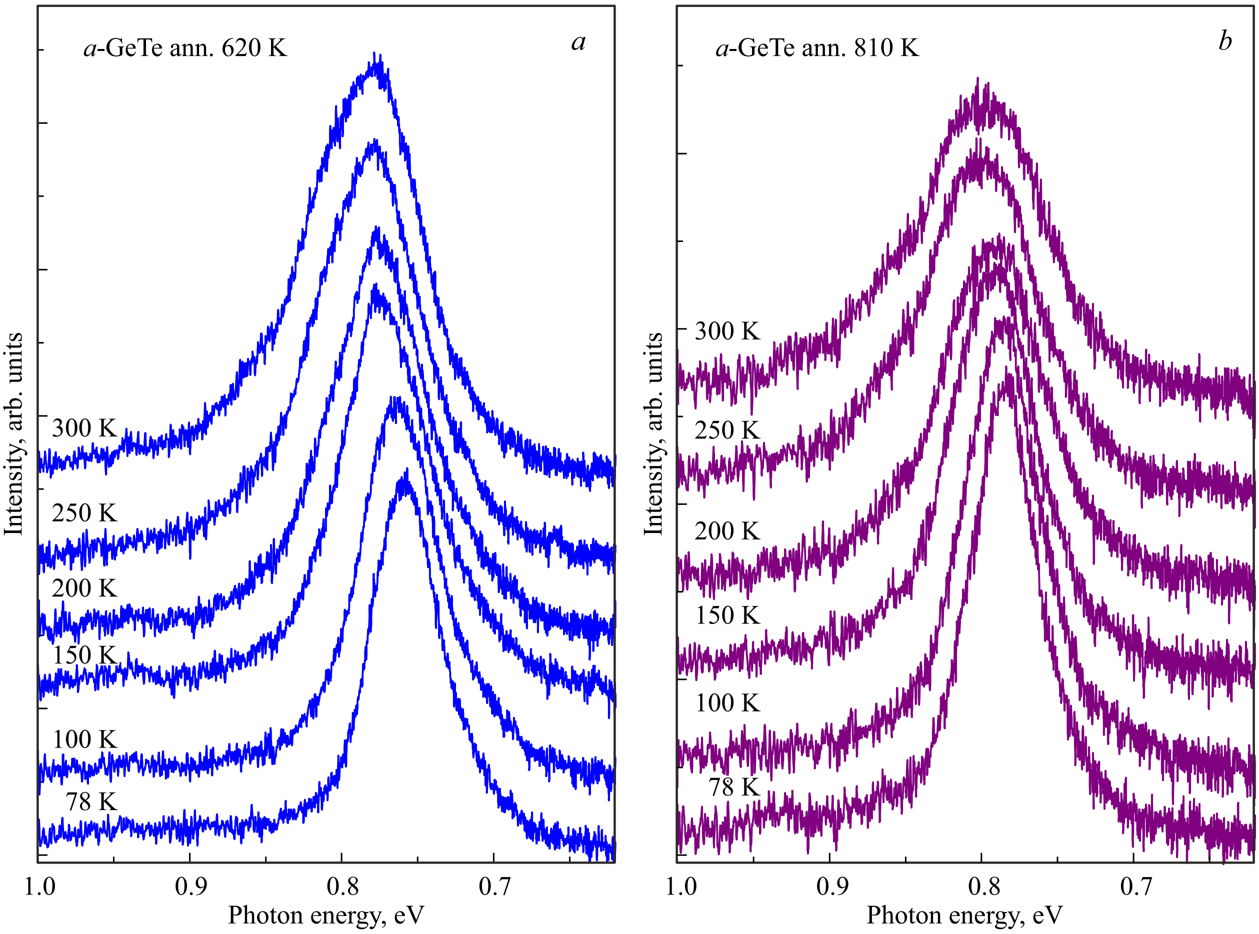

Figure 2. Dependence of PL spectra in the temperature range of $T = 300{-}78$ K for samples: *a* — α-GeTe (annealing at 620 K); *b* — α-GeTe (annealing at 810 K). $\lambda_{\text{ex}} = 633$ nm.

transverse optical phonon mode of A_1 ($\sim 138.5\,\text{cm}^{-1}$) [8]. In addition, in the spectrum of the sample that was not subjected to additional annealing, along with the phonon symmetry lines E and A_1 inherent in the rhombohedral structure, a feature with a maximum at $124\,\text{cm}^{-1}$ is clearly recorded, which either is significantly weakened or is not present in the spectra of samples annealed at temperatures of 620 and 820 K, respectively. Currently, the nature of this feature has not been reliably established, but the suppression of its intensity as a result of annealing undoubtedly indicates a decrease in the number of structural defects. The improvement of the structural characteristics of annealed samples is also supported by a significant decrease in the full width at half maximum (FWHM) of the phonon lines of E and A_1 symmetry compared with their FWHM in the spectrum of the non-annealed sample, which is a consequence of an increase in the lifetime of phonons due to a decrease in the number of structural defects.

IR PL was detected in the range of 0.7–0.8 eV in this study for all the studied α-GeTe samples, information about which, as far as we know, is not available in the literature. Figure 2, *a* and *b* show the transformation of the PL spectra of annealed α-GeTe samples in the temperature range of $T = 300{-}78$ K. For both samples, with a decrease in temperature, there is a shift of the PL maximum by $\sim 20{-}30$ meV in the low-energy direction and a decrease in the values of FWHM. The PL spectra of the same samples, measured at 5 K, are shown in Figure 3. It can be seen that the maxima of the PL peaks are shifted relative to each other in energy by ~ 28 meV. It was also found that with an increase in the density of exciting radiation, a high-energy band shift occurs in the PL spectra of both samples. Measurements of the Hall coefficient showed that the concentration of charge carriers (holes) of the sample annealed at 620 K (Figure 4, *a*) increases strongly with an increase in temperature above 600 K. When the sample is cooled after heating to 810 K, the hole concentration at a temperature of 100 K increases by about 30 % (from $6.2 \cdot 10^{20}$ to $8.6 \cdot 10^{20}\,\text{cm}^{-3}$). We assume that the shift of the maximum of the PL line after annealing at 810 K to higher energies is associated with an increase in the concentration of holes during short-term annealing at a temperature of 810 K.

Calculations of the electronic band structure were performed using the density functional theory to analyze the obtained PL spectra. The calculations used the gene-

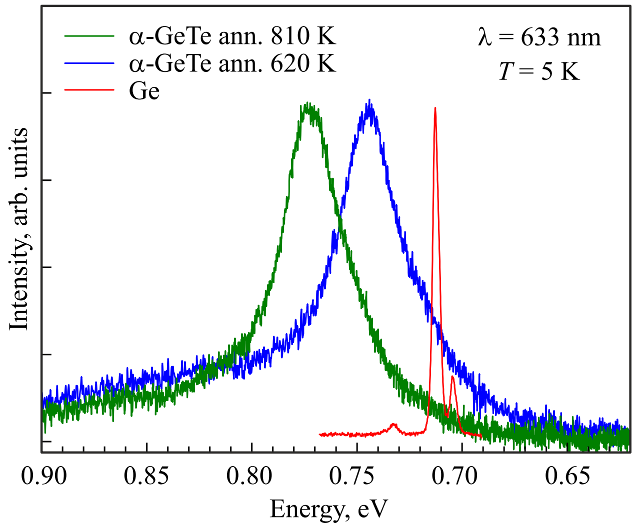

Figure 3. PL spectra of α-GeTe samples annealed at 620 and 810 K, and the PL spectrum of Ge measured at $T = 5$ K.

ralized gradient approximations for the density functional (GGA-PBE) in the VASP program [9,10]. The $12\times12\times12$ mesh in the Brillouin zone and the boundary energy 350 eV, which determines the number of plane waves, were used for the calculation. Optimization of the structure allowed to obtain equilibrium lattice parameters in the rhombohedral phase $a_0 = 4.3738$ Å and $\alpha = 57.9°$. In the PBE approximation, the angle α agrees well with the experimental value 58.0° [11], and the lattice constant turned out to be approximately 1.9 % higher than the experimental value for 309 K (4.2934 Å [11]). The electronic band structure for the rhombohedral phase is shown in Figure 4, *b*. The GeTe band structure in the high-temperature cubic modification is similar to that of lead telluride. Both compounds in the cubic phase are direct band gap semiconductors with the top of the valence band and the bottom of the conduction band located at the *L*-point of the Brillouin zone. There is also a deeper Σ-band in the valence band. In GeTe, as the temperature decreases, a rhombohedral distortion of the lattice occurs, the directions $\langle 111 \rangle$ become symmetry-inequivalent, which leads to the separation of four extrema at *L*-points of the cubic structure into two sets — three at *L* points and one at *Z*-point lying on the third-order axis of the rhombohedral structure. In addition, the valence Σ-band lying on the $\Gamma-P$ line turns out to be higher in energy in the rhombohedral phase than the valence bands at *L*- and *Z*-points. Germanium telluride becomes a indirect band gap semiconductor in the rhombohedral phase. Our calculations in the PBE approximation at the theoretical equilibrium lattice constant gave the value of the indirect band gap width of $E_g = 0.57$ eV, and the direct band gap width of 0.75 eV. GeTe samples almost always have a high concentration of holes due to the presence of Ge vacancies, therefore, the experimental data given in the literature for an optical band gap of 0.73–0.95 eV [12] correspond to a high doping level and a large Burstein-Moss shift.

A comparison of the calculated electronic spectrum with the position of the PL peak in the range of 0.7–0.8 eV suggests that it is associated with direct transitions between states in the conduction band and the valence band near the *L*-point. Estimates of the position of the chemical potential level for the measured Hall concentrations of holes show that it is located near the top of the valence bands at these points (Figure 4, *b*). The states near the top of the valence band are free for transitions of photoexcited electrons from the conduction band. The difference in the position of the chemical potential level for concentrations

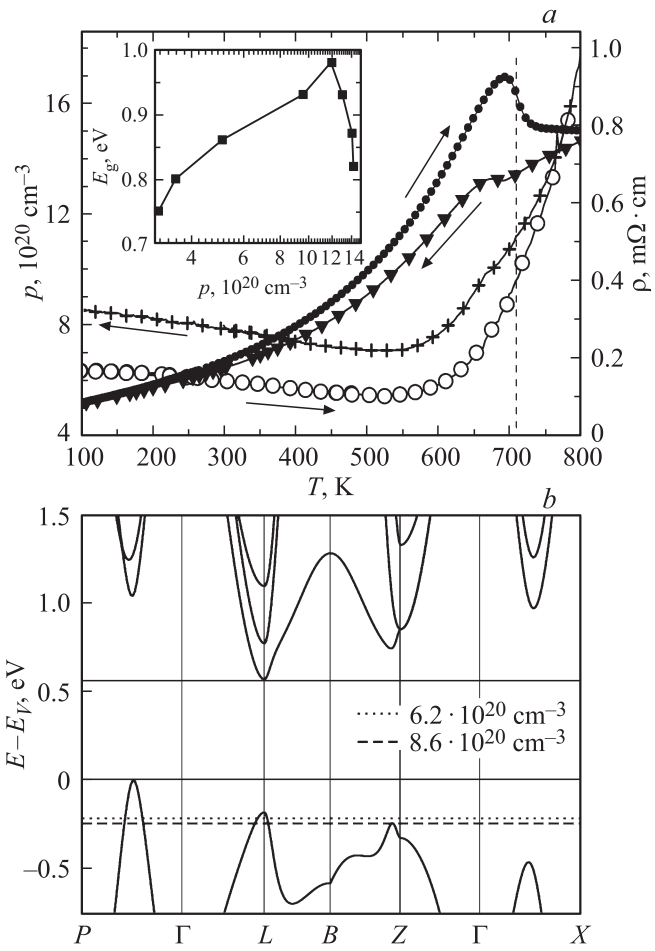

Figure 4. *a* — Hall concentration of holes (open circles — heating, crosses — cooling) and electrical resistance (black circles — heating, triangles — cooling) α-GeTe. The vertical dashed line shows the temperature of the phase transition from a rhombohedral to a cubic structure (when heated). The inset shows the dependence of the optical band gap α-GeTe, determined by the absorption edge [13]; *b* — the band structure of α-GeTe in the vicinity of the Fermi energy. The dotted and dashed horizontal lines show the position of the chemical potential for α-GeTe with the concentration of holes $6.2\cdot10^{20}$ and $8.6\cdot10^{20}$ cm^{-3}, respectively, determined from the Hall effect. The difference in the position of the chemical potential is about 30 meV and is in good agreement with the difference in peak energy of PL.

$6.2 \cdot 10^{20}$ and $8.6 \cdot 10^{20}\,\mathrm{cm}^{-3}$ is about 0.03 eV and is in good agreement with the difference in the energy of the PL peaks. The shift of the PL peak to the region of high energies with increasing temperature may be associated with an increase in E_g. Although there is information in the literature about the negative temperature coefficient E_g [13], the calculations performed indicate an increase in E_g with an increase in the lattice constant. In addition, it is known that in lead chalcogenides, the band gap also increases with temperature [14].

Thus, in this work we carried out a comprehensive studies of the vibrational and electronic properties of α-GeTe using the μ-Raman and μ-PL methods in combination with measurements of temperature dependences of electrical resistance and Hall coefficient over a wide temperature range. For the first time an infrared PL in the range of 0.7–0.8 eV was recorded in α-GeTe. A shift of the PL maximum by $\sim 20{-}30$ meV in the low-energy direction and a decrease in FWHM values is observed with a decrease in temperature. The position of the peaks of the PL maxima also depends on the Hall concentration of charge carriers (holes). A shift to the high-energy region is observed with increasing concentration. At a temperature of 5 K, with a change in concentration from $6.2 \cdot 10^{20}$ to $8.6 \cdot 10^{20}\,\mathrm{cm}^{-3}$, the maxima of PL peaks are shifted relative to each other in terms of energy by ~ 28 meV. It is shown that the magnitude of the shift of the PL maxima is in good agreement with the change in the position of the chemical potential level due to a change in carrier concentration.

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Conflict of interest

The authors declare that they have no conflict of interest.

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