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Structural Relaxation of Glassy $GeSe_2$ during Isothermal Annealing Below and Above T_g

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Abstract—Raman scattering, X-ray diffraction, and differential scanning calorimetry in the temperature range 300–800 K are used to show that, upon isothermal annealing of glass $GeSe_2$ powders below the glass-softening temperature ($T_g = 635 \pm 2$ K), fragments of high-temperature polymorphic modifications having no long-range order (HTPM polymorphoids) decompose and transform into low-temperature polymorphoids (LTPM) with an exothermic effect. A high concentration of LTPM polymorphoids in the glass and their stabilization upon annealing below T_g favor ordering and the appearance of coherent domains of low-temperature α-$GeSe_2$ (3D form). Upon annealing above T_g, the reverse LTPM $\longrightarrow$ HTPM polymorphoid transformation accompanied by an endothermic effect takes place, which results in the predominance of HTPM β-$GeSe_2$ polymorphoids (2D form) in glassy $GeSe_2$ and their crystallization.

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INTRODUCTION

Glassy germanium chalcogenides have long attracted attention due to their temperature-dependent properties and a wide use in integral optical devices [1].

Germanium diselenide has the following crystallographic modifications determined with Raman scattering and X-ray diffraction [2–9]: low-temperature (LT) α-$GeSe_2$ with a complex three-dimensional structure [2], high-temperature β-$GeSe_2$ with a layered two-dimensional structure [3], and γ-$GeSe_2$ with a structure similar to that of $SnSe_2$ [4]. Glassy or amorphous $GeSe_2$ (a-$GeSe_2$) consists of tetrahedral $GeSe_4$ structural units connected to each other through common vertices (LT phase) or common edges (HT phase of $GeSe_2$) [3].

The structural relaxation of glassy $GeSe_2$ in heating was studied in [9–12]. Upon annealing above T_g for ~100 h, crystalline LT and HT phases with a monoclinic structure (2D forms) having different lattice parameters were detected in bulk $GeSe_2$ glasses [9–11]. The HT phase (2D form) and the LT phase (3D form) of α-$GeSe_2$ with an orthorhombic crystal lattice were detected in amorphous $GeSe_2$ films upon annealing for 18 h at various temperatures [12].

According to the concept of a polymer–polymorphoid structure of glass and glass-forming liquids [13–15], the polymorphoids of the HT and LT modifications transform into each other in glass and generally accepted glass-softening temperature T_g is the temperature of the reverse $T_{\text{w-rev}}$ of the HTPM $\longleftrightarrow$ LTPM transformation.

The purpose of this work is to study the structural relaxation in glass $GeSe_2$ powders annealed at temperatures below and above T_g ($T_{\text{w-rev}}$) by Raman scattering, X-ray diffraction, and differential scanning calorimetry. The experimental results are analyzed in terms of the concept of a polymer–polymorphoid structure of glass and glass-forming liquids.

EXPERIMENTAL

$GeSe_2$ glasses were synthesized from special purity grade germanium (GPZ-1) and selenium (OSCh 17-4, TU 6-09-2521-77) in quartz ampules pumped down to 10^{-2} Pa during continuous stirring at a temperature of 1173 K for 20 h. The melts were quenched when the ampules were placed in running water.

Samples in the form of a dispersed $GeSe_2$ glass powder (average particle diameter of ~150 μm) compacted on a quartz glass 10 × 10 × 2 mm in size were situated in an IR-07 (Bruker) diffusion tube furnace heated to a certain temperature in the range (593–753) ± 1 K. Each sample was subjected to isothermal annealing in a nitrogen atmosphere at various temperatures for 20 min, removed from the furnace, and cooled to room temperature.

All annealed samples were studied on a Horiba LabRam HR800 spectrometer during excitation with the radiation of an He–Ne laser at a $\lambda = 632.8$ nm ($h\nu_{\text{exc}} = 1.96$ eV), a radiation power of ~20 mW, similar spectral parameters, and room temperature. A laser beam was focused into a spot 6 μm in diameter. To avoid photostructural changes in the samples, the energy flux density in recording Raman spectra was

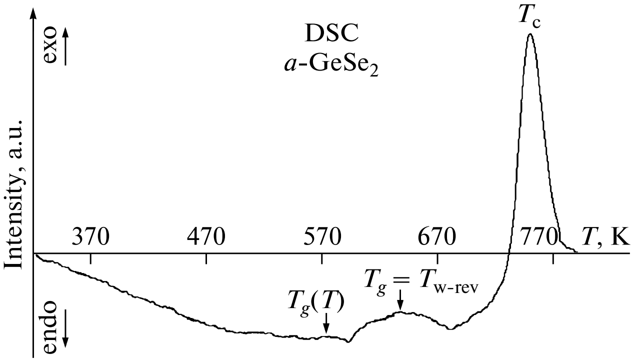

Fig. 1. DSC curve of the $GeSe_2$ glass recorded at a heating rate of 10 K/min. T_g is the generally accepted glass-softening temperature (viscosity $\eta \sim 10^{12.3}$ Pa s), which is the temperature of the reverse T_{w-rev} of the transformation of structural fragments in various high- and low-temperature polymorphic modifications (polymorphoids) of the substance that have no long-range order (HTPM $\longleftrightarrow$ LTPM). $T_g(T)$ is Tammann's glass-softening temperature (viscosity $\eta \sim 10^{15}$–10^{16} Pa s). T_c is the crystallization temperature of a-$GeSe_2$.

chosen to be 6×10^{-2} kWh/cm^2. Scattered light was collected using reflection geometry (180°), and the bandwidth of spectrometer slit was 2 cm^{-1}.

The phase composition of the annealed powder samples was determined by X-ray diffraction (XRD) analysis performed with a D2 Phaser (Bruker) diffractometer using CuK_α radiation at a wavelength $\lambda = 0.1548$ nm.

The characteristic temperatures of the $GeSe_2$ glass were estimated from differential scanning calorimetry (DSC) data obtained at an error of ±2 K and a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curve of the synthesized $GeSe_2$ glass that was recorded during its heating to complete crystallization at a rate of 10 K/min. The following effects are visible in this curve: two endothermic effects in the ranges 573–600 and 635–710 K with minima at 595 and 683 ± 2 K, respectively, and two exothermic effects in the ranges 600–635 and 710–780 K with maxima at 635 and 754 ± 2 K, respectively.

According to [16], an endothermic effect in the thermograms of glass in heating means its softening. The onset of the first endothermic effect at $T = 573 \pm 2$ K corresponds to Tammann's glass-softening temperature $T_g(T)$ (viscosity is $\eta \sim 10^{15}$–10^{16} Pa s). In the DSC curve, this temperature is lower than generally accepted T_g ($T = 635 \pm 2$ K, onset of the second endoeffect, viscosity $\eta \sim 10^{12.3}$ Pa s) [13, 14]. The maximum of the exothermic effect at $T = 754$ K corresponds to glass crystallization temperature T_c. Our data on T_g and T_c for $GeSe_2$ glass agree with the data in [17].

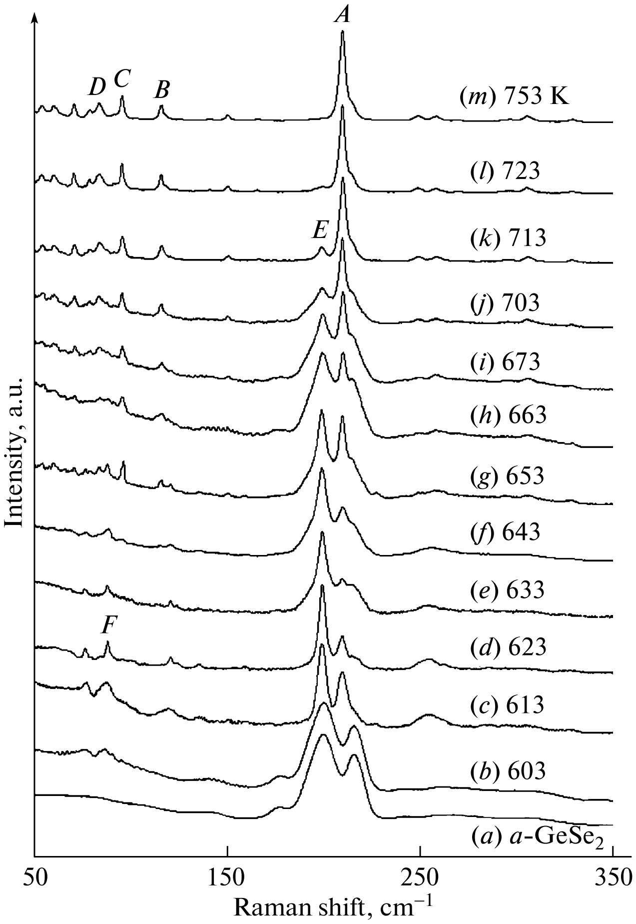

Fig. 2. Raman spectra of glass $GeSe_2$ powders annealed at various temperatures (*b*–*e*) below and (*f*–*m*) above T_g (T_{w-rev}) = 635 ± 2 K for 20 min. (*a*) Raman spectrum of an unannealed glass $GeSe_2$ powder. The annealing temperatures are indicated at the curves. The spectra were recorded in the frequency range 50–350 cm^{-1} at room temperature and were normalized by the maximum peak. Excitation was performed by the radiation of an He–Ne laser with $\lambda = 632.8$ nm ($h\nu_{exc} = 1.96$ eV) at a radiation power of 20 mW. Lines *A*, *B*, *C*, and *D* belong to a high-temperature (HT) phase with a layered structure (2D form), and lines *E* and *F*, to a low-temperature (LT) phase (3D form) of $GeSe_2$ [12].

According to the concept of a polymer–polymorphoid structure of glass and glass-forming liquids [13–15], we can assume that, in heating at a rate of 10 K/min in the temperature range 600–635 K (Fig. 1, below $T_g(T_{w-rev})$), the HTPM polymorphoids that are unstable at these temperatures decompose and transform into LTPM polymorphoids (HTPM $\longrightarrow$ LTPM) with heat release (exothermic effect). The exoeffect is followed by endoeffect (635–710 K) with an extremum at $T = 683$ K, which is the effect of the LTPM $\longrightarrow$ HTPM polymorphoid transformation.

Figure 2 shows the Raman spectra of the $GeSe_2$ samples annealed at temperatures below and above T_g (T_{w-rev}) = 635 ± 2K. These spectra were recorded in

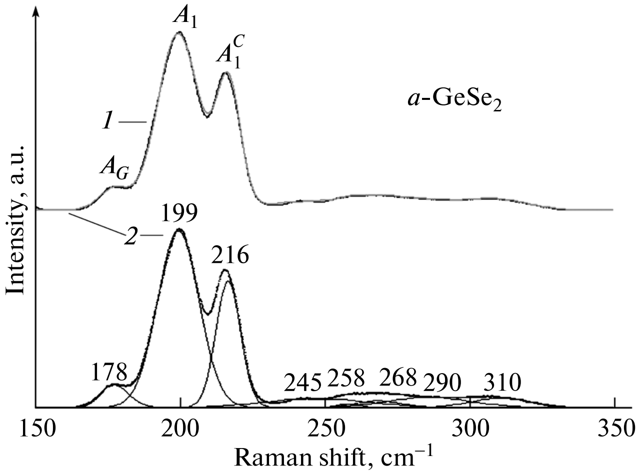

Fig. 3. Decomposition of the Raman spectrum of the $GeSe_2$ glass (without annealing) into Gaussian components: (*1*) experimental and (*2*) calculated resulting spectra. A_G mode corresponds to a weak Ge–Ge bond [19]; A_1, to the vibrations of $GeSe_{4/2}$ tetrahedra in LT α-$GeSe_2$ with common vortices (3D form); and A_1^C (216 cm^{-1}), to the vibrations of bridge $Ge_2Se_{8/2}$ bitetrahedra in HT β-$GeSe_2$ (2D form) [8].

the frequency range 50–350 cm^{-1} at room temperature and were identified with the PeakFit software package by decomposition into Gaussian components.

As a result of studying the Raman spectra recorded in the spectral range 150–350 cm^{-1}, we detected the following most intense vibrational modes: 178 (A_G), 199–200 (A_1), and 216 (211) (A_1^C) cm^{-1} (Figs. 3, 4). Modes at 178, 198, and 216 cm^{-1} appear in glassy $GeSe_2$ [18]. Mode A_G characterizes the weak Ge–Ge bond [19], and mode A_1 characterizes the vibrations of $GeSe_{4/2}$ tetrahedra in LT $GeSe_2$ (3D form) with common vertices (Fig. 2, peak *E*; Figs. 3, 4) [8, 12, 20, 21]. According to [5], mode A_1^C consists of the following two modes (Fig. 2, peak *A*; Fig. 3): a strong mode at 211 cm^{-1}, which belongs to the vibrations of $GeSe_{4/2}$ tetrahedron chains connected through vertices, and a weak mode at 216 cm^{-1}, which belongs to the vibrations of bridge $Ge_2Se_{8/2}$ bitetrahedra (as in HT $GeSe_2$ (2D form)). The coexistence of modes A_1 and A_1^C in glassy $GeSe_2$ indicates the presence of the polymorphoids of two crystalline forms of $GeSe_2$, namely, HT and LT forms, in the glass [8].

The Raman spectra of the annealed samples also have the following low-intensity modes: 245 (single Se_8 rings); 290 (Ge–Se–Ge bonds) [22]; 250–256 (line characteristic of a high Se_8 ring concentration); 257–260 (stretching vibrations in Se_n chains) [23];

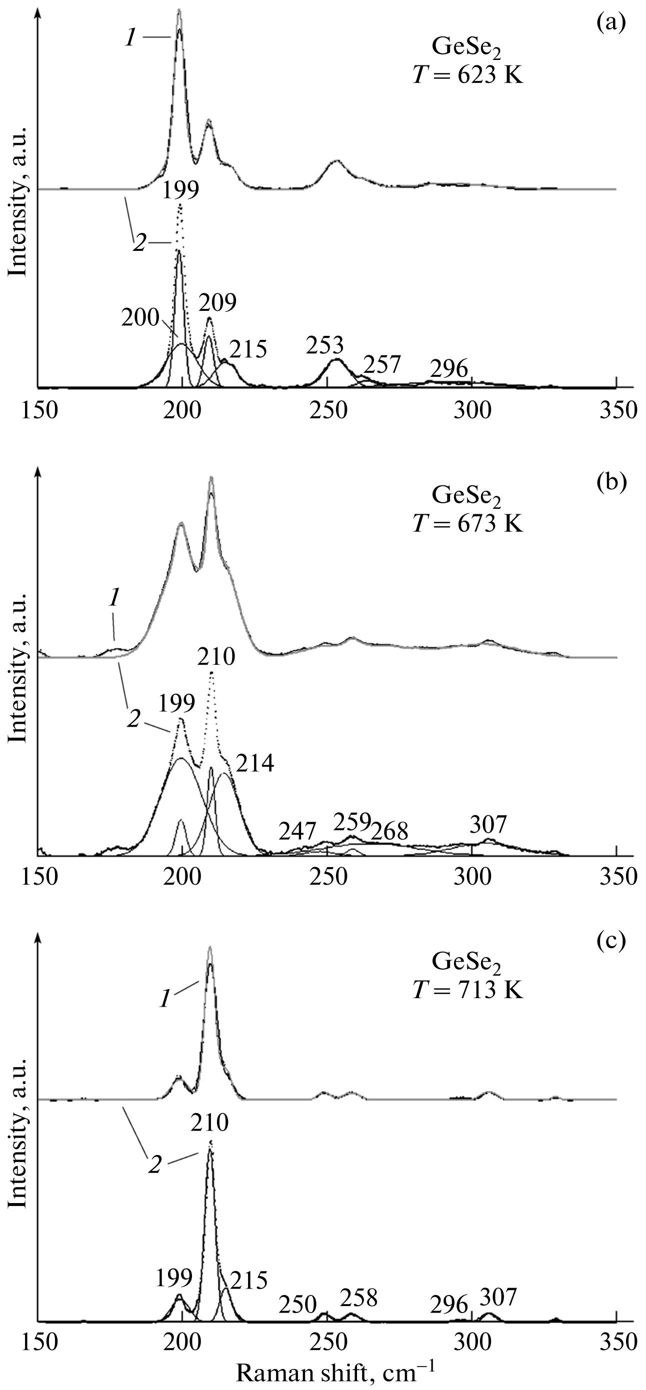

Fig. 4. Decomposition of the Raman spectra of the $GeSe_2$ glass powders annealed for 20 min at (a) 623, (b) 673, and (c) 713 K into Gaussian components: (*1*) experimental and (*2*) calculated resulting spectra. A_1^C mode consists of the following two modes: a strong mode at 211 cm^{-1}, which is related to the vibrations of the chains of $GeSe_{4/2}$ tetrahedra connected by common vertices, and a weak mode at 216 cm^{-1}, which is related to the vibrations of bridge $Ge_2Se_{8/2}$ bitetrahedra in HT β-$GeSe_2$ (2D form) [8].

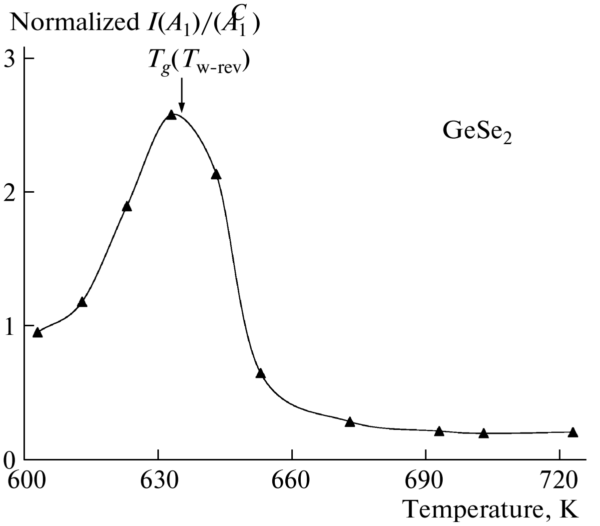

Fig. 5. Ratio of the integrated intensities of modes A_1 (LTPM) and A_1^C (HTPM) as a function of temperature. The data were taken from the Raman spectra of glass $GeSe_2$ powders after isothermal annealing. The ratios were normalized by the ratio obtained at $T = 293$ K. The errors are within the symbols.

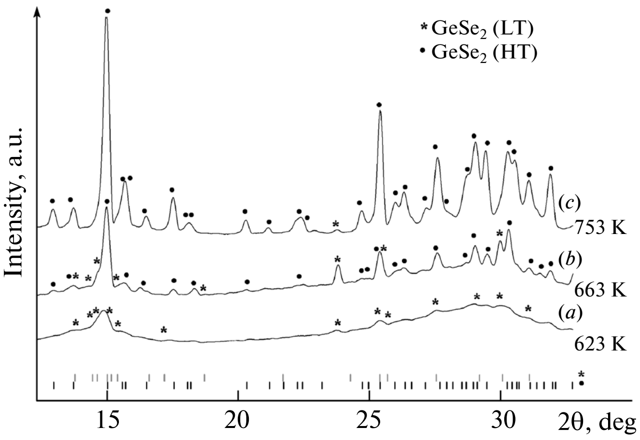

Fig. 6. (Curves *a*–*c*) X-ray diffraction patterns of glass $GeSe_2$ powders annealed at various temperatures (±1 K) in the range 593–753 K at a step of 10 K for 20 min in a nitrogen atmosphere. The annealing temperatures are indicated at the curves. The X-ray diffraction patterns were normalized by the maximum peak intensity. (*), (●) Reflection lines of the crystal lattices of the LT (3D form) and HT (2D form) phases of $GeSe_2$, respectively. At the bottom, the bar X-ray diffraction patterns of these phases ([PDF 01-071-0117] and [PDF 00-016-0080], respectively).

and 252, 268, 297, and 307 cm^{-1} (bond vibrations in HT $GeSe_2$) [24].

The Raman spectra of the powder samples annealed at below 600 K for 20 min turn out to be similar to the spectrum of the unannealed sample (Fig. 2, curve *a*), which in turn is identical to the Raman spectrum of $GeSe_2$ glass presented in [9, 25]. At annealing temperatures below 600 K, the ratio of the integrated intensities of modes A_1 and A_1^C (i.e., the concentration ratio of the polymorphoids (CRP) of the 3D and 2D forms) in the glass remains almost the same.

At $T_{ann} \longrightarrow T_g$ (T_{w-rev}) = 635 ± 2 K, the Raman spectra have line *F*, which is attributed to the LT phase (3D form, Fig. 2, curves *c*–*e*) [12]. The ratio of the integrated mode intensities $I(A_1)/I(A_1^C)$ normalized by this ratio at $T = 293$ K becomes higher than unity (Fig. 5). This finding points to the fact that 3D form polymorphoids (mode A_1) in glassy $GeSe_2$ begin to dominate over 2D polymorphoids (mode A_1^C) to a greater extent than in the unannealed sample. The concentration of LTPM polymorphoids increases sharply due to the decomposition of HTPM polymorphoids (Fig. 2, curves *d*, *e*, Fig. 5), which are unstable at these temperatures, and to the HTPM ⟶ LTPM transformation, which has an exothermic effect (Fig. 1).

The X-ray diffraction patterns of the powder samples subjected to isothermal annealing for 20 min at $T_{ann} \longrightarrow T_g$ (T_{w-rev}) = 635 ± 2 K contain reflection lines in the angular range $2\theta = 5°–100°$ against the background of an amorphous halo (Fig. 6a). These lines are close to the reflection lines of the crystalline phase of orthorhombic LT α-$GeSe_2$ (space group *Pmnm*; lattice parameters $a = 0.6953$ nm, $b = 1.222$ nm, $c = 2.304$ nm [2, PDF 00-016-0080]. A high concentration of LTPM polymorphoids in the glass and their stabilization upon annealing below T_g (T_{w-rev}), $T_{ann} < T_c$, are likely to favor ordering and the appearance of coherent domains. In [26], we also detected nonequilibrium LT crystalline phases stabilized in a glassy matrix in amorphous Ge–Se nanofilms.

The stability of the 3D form was also detected in amorphous $GeSe_2$ films annealed below T_g (T_{w-rev}) [12]. Our results correlate with the results of that work, where the crystalline LT α-$GeSe_2$ phase with an atomic surrounding that is similar to that of the α-GeS_2 phase was also detected in the samples annealed at $T_{ann} < T_g$ (T_{w-rev}) for 18 h.

The authors of [11] found that bulk $GeSe_2$ glasses are resistant to crystallization and that their crystallization requires thermal annealing for 60–100 h. In [9–11], bulk $GeSe_2$ glass was annealed at $T_{ann} > T_g$; as a result, it fully crystallized into the LT and/or HT phase of $GeSe_2$ with a monoclinic crystal lattice (2D form).

When our samples were heated at $T_{ann} > T_g$ (T_{w-rev}) = 635 ± 2 K, glassy $GeSe_2$ transformed into the region of stable HTPM polymorphoids and unstable LTPM polymorphoids, as in [9–11]. Up to ~650 K, 3D polymorphoids still dominate over 2D polymorphoids (Fig. 2, curve *f*, 5), as in the unannealed sample (Fig. 2, curve *a*), but actively transform into them (LTPM ⟶ HTPM) with heat absorption (endoeffect with an extremum at $T = 683$ K; Fig. 1). At $T_{ann} > 650$ K, the ratio of the integrated mode intensities $I(A_1)/I(A_1^C)$ (LTPM/HTPM CRP) becomes lower than in the unannealed sample; at $T_{\text{ann}} = 653$ K, the integrated intensities of modes A_1 and A_1^C become equal to each other (Fig. 2, curve *g*).

As T_{ann} increases further, 2D form polymorphoids (A_1^C) begin to dominate in glassy GeSe_2 (Fig. 2, peak *A*; Figs. 4b, 4c, 5). Lines *B*, *C*, and *D*, which were attributed to HT β-GeSe_2 [12], appear in the Raman spectra (Fig. 2, curves *g*–*m*). The X-ray diffraction patterns of the annealed GeSe_2 samples (Fig. 6, curves *b*, *c*) have the reflections of monoclinic HT β-GeSe_2 (space group *P*21/*c*; lattice parameters $a = 0.7016$ nm, $b = 1.6796$ nm, $c = 1.1831$ nm, $\beta = 90.65°$ [3, PDF 01-071-0117]). At $T_{\text{ann}} > 710$ K, X-ray diffraction patterns have reflections from only HT β-GeSe_2 (Fig. 6, curve *c*). At $T_{\text{ann}} \longrightarrow T_{\text{c}}$, complete crystallization of the samples take place (Figs. 1, 2, curve *m*).

CONCLUSIONS

Based on the concept of a polymer–polymorphoid structure of glass and glass-forming liquids, we performed a comparative structural analysis of the results of investigating GeSe_2 glass powders annealed at various temperatures below and above T_g ($T_{\text{w-rev}}$) = 635 ± 2 K by Raman scattering, XRD, and DSC.

It was found that the temperature dependence of the normalized ratio of the integrated mode intensities $I(A_1)/I(A_1^C)$ (HTPM/LTPM CRP) in the glass was nonmonotonic. During isothermal annealing below T_g ($T_{\text{w-rev}}$), HTPM polymorphoids decompose and transform into LTPM polymorphoids (HTPM ⟶ LTPM) with heat release (exothermic effect) up to the appearance of coherent LT-GeSe_2 domains (3D forms). In this case, the normalized ratio is $I(A_1)/I(A_1^C) > 1$.

When the samples are annealed at temperatures above T_g ($T_{\text{w-rev}}$), the LTPM ⟶ HTPM transformation accompanied by heat absorption (endoeffect) occurs. As a result, HTPM polymorphoids (2D forms) are predominant in glassy GeSe_2 and crystallize ($I(A_1)/I(A_1^C) < 1$).

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