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Raman and Photoluminescence Spectra of Crystalline and Glassy GeS$_{2x}$Se$_{2-2x}$ Solid Solutions

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Abstract—We have studied the effects of compositional and structural disorder on the Raman and photoluminescence (PL) spectra of crystalline and glassy GeS$_{2x}$Se$_{2-2x}$ solid solutions. The influence of structural disorder (variations in bond lengths and bond angles at the vertices of [GeX$_4$] (X = S, Se) tetrahedra) is shown to be comparable to that of local inhomogeneities in the solid solutions. The PL spectra of the crystalline phases are, on the whole, similar to those of the glasses: they show one, broad emission band, which shifts to lower photon energies in going from the crystals to glasses over the entire solid-solution series. The luminescence excitation spectra of the crystals differ markedly from those of the glassy solid solutions. In contrast to crystalline GeS$_2$ and GeSe$_2$, the solid solutions exhibit PL fatigue. Our results indicate that radiative processes in the crystalline and glassy GeS$_{2x}$Se$_{2-2x}$ solid solutions are determined by native point defects and depend little on the degree of long-range ordering, whereas nonradiative processes are rather sensitive to topological disorder in the structure of the solid solutions.

INTRODUCTION

The high-temperature (β) forms of crystalline GeS$_2$ and GeSe$_2$ have monoclinic structures (sp. gr. $P2_1/c$) and are close in unit-cell parameters [1], which suggests that they are likely to form solid solutions. Indeed, differential thermal analysis, x-ray diffraction (XRD), and far-IR spectroscopy results [2, 3] demonstrate that these chalcogenides form a continuous series of substitutional solid solutions, GeS$_{2x}$Se$_{2-2x}$ (0 < x < 1).

Crystalline substitutional solid solutions are of considerable interest because they are intermediate in structure between ideal crystals and disordered condensed systems (glasses and liquids). A salient feature of the GeS$_2$–GeSe$_2$ system is that its end-members form a continuous series of solid solutions in both crystalline and glassy states [1, 3].

Theoretically, the two states of GeS$_{2x}$Se$_{2-2x}$ solid solutions correspond to two distinct types of disorder: compositional (substitutional) and structural (topological) [4]. The glassy solid solutions are disordered both structurally and compositionally.

The effect of structural disorder on vibrational spectra and photoluminescence (PL) has only been studied for glassy GeS$_{2x}$Se$_{2-2x}$ solid solutions [3, 5, 6]. No less important is to study the effect of compositional disor-der on the spectra of crystalline solid solutions since real solid solutions are, as a rule, locally inhomogeneous.

Most solid solutions of crystalline semiconductors are weakly disordered systems in which the large-scale fluctuation potential resulting from random atomic substitutions leads to localization and scattering of charge carriers and excitons, which shows up in their optical spectra. At the same time, large-scale composition fluctuations, characterized not only by large sizes but also by large amplitudes, give rise to antiparallel modulation of energy bands (the characteristic length scale of fluctuations exceeds the de Broglie wavelength and mean free path of charge carriers) and more significant changes in the electronic properties of the solid solution.

In this paper, we analyze the effect of structural disorder on the Raman and PL spectra of crystalline and glassy GeS$_{2x}$Se$_{2-2x}$ solid solutions.

EXPERIMENTAL

Polycrystalline GeS$_{2x}$Se$_{2-2x}$ solid solutions were synthesized by melting appropriate mixtures of elemental Ge, S, and Se sealed in silica ampules 20–22 mm in diameter and 160–180 mm in length under a vacuum of 10^{-3} Pa. The melt was homogenized

by vibration stirring. The highest synthesis temperature was 1300 K.

To prepare glass samples, the melt (10 g) was cooled from 40–50 K above the corresponding liquidus temperature by lowering the ampule to ice water. The glassy state was evidenced by characteristic luster and conchoidal fracture, and was checked by XRD and microstructural examination.

Samples for spectroscopic measurements had the form of rectangular plates, which were cut from glass monoliths and were then ground and polished.

Single crystals of $GeS_{2x}Se_{2-2x}$ solid solutions were grown by closed-tube physical vapor transport. To this end, the synthesized polycrystalline material was driven to one end of the ampule by shaking it, without breaking the vacuum. Next, the ampule was mounted in a two-zone tubular electrical furnace (tilted 30° to the horizontal), and the desired temperature gradient was applied.

The (empirically selected) optimal conditions for the growth of perfect $GeS_{2x}Se_{2-2x}$ crystals were as follows: sublimation source temperature, 1000 K; growth temperature, 900 K; growth time, 24–30 h.

The formation of a continuous series of crystalline substitutional solid solutions in the GeS_2–$GeSe_2$ system was ascertained by XRD (the unit-cell parameters as functions of composition were found to follow the additivity rule). The composition (x) of the $GeS_{2x}Se_{2-2x}$ mixed crystals was determined by x-ray microanalysis. Forward-reflection x-ray Laue photographs confirmed that all of the solid solutions were isostructural with the high-temperature, monoclinic (β) forms of the end members (sp. gr. $P2_1/c$). The solid solutions were similar in crystal habit to the constituent chalcogenides. The vapor-grown crystals of the layered solid solutions had tabular habits with mirror-smooth faces and were up to $10 \times 15 \times 2$ mm in dimensions. The c axis was normal to the cleavage plane.

In Raman measurements, excitation was provided by a 40-mW 638.2-nm He–Ne laser beam, and the spectra were taken on a DFS-24 spectrometer in a 90° geometry with a 0.5-cm^{-1} resolution.

PL and excitation spectra were recorded with a standard system, using two (MDR-23 and DMR-4) monochromators, one for measuring the excitation spectrum and the other for analyzing the spectral distribution of the PL. The PL was excited by a DKSSh-1000 lamp or LGI-21 pulsed laser. The PL signal was synchronously detected using a standard setup. Recombination radiation was detected using a PbS photoresistor.

RESULTS AND DISCUSSION

Raman spectra. Figures 1 and 2 show the Raman spectra of crystalline and glassy $GeS_{2x}Se_{2-2x}$ solid solutions. Factor group analysis and polarized Raman

spectra of the stable crystalline phases (α and β) of germanium dichalcogenides were presented in [7–9]. The basic structural components of the high-temperature (β) phases are four types of $[GeX_4]$ tetrahedra, differing in distortion [1]. The tetrahedra are arranged so as to form double chains, which are linked by edge-shared double tetrahedra, $[Ge_2X_6]$. These tetrahedra serve as bridging elements in the layered basis of the β phase. Within the layers, the tetrahedra share edges or vertices so as to form pairs, which, in turn, form rings of eight tetrahedra, $[Ge_8X_{22}]$ $(2[Ge_2X_7] + 2[Ge_2X_6] - 4X)$. The unit cell of the β phase contains 48 atoms, residing in two layers. The layers are linked by chalcogen–chalcogen bonds, which are considerably longer than those in the chains and rings.

Analysis of the Raman results for the crystals and glasses shows that the Raman spectra are dominated by the normal modes of the $[GeX_4]$ tetrahedra. Any tetrahedron has four Raman-active modes (A_1, E, E_1, and F_2); A_1 possesses the highest symmetry and is usually the strongest. The spectra of dilute crystalline $GeS_{2x}Se_{2-2x}$ solid solutions show a large number of high- and low-frequency Raman bands identical in position and relative intensity to those in the spectrum of the host component. Interpretation of the spectra is facilitated by the fact that the high- and low-frequency groups of vibrational modes do not overlap and are easy to identify.

The compositional disorder in the layered structure of the crystalline $GeS_{2x}Se_{2-2x}$ solid solutions leads to drastic changes in phonon spectrum, both at low and high frequencies (Fig. 1). Even comparatively low solute concentrations sharply reduce the number of low-frequency modes and change their position and relative intensity. This indicates that the low-frequency interlayer vibrations in the dilute crystalline solid solutions are the first to be disturbed by substitutions on the chalcogen site. At the same time, the high-frequency, intralayer modes in the dilute solid solutions are considerably less disturbed and remain essentially unchanged even at significant solute concentrations: from $x = 0$ to 0.2 and from $x = 0.8$ to 1. These findings lead us to conclude that, in the layered structure of the compositionally disordered crystalline $GeS_{2x}Se_{2-2x}$ solid solutions, the chalcogen atoms which are linked by bridge bonds to form chains of tetrahedra are the first to be substituted by solute atoms.

Further increase in solute concentration ($x > 0.2$) in the crystalline solid solutions is accompanied by gradual changes in the relative intensity of the stretching modes of the host component and an increase in their width. The Raman lines of the solid solutions become notably broader because the disordered distribution of atoms gives rise to significant local strain and a scatter in the bond angle at the vertices of the $[GeX_4]$ tetrahedra forming the chains, resulting in distortion of the
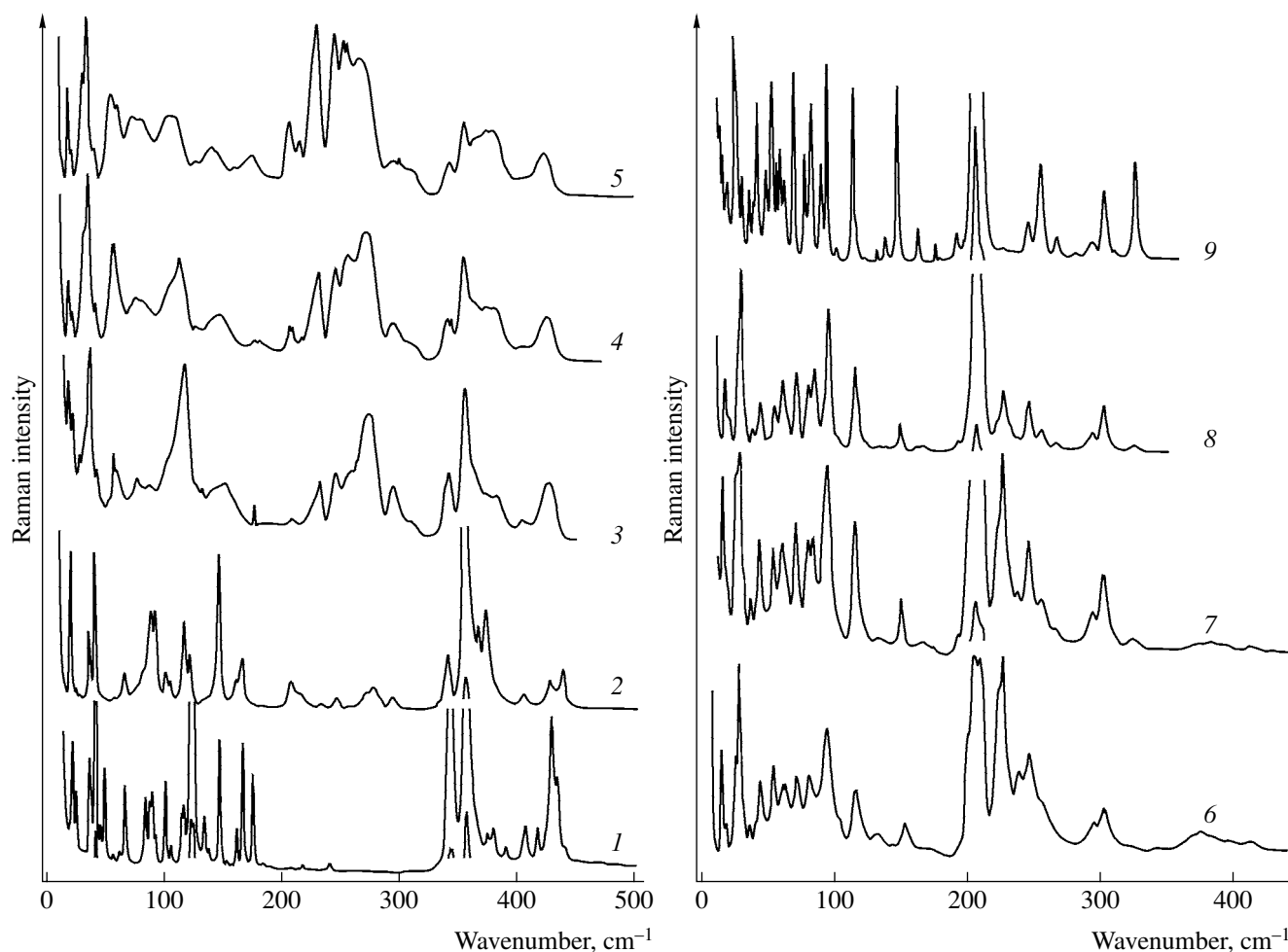
Fig. 1. 293-K Raman spectra of crystalline $GeS_{2x}Se_{2-2x}$: $x = (1)$ 1, (2) 0.95, (3) 0.7, (4) 0.6, (5) 0.5, (6) 0.2, (7) 0.1, (8) 0.05, (9) 0.

chains. At a sufficiently high solute concentration, the spectrum shows complex (local) gap Raman modes due to the solute atoms.

It is of interest to note that the gap modes, due to the solute tetrahedra, are not characteristic of the tetrahedra in the host crystalline germanium dichalcogenide and differ in frequency from the strongest stretching modes of the $[GeX_4]$ tetrahedron. In particular, the Raman spectra of the GeS_2-based solid solutions show gap modes at 297, 282, and 274 cm^{-1}, whereas the strongest band in the spectrum of germanium selenide, A_1, is peaked at 211 cm^{-1}. At moderate solute concentrations, the Raman spectra of the solid solutions do not show the strongest bands of the solute, and we observe only changes in relative intensity in the frequency range of the bands already present in the spectrum. Note also that the frequencies of the gap modes are higher than the stretching frequencies of the constituent chalcogenides.

The high-frequency features in the Raman spectra of the crystalline solid solutions containing nearly equimolar amounts of the constituent chalcogenides vary significantly in intensity, number, and width (Fig. 1, spectra *3–5*). Clearly, the marked changes in the shape of the Raman spectrum reflect the topological (structural) disordering associated with the severe distortion of the $[Ge(S,Se)_4]$ tetrahedra and, accordingly, the chains formed by these tetrahedra because of the differences between the Ge–S and Ge–Se bond lengths and between the Ge–S–Ge and Ge–Se–Ge bond angles.

If the solute is $GeSe_2$, its vibrational modes are close in parameters to those in the Raman spectrum of the glassy solid solution with the same composition (Figs. 1, 2, spectra *3–5*). If the solute is GeS_2, an analogous conclusion cannot be drawn at relatively low solute concentrations because the Raman bands of GeS_2 are then too weak. Topological disorder in the nearly equimolar crystalline solid solutions is evidenced by the similarity between the Raman spectra of crystalline and glassy phases of the same composition. At the same time, the high- and low-frequency features due to weak interaction are missing in the spectrum of the glassy phase.
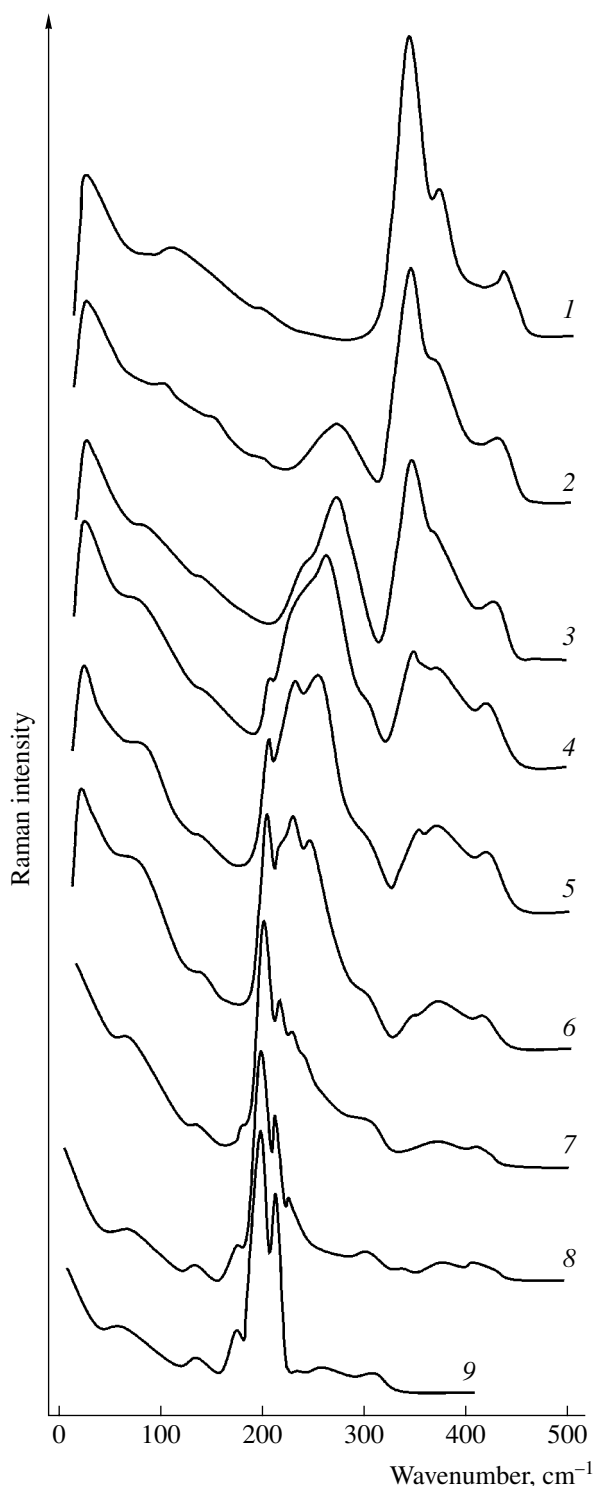
Fig. 2. 293-K Raman spectra of glassy $GeS_{2x}Se_{2-2x}$: $x =$ (*1*) 1, (*2*) 0.9, (*3*) 0.8, (*4*) 0.6, (*5*) 0.5, (*6*) 0.4, (*7*) 0.2, (*8*) 0.1, (*9*) 0.

The glassy $GeS_{2x}Se_{2-2x}$ solid solutions consist of self-limited ordered clusters (SLOCs) a few nanometers in average size, similar in structure to the crystalline solid solutions. The SLOCs are close in at least

medium-range order to the corresponding crystals. However, because of the small bond angle at the vertices of the tetrahedra ($\sim$100°), the glassy solid solutions contain loosely packed, heavily distorted tetrahedra. As a result, the SLOCs are separated by a system of molecular-scale dipole channels and dislocation quadrupoles, there is no long-range order, and the glassy material has a reduced band gap. In addition, the fine structure of the Raman spectrum, as is observed in the case of isotopic disorder, disappears. Because the Raman spectra of glasses lack fine structure, interlayer vibrations cannot be analyzed based on low-frequency features, and one have to rely only on the intensity of the companion mode A_1^c, peaked at 212 cm^{-1} in the spectrum of glassy $GeSe_2$ [10–12]. This mode is due to vibrations of bridging selenium atoms and disappears even at low sulfur concentrations in the solid solutions.

Note that the high-frequency spectrum of the glassy solid solutions is bimodal and that the intensity of the longest wavelength bands of the [GeS$_4$] and [GeSe$_4$] tetrahedra decreases most significantly. This attests to replacement of chalcogen atoms in the four-membered rings—first of all, in those with the weakest bonds. The first incorporated solute atoms are however incapable of forming bonds characteristic of them because the covalently bonded atoms of the rings prevent it. As a result, the spectrum of the topologically disordered solid solutions is bimodal, and the strongest band shifts systematically to longer wavelengths with increasing solute concentration because of gradual changes in the composition and structure of the ring. In this regard, the vibrational spectra of isotopically and topologically disordered $GeS_{2x}Se_{2-2x}$ solid solutions are identical.

The data above lead us to conclude that, in both isotopically and topologically disordered $GeS_{2x}Se_{2-2x}$ solid solutions, the solute atoms substitute first for the bridging chalcogen atoms and then for the chalcogen atoms in the four-membered rings.

PL spectra. Figures 3–5 present the 77-K PL and excitation spectra of crystalline and glassy $GeS_{2x}Se_{2-2x}$ solid solutions. Comparison of the PL data for crystalline and glassy $GeSe_2$ and GeS_2 with those of the $GeSe_2$- and GeS_2-based solid solutions reveals the following general trends:
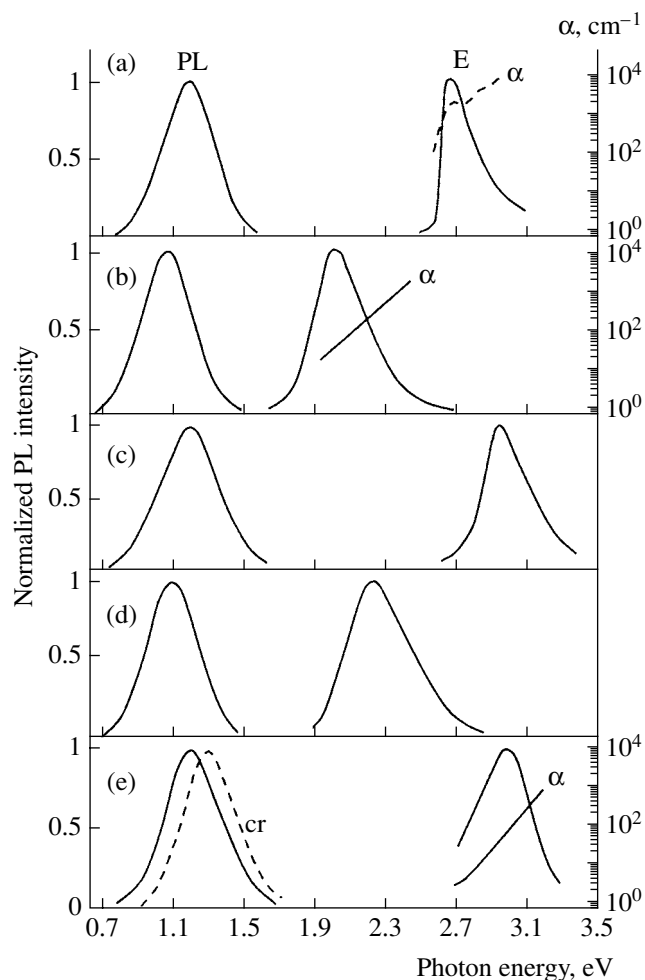
1. The PL spectra of the crystalline chalcogenide solid solutions are, on the whole, similar, to those of the glasses: the spectra show one strong, broad emission band centered at a photon energy less than half the band gap. In going from crystals to the glass of the same composition, the PL band shifts to lower photon energies. The large width and asymmetric shape of the PL band suggest that it consists of several elementary components. This assumption is also supported by the results of decomposing the emission spectra of Ge_xSe_{1-x} nonstoichiometric glasses [13].
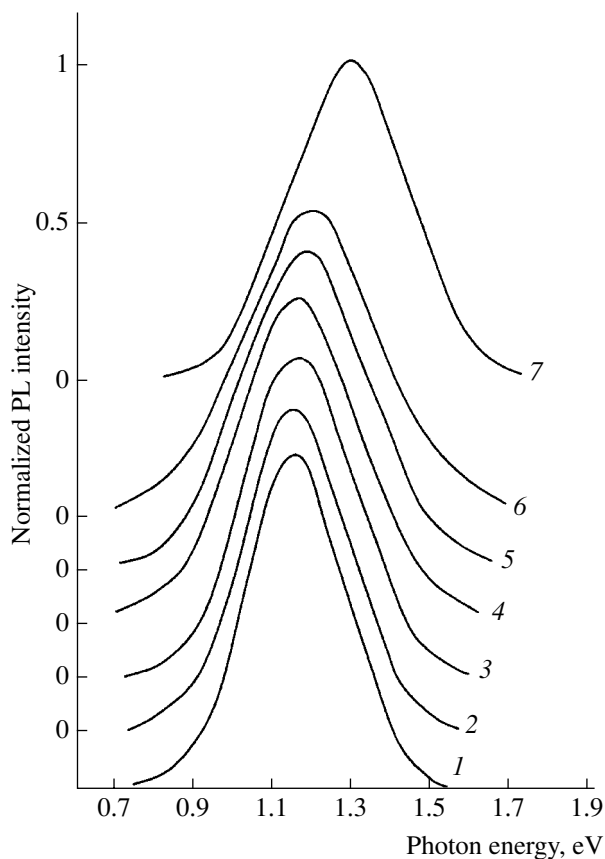
Fig. 3. 77-K PL spectra of crystalline GeS$_{2x}$Se$_{2-2x}$: $x =$ (*1*) 0, (*2*) 0.2, (*3*) 0.5, (*4*) 0.6, (*5*) 0.7, (*6*) 0.85, (*7*) 1.

Fig. 4. 77-K PL, excitation (E), and edge absorption (α) spectra of (a, c) crystalline and (b, d, e) glassy (a, b) GeSe$_2$, (c, d) GeS$_{2x}$Se$_{2-2x}$, and (e) GeS$_2$.

2. The PL of all the crystalline solid solutions results from above-band-gap excitation. The peak emission energy in the excitation spectra of the crystalline phases corresponds to absorption coefficients $\alpha > 10^2$ cm^{-1} at the intrinsic edge. In the temperature range 4.2–77 K, the maximum in the excitation spectrum of crystalline GeSe$_2$ matches the excitonic absorption (Fig. 4). In contrast, the peak emission energy in the excitation spectra of the glasses corresponds to $\alpha = 80$–100 cm^{-1} in the exponential portion of the intrinsic edge. This indicates that the luminescence excitation is due to optical transitions involving localized states in band tails. Sulfur substitution for selenium in both the crystalline and glassy solid solutions shifts the excitation band to higher photon energies (Figs. 4, 5), and the shift correlates with the increase in band gap in going from GeSe$_2$ to GeS$_2$.

3. Crystalline and glassy GeSe$_2$ and GeS$_2$ exhibit no PL fatigue effect (at least at low excitation intensities), in contrast to arsenic chalcogenides (As$_2$S$_3$ and As$_2$Se$_3$) [14]. Both types of disorder in the solid solutions under consideration gives rise to PL fatigue. The magnitude of the effect depends on composition, with a maximum at $x = 0.5$.

4. We observe a significant Stokes shift, $W_S = E_{ex} - E_{PL}$, which is substantially larger for the crystalline phases. Thus, the luminescence of the crystalline and glassy germanium dichalcogenide solid solutions is always accompanied by nonradiative excitation relaxation in the excited and ground states of the emission center. Nonradiative transitions underlie Stokes' law and energy-to-heat conversion. The excitation energy may relax through vibrational sublevels of one electronic state and through nonradiative transitions between different electronic levels. In both cases, the luminescence center emits nonequilibrium phonons.

5. The crystalline and glassy germanium dichalcogenides are close in luminescence intensity, which, however, always decreases in going from GeS$_2$ to GeSe$_2$. This accounts for the observed decrease in PL intensity with increasing S concentration in the solid solutions. The difference in PL intensity between the constituent chalcogenides seems to account for the fact that the shift of the emission band in the spectra of the
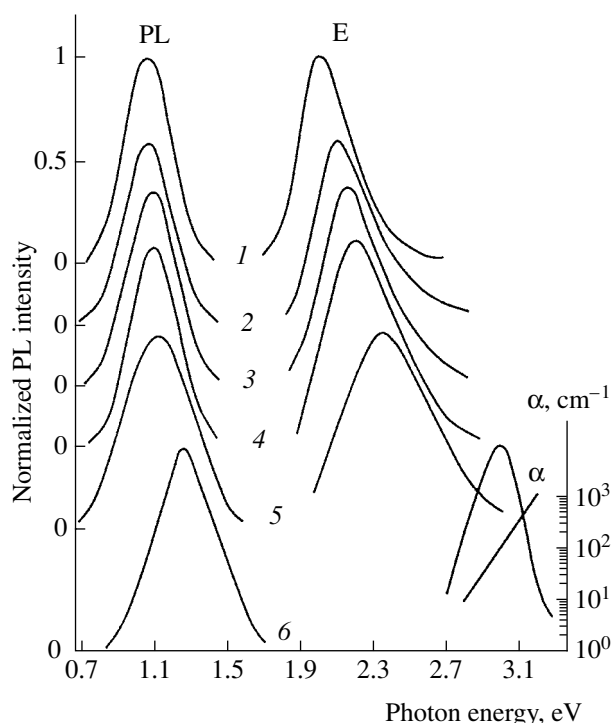
Fig. 5. 77-K PL, excitation (E), and edge absorption (α) spectra of glassy $GeS_{2x}Se_{2-2x}$: $x =$ (*1*) 0, (*2*) 0.2, (*3*) 0.4, (*4*) 0.6, (*5*) 0.8, (*6*) 1.

crystalline and glassy solid solutions is only slight up to $x = 0.8$ (Figs. 3, 5), in spite of the significant changes in band gap.

6. Both the crystalline and glassy solid solutions have linear brightness–illuminance characteristics. The only effect of increasing excitation intensity is a slight shift of the emission band to higher energies. The linear brightness–illuminance characteristics, together with the exponential PL decay [15] in the glassy and crystalline solid solutions at 77 K, indicate that the recombination in both phases follows a monomolecular mechanism.

7. In both the crystalline and glassy solid solutions, we observe temperature quenching of PL, but the ordered and disordered phases differ in PL quenching behavior.

8. PL studies of β-$GeSe_2$ single crystals grown by three different processes—physical vapor transport, chemical vapor transport, and melt growth—demonstrate that the peak emission energy, band width, PL intensity, brightness–illuminance behavior, and temperature variation of PL intensity are essentially independent of the growth method.

CONCLUSIONS

The present results indicate that radiative processes in crystalline and glassy germanium dichalcogenides and $GeS_{2x}Se_{2-2x}$ solid solutions are dominated by

native point defects and depend little on the degree of long-range ordering, whereas nonradiative processes are rather sensitive to topological disorder in the structure of the solid solutions. At the same time, local inhomogeneities, typical of solid solutions, lead to the formation of density-of-states tails of the upper valence band and conduction band and broadening of energy levels. The reason for the broadening of the band edges is that the energy position of the conduction band minimum and valence band maximum depends on composition, so that local inhomogeneities broaden the band edges. This, in turn, gives rise to changes in the optical spectra of the solid solutions, leading to broadening of the fundamental edge, Raman bands, and intrinsic and impurity absorption and luminescence bands.

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