

PHOTOLUMINESCENCE AND PHOTOSTRUCTURAL CONVERSION IN DEFORMED LAMINATED CRYSTALS OF As_2S_3 , GeSe_2 , As_2Se_3

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Reversible photostructural conversions (darkening and bleaching) accompanied by a shift of transmittance edge and by the photoluminescence fatigue effect are revealed in binary chalcogenides. Upon mechanical treatment of crystals the maximum of the luminescence excitation spectrum shifts toward higher energies. The low-energy edge of the luminescence spectrum flattens, and emission intensity increases. The experimental results are interpreted within a configuration model with two stable structural states of characteristic molecular groupings.

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1. Introduction

Transition of crystalline solids to an amorphous state induced by nonthermal factors (mechanical treatment, radiation, and shock waves) results from strong impact of external forces. Atoms of impacted samples may leave their equilibrium positions, e.g., after receiving an energy pulse. Under certain conditions, structures with periodically arranged atoms are often distorted in the course of chemical reactions in solids to produce amorphous phases or some intermediate form. When considering solid materials that are treated mechanically one should keep in mind that an intense disorder arising initially in surface layers spreads inward the sample and may eventually lead to complete conversion of the material into an amorphous state [1]. The transition of quartz into amorphous state upon its treatment in a vibrational mill was observed in [2]. Of particular interest is the investigation of transition of single crystals - analogs of chalcogenide glassy semiconductors (CGS) - to a disordered state induced by non-thermal impacts. Among the most interesting phenomena characteristic to CGS, but not observed in the crystalline analogs, we mention light-induced atomic processes whose mechanism is not completely understood. In the first place, these are reversible photostructural conversions leading to changes in many properties of CGS.

The authors of classical works [3,4] have shown that photoluminescence spectra of As_2Se_3 , As_2S_3 , and GeSe_2 single crystals and appropriate CGS exhibit a single photoluminescence band (PL) with $h\nu \leq E_g/2$ (E_g is the width of the forbidden band), quantum efficiency of $\eta=0.2-0.5$, and large Stokes shift, $W_s \geq 1$ eV. The maxima of luminescence excitation spectra (LES) of single crystals correspond to the energy of exciton absorption and feature high absorbance $\alpha=10^4 \text{ cm}^{-1}$, while CGS spectra feature low absorbance $\alpha=10-10^2 \text{ cm}^{-1}$ [5,6]. It has been established that excitons strongly interacting with the lattice play the key role in PL and that structure defects are the sites of radiationless recombination. This interaction produces auto-localized excitons (ALE) at $h\nu \approx E_g/2$. In analyzing radiative recombination in the related CGS formation of ALE and its interaction with the

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localized states formed due to structure defects are taken into account [7]. In the course of continuous excitation of PL in CGS, the intensity of recombination-generated radiation drops drastically with time to a quasi-steady state. No such a long-time process, called the fatigue effect, is observed in single crystal analogs [8,9].

2. Measurements

The objective of this work is to study by optical methods the effect of mechanical treatment on disordering of the structure of As_2S_3 , As_2Se_3 , and GeSe_2 single crystals. To this end, PL properties and optical transmittance of non-deformed (original) and deformed single crystals and also of powders prepared by treating single crystals in a vibrational mill-mortar were studied.

Laminated GeSe_2 and As_2Se_3 crystals were grown in liquid phase in a gradient furnace from the original materials - Ge (50 Ω), As, and Se (99.9999 %). GeSe_2 crystals are gold-yellow plates, belonging to the structural modification of germanium diselenide characterized by a specific resistance $\rho = 10^{10}\text{--}10^{11} \Omega\cdot\text{cm}$. As_2Se_3 single crystal is natural yellow arsenic. The crystals are isomorphous analogs of the laminated structure possessing a monoclinic lattice, and they can easily be cut along the cleavage plans (010). In addition, they are genuine superlattices in the direction of axis b with a period $a \approx 5\text{--}8 \text{ \AA}$. The emission and PL excitation spectra were studied in a set-up described in [3]. Monochromatic light from a 1000-W Xe lamp was used as an PL excitation source. To study optical transmittance of powders, we manufactured special glass cell in which the distance between optical windows was $d = 100 \mu\text{m}$.

3. Results

Fig. 1a shows the PL spectra (1, 2, 3) and LES at $T = 77 \text{ K}$ of the original ($1'$, $2'$, $3'$) and deformed crystals and powders ($1''$, $2''$, $3''$) of As_2Se_2 , GeSe_2 and As_2S_3 , respectively. As follows from Fig. 1, the PL spectra of original and deformed crystals and of powders are identical, whereas LES change significantly. Whereas in original crystals the LES maxima correspond to the energy of exciton absorption, in mechanically treated samples they are shifted toward greater energies equal to E_q of the original materials. This shift to greater absorbances is accompanied by an increase in the PL intensity in deformed crystals and powders, the low-energy edge of LES becomes much less steep in this case.

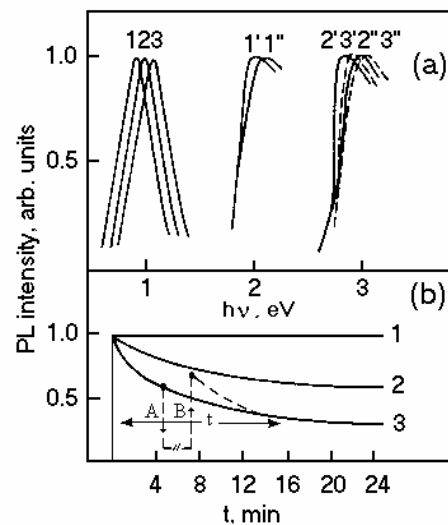


Fig. 1. (a) PL spectra (1,2,3) and LES of original ($1'$, $2'$, $3'$) and deformed As_2Se_3 , GeSe_2 and As_2S_3 crystals and powders ($1''$, $2''$, $3''$), respectively, $T = 77 \text{ K}$. (b) Long-term PL fading under continuous excitation in original (1) and deformed (2) crystals, and powder of As_2S_3 (3) at 77 K .

The observed Stokes shift, positions of the PL spectrum band and its large half-width suggest strong electron-phonon interaction. Conductivity band in studied crystals is produced by antibonding orbitals of chalcogen electron pairs [10,11]. Mechanical treatment of crystals apparently generates effects similar to those observed in CGS [12]. Interaction between unshared electron pairs of different atoms between themselves and with their local surrounding produces in the optical gap a spectrum of localized states part of which are charged defects. Triply coordinated chalcogen atom C_3^0 may serve as a neutral defect with the minimum energy. Each of these states is associated with different local atom configuration, therefore they can be considered as three distinct defects. Two neutral centers are unstable with respect to the exothermic reaction $3C_3^0 \rightarrow C_3^+ + C_1^-$, that is, the total energy (electron plus lattice) associated with a pair of charged defects is lower than the energy of two neutral defects.

Note that charged defects in CGS are diamagnetic, while the neutral one produced by photoexcitation are paramagnetic [12]. Original single crystals show neither electron spin resonance (ESR) nor photo-induced ESR at the 10^{14} - 10^{15} cm⁻³ as do intrinsic defects. An additional support for the formation of defects similar to those in CGS may be provided by ESR investigations in deformed crystals and powders in which at $T=77$ K PL fatigue effect and photostructural conversions characteristic of CGS are discovered. Fig. 1b illustrates typical curves demonstrating PL fatigue of deformed crystals and powders on the case of As_2S_3 .

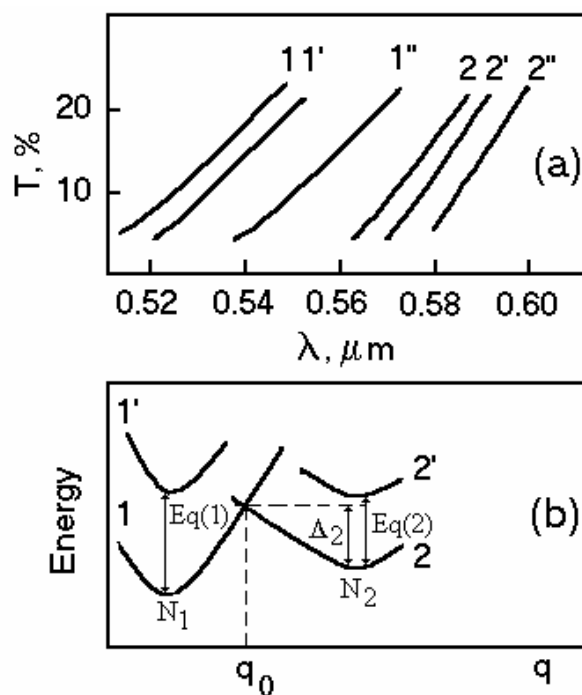


Fig. 2. (a) Edge transmittance of As_2S_3 and $GeSe_2$ powders: (1,2) before and (1'',2'') after illumination; (1', 2') annealed; (b) Configuration diagram: electron energy in ground (1) and excited (1') states; (2, 2') their metastable states.

The PL fatigue effect in crystals has a peculiarity which makes it different from the similar effect observed in CGS. In the course of PL decay after switching off continuous excitation, the PL intensity, likewise in the case of CGS, drops steeply within time $t < 10^{-2}$ s(A). Upon subsequent excitation, the signal level (B) does not resume its former level, as it does in the case of CGS [13], but exceeds it.

Photostructural conversions are expressed by darkening at low temperatures and bleaching after annealing and also by the corresponding shift of the transmittance edge (see Fig. 2a). Any temperature increase results in partial recovery of the initial transmittance, the degree of the transmittance recovery increases when the temperature of the sample increases. The parameter

characterizing the rate of optical transmittance recovery depends also on the structure rigidity. In As_2Se_3 , whose structure is fairly mobile, the optical transmittance is fully recovered at $T=423$ K, whereas for the more rigid structure of GeSe_2 crystals a temperature of $T=453$ K is needed. Since upon annealing of powders samples are bleached, we may also speak about thermally induced conversions. Measurements of light-induced changes in the optical transmittance were conducted at $T=77$ and 300 K. These changes were monitored at a wavelength the initial transmittance at which was 20 %. At 77 K the transmittance of a powder layer decreases in time according to a law similar to the PL fatigue effect. It is noteworthy that the PL fatigue time t corresponds to the optimal time of photostructural conversions. Reversible photostructural atomic processes taking place in deformed crystals and powders are qualitatively similar, that is, illumination produces darkening while annealing, recovery of the initial parameters. Based on the model of photostructural conversions in CGS [14,15] we can propose for an analysis of this process in deformed crystals and powders a configuration model of two stable structural states of molecular grouping (analogs of a unit cell in the original crystal) differing in their energy (ground and metastable states) (see Fig. 2b).

4. Discussion

The ratio between the molecular grouping controls the structure of a deformed crystal or powder. This ratio varies as a result of optical and thermal transitions. As in the case of CGS, the basic changes in deformed crystals and powders take place in the chalcogen sublattice. The probability of optical transitions between the states depends on mutual disposal of the atoms due to thermal vibrations. Within the configuration model, transmission of a sample is governed by the population of the metastable state β :

$$\beta = N_2 / (N_1 + N_2) \quad (1)$$

where N_1 and N_2 are the number of molecular groups in the ground and metastable states, respectively. The balance equation for quantity β can be written as follows

$$\frac{d\beta}{dt} = -\left[-\frac{1}{\tau} + Q(\alpha_1 + \alpha_2)\right]\beta + Q\alpha \quad (2)$$

where Q is the light flux, $\alpha(\alpha_2)$ is the absorption cross section for the optical transition from the ground state to the metastable one (an vice versa), and τ is the lifetime of the system in the metastable state. At

$$Q(t) = \begin{cases} 0, & t = 0 \\ Q_0, & t > 0 \end{cases} \quad (3)$$

the balance equation yields

$$\beta = (\beta_0 - \beta_\infty) \exp(-\alpha t) + \beta_\infty \quad (4)$$

$$\beta_\infty = Q_0 \alpha_1 / \alpha \quad (5)$$

$$-\alpha = Q_0(\alpha_1 + \alpha_2) - 1/\tau \quad (6)$$

where β_0 is the initial population at $t=0$. Quantity α characterizes the dependence of the population on temperature and wavelength of exciting light. After switching off illumination the population of the metastable state decays by an exponential law $\beta = \beta_0 \exp(-\alpha t)$ where $\alpha_T = \tau^{-1} = \nu \exp(-\Delta_2/kT)$, Δ_2 is the depth of the potential well of the metastable state (see Fig. 2b), and ν is a frequency of the order of phonon frequency.

5. Conclusions

A model with two stable structural states of the molecular groupings has been developed for the photo-luminescence phenomena in deformed laminated chalcogenide crystals

The suggested configurational model is semi-phenomenological and in no way specifies the real changes in the structure of illuminated deformed crystals and powders. To elucidate the microscopic nature of photostructural conversions EXAFS, photoelectron spectroscopy, and ESR methods should be used.

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