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Nonlinear light absorption in $GaSe_{1-x}S_x$ solid solutions under high excitation levels

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Abstract : Transmission, photoluminescence and photoconductivity spectra of $GaSe_{1-x}S_x$ solid solutions have been investigated experimentally in the exciton resonance region at high optical excitations. The absorption edge of $GaSe_{1-x}S_x$ is caused by exciton transitions and linear shifts towards short wavelengths by raising the value of x in the solution. The exciton peak disappears and nonlinear absorption appears in $GaSe_{1-x}S_x$ crystals by increasing the excitation intensity. The new luminescence band appears at about 20 meV below the free exciton line at high excitation levels. These peculiarities are interpreted by means of the exciton-exciton scattering process.

Keywords : Exciton, $GaSe_{1-x}S_x$ solid solutions, nonlinear light absorption

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1. Introduction

Gallium Selenide (GaSe), Gallium Sulfide (GaS) and Gallium Selenium Sulfide ($GaSe_{1-x}S_x$) are III–VI semiconductors which crystallize with a lamellar structure. The bonding between two adjacent layers is of the Van der Waals type, while within the layer the bonding is predominantly covalent. Therefore, the bulk material obtains a strong mechanical anisotropy which allows easily to prepare thin samples using a simple peeling procedure. The optical c-axes of crystals are orthogonal to the layers having thicknesses of ~0.8 nm [1]. The exciton binding energy is equal to 20 meV, which is close to the room temperature thermal energy [2]. Therefore, one can observe the exciton in $GaSe_{1-x}S_x$ at room temperature from optical transmission experiments. Exciton absorption and luminescence in $GaSe_{1-x}S_x$ have been investigated by a number of investigators [3–7]. In these crystals (with the exception of GaSe [8–18]), the optical absorption has not practically been considered at high excitation levels.

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In the present work, the nonlinear light absorption has been investigated experimentally in the exciton resonance region at high optical excitation levels in $GaSe_{1-x}S_x$ layered crystals.

2. Experimental method

$GaSe_{1-x}S_x$ crystals (x = 0, 0.05, 0.1, 0.2 and 0.25) were grown by Bridgman technique. Thicknesses of samples were about 30–100 μm. Ohmic contacts were obtained by deposition of high-purity indium on the surface of samples. As an excitation source, a dye laser (PRA, LN-107) pumped by the output of a N_2-laser (PRA, LN-1000) were used. The dye laser gave possibility of selecting different wavelengths (473–547) nm, (568–605) nm and (594–643) nm with the resolution 0.04 nm. The pulse power was 120 kW at the repetition frequency of 10 Hz and at pulse width 1 ns. The laser light was focussed onto the sample with the focus diameter of about 0.5 mm. Laser beam intensity was varied by inserting calibrated neutral density filters. Luminescence was excited by dye laser photons with energy more than the band gap width E_g of the $GaSe_{1-x}S_x$ crystals (λ_{exc} = 500 nm). Luminescence was detected under a small angle with respect to the c-optical axis of the crystal. Photoluminescence spectra were analysed by means of a diffraction grating monochromator (JOBIN-YVON) with the reciprocal dispersion 2.4 nm/mm. The output signal was detected by a photomultiplier and then was sent to a recorder (HP-7475A) through a storage oscilloscope (Le Croy 9400).

3. Results and discussion

Transmission spectra of $GaSe_{1-x}S_x$ crystals are shown in Figure 1 near the fundamental absorption edge at low excitation intensities. These spectra show positions of the free-exciton peaks for different x-values [4]. Nonlinear light absorption is observed in these

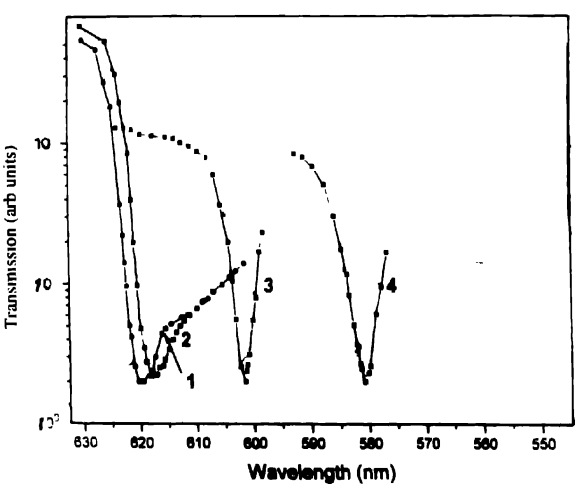

Figure 1. Transmission spectra of $GaSe_{1-x}S_x$ (300 K) for various values of x: 1–0, 2–0.05, 3–0.1, 4–0.2.

crystals at the high pumping levels. Figures 2 and 3 show transmission spectra of GaSe and $GaSe_{0.95}S_{0.05}$ crystals at different excitation levels, respectively. Bleaching of the samples takes place in the region of the exciton resonance by increasing the excitation intensity.

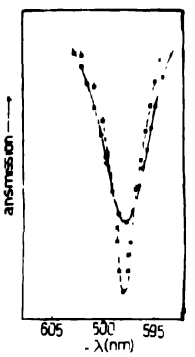

Figure 2. Transmission spectra of GaSe (80 K) at two pumping intensities (in MW/cm^2) 1–1.7, 2–12.

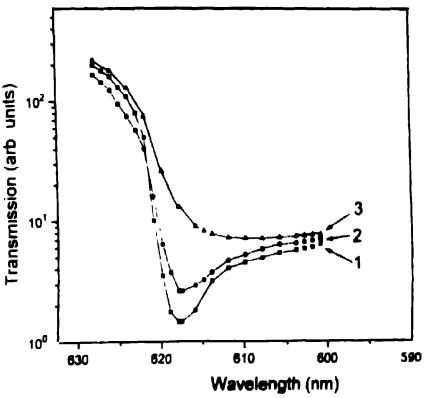

Figure 3. Transmission spectra of $GaSe_{0.95}S_{0.05}$ (300 K) at different pumping intensities (in MW/cm^2) 1–0.13, 2–2.01, 3–12.

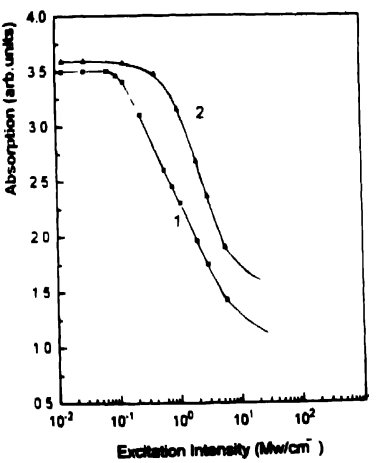

Figure 4. Exciton absorption peaks (300 K) *versus* pumping intensities for (1) GaSe and (2) $GaSe_{0.9}S_{0.1}$.

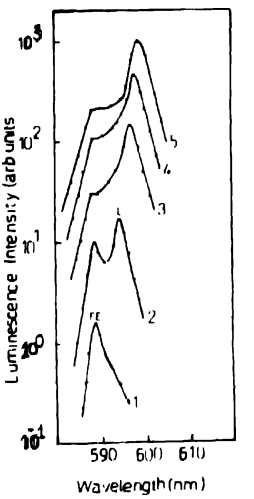

Figure 5. Luminescence spectra (80 K) of $GaSe_{0.95}S_{0.05}$ for various pumping intensities (in MW/cm^2): 1–0.12, 2–1.01, 3–4.02, 4–6.03, 5–12.

Figure 4 illustrates the dependence of absorption on the excitation intensity at the wavelength where the exciton absorption is maximum. According to Figure 4, the absorption is constant up to the intensity $I_0 = (0.1–0.2)$ MW/cm^2, and then decreases more than three times in the region $0.15 < I_0 < 12$ MW/cm^2.

Figure 5 shows luminescence spectra of $GaSe_{0.95}S_{0.05}$ at various pumping levels. These spectra include the low-energy band (L band) besides the free-exciton peak ($\lambda = 589$ nm). The exciton peak takes place also at low excitation intensities. On the other hand, the L band appears when $I_0 > 0.5$ MW/cm^2 at $\lambda = 595$ nm (*i.e.* 20 meV below energy of the free exciton) The peak of the L band exhibits a red shift by increasing the pumping excitation. L emission strongly predominates at highest pumping levels. Dependence of the L-emission on excitation levels is a square-law, while the free exciton dependency is a linear one.

The photoconductivity spectra of $GaSe_{0.9}S_{0.1}$ at various pumping levels are shown in Figure 6. One can see from this figure, that both exciton (A) and impurity (B) photoconductivities are observed in the spectrum (curve 1). The exciton peak first increases

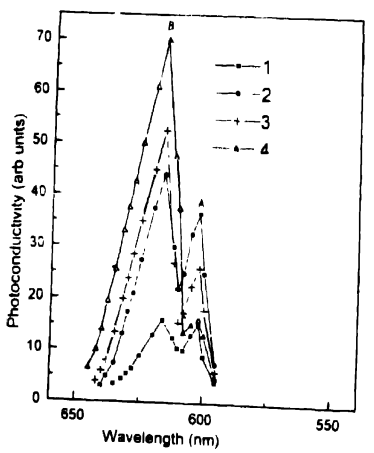

Figure 6. Photoconductivity spectra (300 K) of $GaSe_{0.9}S_{0.1}$ for various pumping intensities (in MW/cm^2) 1–1.01, 2–4.02, 3–6.03, 4–12.

by increasing the laser intensity (curve 2), then begins to diminish (curve 3), and almost disappears at higher intensities (curve 4). The dependence of the exciton photoconductivity on the pumping intensity is shown in Figure 7. It is clearly seen that the exciton photoconductivity $\Delta\sigma$, first increases linearly with growth of the incident intensity I_0, up to $I_0 = 1$ MW/cm^2, then varies according to $\Delta\sigma \sim I_0^{1/2}$, and at last decreases at $I_0 >$ 4 MW/cm^2 (curve 1). In the case of the impurity excitation, the photoconductivity changes first linearly, and then approaches with a farther trend to the saturation (curve 3). The concentration of impurities determined from the region of the saturation is equal to 1.0×10^{14} cm^{-3}.

It is known that photoconductivity of nonequilibrium carriers in semiconductors is of the form $\Delta\sigma \sim \alpha I_0$, where α is the optical absorption coefficient and I_0 is the excitation intensity [19]. Dependences of αI_0 on I_0 are shown in Figure 7 (curve 2), where values of α correspond to Figure 4. It is seen that, dependences of αI_0 and $\Delta\sigma$ on I_0 are similar. Thus, the disappearance of the exciton peak in the photoconductivity spectrum is caused by the same mechanism, as in the transmission spectrum.

Exciton-exciton collision process is one of the possible mechanisms of the nonlinear light absorption in $GaSe_{1-x}S_x$ solid solutions [20,21]. Disappearance of the exciton absorption and appearance of the new band of the luminescence (at 20 meV below the free

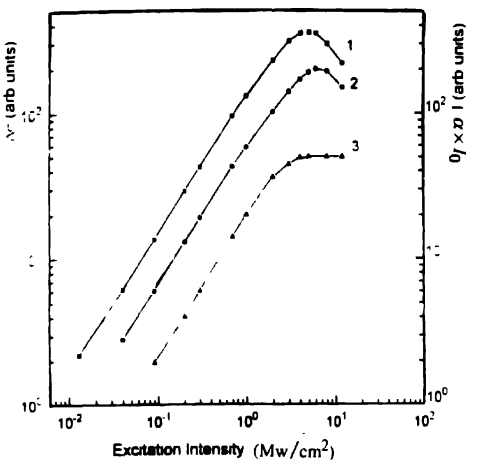

Figure 7. Photoconductivity of $GaSe_{0.9}S_{0.1}$ *versus* incident intensity. 1, 3-exciton and impurity photoconductivity, 2-αI_0.

exciton) at high pumping levels indicate such possibility. The density of the absorbed photons, averaged over the sample thickness, reached 3×10^{19} cm^{-3} which exceeds the exciton density necessary for the Mott transition in $GaSe_{1-x}S_x$ [12,22].

4. Conclusion

Transmission, luminescence and photoconductivity spectra of $GaSe_{1-x}S_x$ solid solution (upto 25% S) contain only lines corresponding to free-excitons at low pumping intensities. Thus, $GaSe_{1-x}S_x$ present materials which are especially convenient for the study of the interactions between excitons. Such interaction leads to disappearance of the exciton lines and gives rise to new radiative transitions.

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