

NONLINEAR OPTICAL PHENOMENA

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Resonance enhancement of nonlinear photoluminescence in gallium selenide and related compounds

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Abstract. **Maker fringe experiments on the layered chalcogenide semiconductor gallium selenide (GaSe) with weak cw diode lasers are presented. It is demonstrated that nonlinear photoluminescence emitted by this material and by the similar compound $GaSe_{0.9}S_{0.1}$ under illumination with a 632.8-nm He–Ne laser shows very strong resonance enhancement upon heating when the absorption edge and exciton levels are shifted towards the laser line. The photoluminescence appears to be strongest when the energy level of the direct exciton, which emits it, is resonant with the photon energy of the laser. The previously observed enhancement of the photoluminescence by electric fields is interpreted in this context.**

Keywords: *gallium selenide, photoluminescence, nonlinear optics, Maker fringes, excitons.*

1. Introduction

Gallium selenide (GaSe), gallium sulfide (GaS), and mixed compounds $GaSe_{1-x}S_x$ ($0 \leqslant x \leqslant 1$) belong to a class of layered chalcogenide semiconductors which are characterised by strong covalent bonds within thin (thickness of four atoms) layers and weak interactions of mainly van-der-Waals type between them. The absorption edge is in the visible region of the spectrum and varies from ~630 nm in GaSe to 490 nm in GaS at room temperature. With increasing temperature it shows a pronounced red shift in all compounds [1]. The layers are stacked along the crystallographic axis c. The crystals usually exist in several modifications or polytypes which differ in the arrangement of the layers and their number per elementary cell. The most thoroughly studied material of this class is GaSe due to its very high nonlinear optical second-order susceptibility, $\chi^{(2)}$ [2–8]. More detailed reviews of the properties of these crystals are presented elsewhere [9–11].

Investigations of GaSe with a confocal Raman microscope equipped with a He–Ne laser showed that the material emits strong photoluminescence (PL) which is mainly blue-shifted from the laser line and exhibits a quadratic dependence on the laser intensity [12]. The mechanism of its generation was assumed to be second-harmonic generation (SHG) in the laser focus creating UV photons which excite electrons high into the conduction band; after their relaxation to the band edge, the excitons are formed. An intriguing and promising effect was that, in an external electric field, the PL showed a red shift and an increase in intensity, both with a roughly quadratic dependence on the field strength E [12]. The magnitude of the shift was of the order expected from the Franz–Keldysh effect. Of particular interest was the field-induced increase in the PL signal, because one possible explanation was that the already high nonlinear susceptibility $\chi^{(2)}$, responsible for the effect, may become even larger in the presence of the field E.

Photoluminescence measurements were later also conducted in mixed crystals $GaSe_{1-x}S_x$ with $0.02 \leqslant x \leqslant 0.8$ [13]. Photoluminescence signals were only observed in crystals with sulfur content $x \leqslant 0.05$. Since pure GaSe and compounds with low sulfur content are known to form primarily non-centrosymmetric ε or δ modifications and those with high sulfur content – mainly the centrosymmetric β polytype, the data seemed to confirm that the effect is indeed due to SHG, which cannot occur in centrosymmetric crystals. On the other hand, in earlier studies SHG signals had been observed in mixed crystals with a higher sulfur content and even in pure GaS [14,15]. Also Maker fringes could be recorded in a GaS crystal [16]. Their irregular appearance and modulation was ascribed to the presence of domains of centrosymmetric and non-centrosymmetric polytypes.

The purpose of the present paper is twofold. In Section 2 we describe Maker fringe experiments on GaSe performed with weak cw diode lasers to show that the direct detection of cw SHG signals is easily possible. In Section 3 we present temperature-dependent measurements of the nonlinear PL signal excited with a He–Ne laser and of the absorption edge of GaSe and $GaSe_{0.9}S_{0.1}$. We also demonstrate that, in both materials, the PL exhibits very strong enhancement when the absorption edge is shifted close to the laser frequency. We arrive at the conclusion that the most probable mechanism behind the nonlinear PL consists in two successive one-photon transitions involving an exciton as an intermediate state; however, resonance-enhanced SHG, as assumed previously, and two-photon absorption (TPA) are, in principle, also possible. An enhancement of the SHG coefficient by electric fields is ruled out.

2. Maker fringe experiments on gallium selenide performed using a cw laser

SHG Maker fringe experiments are usually conducted with a wavelength for which neither the fundamental nor the second

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harmonic are strongly absorbed by the sample material. SHG measurements in GaSe had been previously performed with a fundamental wavelength of 1579 nm which was generated by stimulated Raman scattering of radiation from a 532-nm picosecond laser in pressurised hydrogen gas [17]. The signals showed good agreement with ray tracer calculations when multiple reflections of the irradiated beam in the crystal were taken into account.

Due to the large optical nonlinearity of GaSe, Maker fringe experiments are also feasible with much weaker cw lasers. In the present study, two linearly polarised diode lasers were used: one at 1300 nm with a power of 30 mW and the other at 1550 nm with only 4.5 mW power [Power Technology PMT20(1300-30)G2X22 and PMT4.5(1550-6)G25, respectively]. The laser beam passed through a Schott RG850 glass filter to block very weak, but detectable, second-harmonic light which is emitted by the diode lasers themselves. The 1300-nm laser light was focused onto the sample with achromatic lenses of different focal lengths between 40 mm and 80 mm and combinations thereof. As expected, the SHG signal increased strongly with decreasing focal length.

Achromatic lenses could not be used with the 1550-nm laser, since their antireflection coatings, which are optimised for the visible range, block too much of the IR light. Instead, the beam was focused by two uncoated plano-convex lenses with a focal length of 50 and 150 mm, whose plane sides were in contact with a drop of glycerol used as an index-matching fluid in between.

Behind the sample, the fundamental beam was blocked with an IR filter and the second harmonic was detected in transmission geometry with a Hamamatsu R928 photomultiplier. The laser light was modulated at 1.8 kHz for using lock-in detection. As usual, the signal was measured as a function of the external angle of incidence, while the crystal was rotated around an axis perpendicular to the c axis. Since the main goal of the experiment was to demonstrate that second-harmonic signals can be detected with weak cw diode lasers, the polarisation axis of the laser was arbitrary and no polariser was used in the path of the SHG light. Thus, both polarisation components, parallel and perpendicular to the plane of incidence, were detected [18].

Maker fringe signals could be recorded with both diode lasers. An example obtained with the 1300-nm laser and a focusing achromatic lens of 80 mm focal length is shown in Fig. 1. The fringe minima do not reach zero, since the Rayleigh range, in which the light field is approximately equal to a plane wave, is of similar magnitude as the crystal thickness of 150 μm.

Maker fringe signals were also recorded with electrical fields applied to the GaSe sample. The field was applied in two different geometries. The crystal was either sandwiched between two ITO-coated glass slides with thin microscope cover glasses in between to prevent current flow. In the second configuration the crystal was placed on top of interdigitating gold electrodes as in Ref. [12]. Field strengths up to ~20 kV cm^{-1} were applied. The result of all of these experiments was that the amplitude of the SHG signal is not affected by the field E. This contradicts our previous measurements [12].

3. Photoluminescence measurements

3.1. GaSe sample

When GaSe and the mixed crystal with 10% sulfur are excited with 532-nm laser light, the photon energy of which is larger than the band gap, they emit strong PL due to the decay of direct-gap excitons [13]. Irradiation of GaSe by the He–Ne laser light (632.8 nm) results in the emission of the same PL, which is slightly blue-shifted from this laser line and has a quadratic dependence on its intensity [12]. In order to reinvestigate the origin of the nonlinear PL, our first attempt was to irradiate samples at a wavelength which is spectrally well separated from the PL. We used a 783.2-nm cw diode laser (Point Source, model iFlex-1000). The energy of two photons, corresponding to a wavelength of 391.6 nm, should be sufficient to excite the PL. In spite of its relatively high power of 38 mW, however, no PL signal was detected.

Therefore, the diode laser was replaced with a He–Ne laser (632.8 nm, 15 mW, unpolarised). A confocal configuration similar to that in Ref. [12] was used; it is schematically shown in Fig. 2. The clean-up filters (AHF Analysentechnik) were required for suppressing plasma lines of the He–Ne discharge tube which were superimposed on the PL spectrum. The laser beam was focused onto the sample with a microscope objective Leica N Plan 40$^{\times}$/0.55, which also collected and collimated the PL. The very strong line of reflected and scattered laser light was efficiently suppressed by a holographic Super-Notch filter (Kaiser Optical Systems); then the PL spectrum was dispersed in a small BM25 monochromator. A mechanical chopper modulated the laser beam at 1.8 kHz to use lock-in detection.

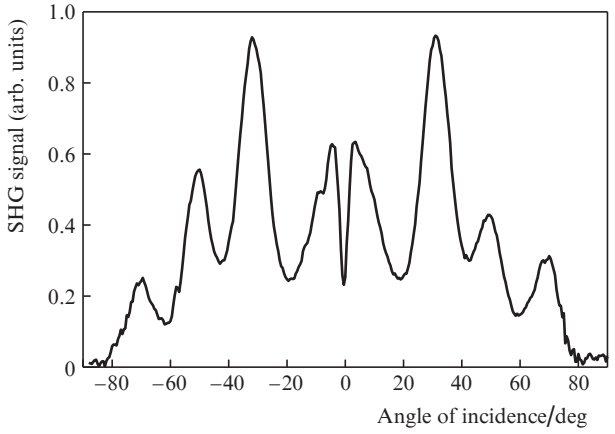

Figure 1. Maker fringe signal of a 150±30-μm-thick GaSe crystal, measured with the 1300-nm diode laser.

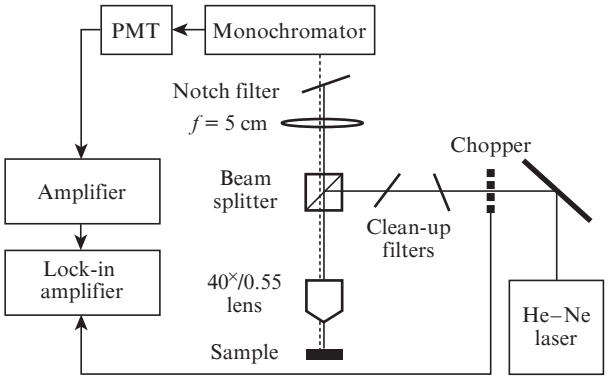

Figure 2. Confocal setup for investigating the PL of GaSe and $GaSe_{0.9}S_{0.1}$. Details are explained in the text.

The PL of GaSe was measured at different temperatures. To this end, the crystal was placed on a glass chip with an evaporated meandering gold path which was connected to a power supply. Since the sample temperature could not be measured directly, the transmission spectrum was recorded at each heating voltage and the temperature scale was calibrated by comparison with the data in Ref. [1].

Figure 3 shows the band edge and Fig. 4 the He–Ne laser-induced PL of GaSe at different temperatures. At room temperature (293 and 300 K), the PL is barely visible on the scale of Fig. 4 and located mainly to the blue of the laser line. At higher temperatures it increases dramatically in intensity and shifts to the red across the laser line, reflecting the shift of the band edge and the exciton frequency. At the highest temperatures, the PL signal decreases again and its spectrum exhibits strong thermal broadening. The strongest enhancement occurs around 370 K, when the peak of the exciton transition crosses the laser frequency. Parallel to the enhancement of the PL, the laser line decreases in intensity. The exact origin of this effect is not clear. We speculate that it is related to the varying effective absorption coefficient and/or refractive index (corresponding to the Kramers–Kronig relations).

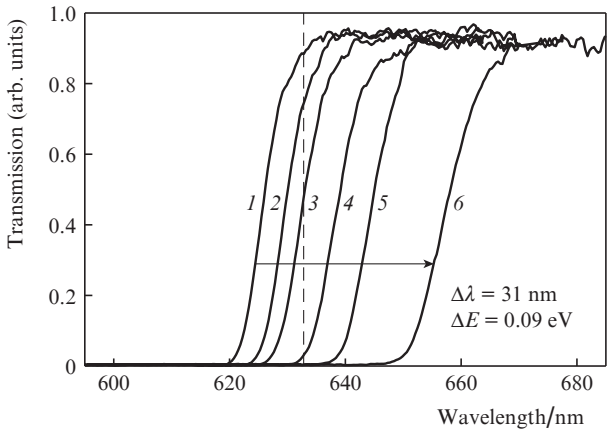

Figure 3. Absorption edge of GaSe at different temperatures: (*1*) 304, (*2*) 323, (*3*) 346, (*4*) 369, (*5*) 393, (*6*) 430 K. The dashed line indicates the wavelength of the He–Ne laser.

The data in Fig. 4 explain, why no PL was observed with the diode laser at 783.2 nm. The mechanism behind the nonlinear PL shows very strong resonance enhancement when the absorption edge and the exciton transition virtually coincide with the laser wavelength. Without this enhancement, the effect is too small to generate detectable luminescence.

As the absorption edge of the crystal crosses the laser line, PL can be excited not only by the nonlinear mechanism but also by regular one-photon excitation of electrons into the conduction band. This is reflected by the dependence of the PL signal on the laser intensity I_{las}. At each temperature the PL signal was recorded at different laser powers and was integrated over a wavelength interval outside the blocking region of the notch filter. We assumed for simplicity that the integrated signal I_{PL} has a power law dependence on I_{las} with an effective exponent α:

$$I_{PL} \propto I_{las}^{\alpha}. \qquad (1)$$

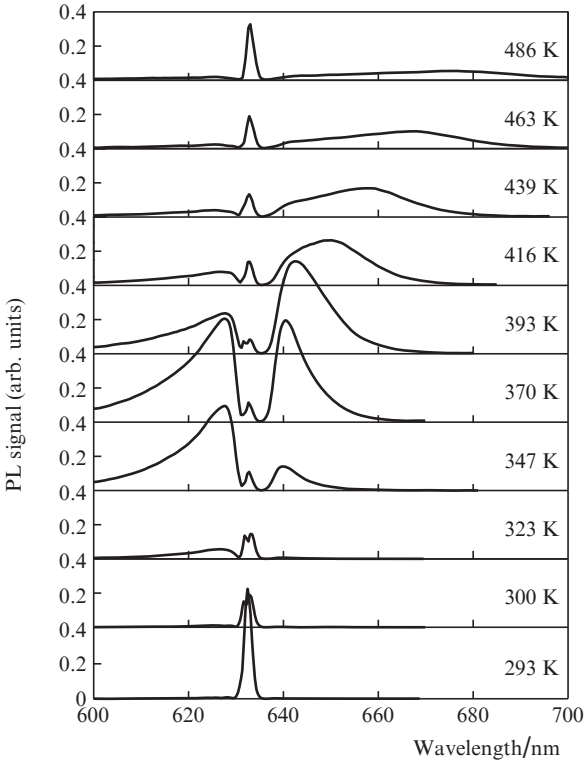

Figure 4. Photoluminescence spectrum of GaSe at different temperatures. The gap around the He–Ne laser wavelength is caused by the notch filter.

In Fig. 5, the exponent α is plotted versus temperature. The exponent decreases from values close to 2 at room temperature to roughly 1.65 above 450 K, thus indicating the increasing contribution of linear absorption processes. Even at these high temperatures, however, there is a substantial nonlinear contribution to the PL. The photon energy of the laser is distinctly higher than the maximum of the PL spectrum in this regime, yet, due to the broad width of the latter there is still some overlap. The signal strength of the PL was also measured with an electrical field applied. As in the case of SHG, no influence of the field strength was found.

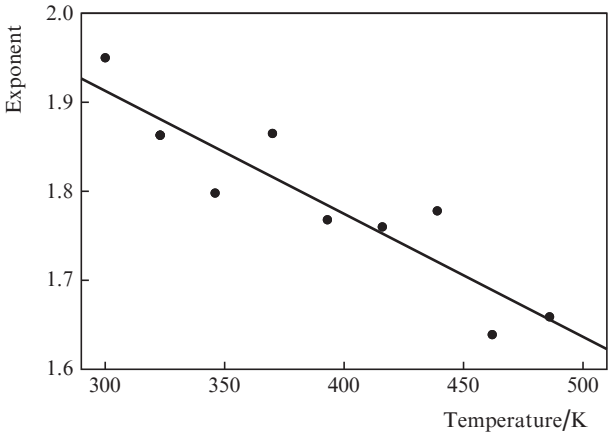

Figure 5. Effective exponent α indicating the variation of the PL signal of GaSe with laser intensity [Eqn (1)] as a function of temperature. The straight line represents a linear fit.

3.2. $GaSe_{0.9}S_{0.1}$ sample

In the previous study [13], mixed crystals $GaSe_{1-x}S_x$ with sulfur content $x \geqslant 10\%$ had not shown any nonlinear PL excited by the He–Ne laser at room temperature. This result had been ascribed to the presence of a centrosymmetric crystal structure (the β polytype) which prevents the generation of second-harmonic photons. The strong temperature dependence of the PL in GaSe presented above, however, prompted us to repeat the measurements also in $GaSe_{0.9}S_{0.1}$ at elevated temperatures.

Figure 6 shows the absorption edge and Fig. 7 the PL signal of this compound up to 474 K. Since the mixed compound has a larger band gap than GaSe, it does not emit PL at room temperature. Above 400 K, however, when the absorption edge comes sufficiently close to the laser line, the signal appears. With increasing temperature it grows in intensity and shifts to the red as in GaSe. The signal strength of the PL is smaller than in GaSe by at least one order of magnitude, but it also depends on the laser intensity in a superlinear fashion (data not shown). At the highest temperature of 474 K, the exponent α in Eqn (1) amounts to 1.75 ± 0.07. Hence, the mechanism responsible for PL emission is likely the same as in GaSe. The small amplitude of the PL may be related to increasingly efficient nonradiative relaxation processes at elevated temperatures. Also the signal of GaSe decreases strongly above 400 K (Fig. 4). Upon irradiation by green laser light (532 nm) at room temperature, both crystals emit PL signals of comparable amplitude [13].

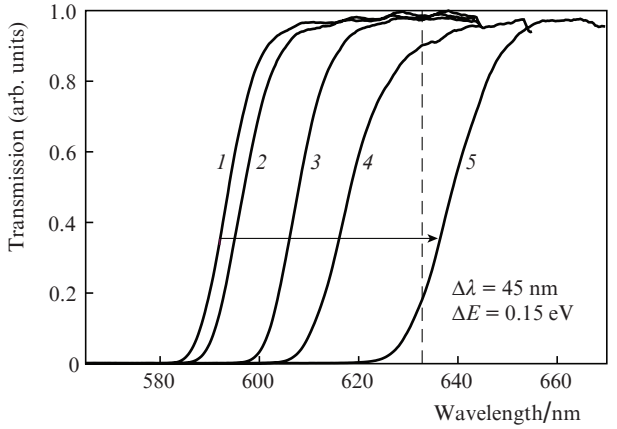

Figure 6. Absorption edge of $GaSe_{0.9}S_{0.1}$ at different temperatures: (*1*) 293, (*2*) 312, (*3*) 358, (*4*) 397, (*5*) 451 K. The dashed line indicates the wavelength of the He–Ne laser.

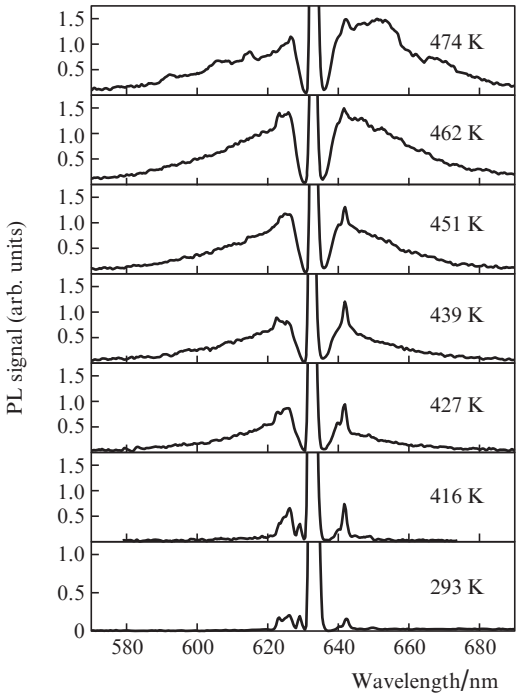

Figure 7. Photoluminescence spectrum of $GaSe_{0.9}S_{0.1}$ at different temperatures. The gap around the He–Ne laser wavelength is caused by the notch filter. Some low-frequency Raman lines are also visible (cf. [13]).

4. Discussion

The results of the PL measurements in GaSe and $GaSe_{0.9}S_{0.1}$ demonstrate that clear PL signals can only be generated with a He–Ne laser of a few mW power, if the laser line overlaps with the exciton spectrum. The nonlinear dependence on the laser intensity can be interpreted in terms of three different excitation mechanisms.

The first possibility consists in two successive linear absorption processes involving the direct exciton. In this case, the first step populates the exciton state and the second one lifts the electron high into the conduction band. Since the absorption of two photons is required, the dependence of I_{PL} on I_{las} is quadratic. The other two mechanisms involve nonlinear-optical processes, either SHG plus the absorption of the generated UV photons or TPA. Both mechanisms must be subject to strong resonance enhancement by the exciton state, since the irradiation by 783.2-nm light with a power of 38 mW does not produce any detectable PL signal.

Substantial resonance enhancement of SHG in GaSe was reported in Ref. [18]. For photon energies of the laser close to the exciton state, the coefficient $\chi^{(2)}$ was measured to be larger by a factor of 18 than far away from the resonance. Since the SHG intensity (which would be proportional to the PL) depends on the square of $\chi^{(2)}$, we expect a resonance enhancement of the PL signal by a factor of $18^2 = 324$. The enhancement factor in the present study must be at least of this order of magnitude, given the complete absence of PL at 783.2 nm and the strong signals shown in Fig. 4. Hence, SHG, although less likely than two successive one-photon transitions, may still be responsible for the PL emission.

Also resonance enhancement of TPA has been reported for GaSe [19]. At 75 K, the TPA coefficient was found to be enhanced by a factor of 5–10 in a spectral interval of width $\sim k_B T$ around the indirect exciton resonance. At room temperature, where the exciton states are broader, the enhancement is expected to be even smaller. Under nonresonant conditions, TPA coefficients of 6 ± 1.2 cm GW^{-1} ($\lambda = 700$ nm [20]) and 0.3 cm GW^{-1} ($\lambda = 626$ nm [21]) were measured for GaSe at room temperature. In the focus of our cw lasers, the intensity is estimated to be no higher than $\sim 10^6$ W cm^{-2}. Hence, it is clear that no PL was observed with the near-IR laser (783.2 nm). An enhancement factor of 5–10, on the other hand, seems hardly sufficient to generate the PL signals (see Fig. 4). Therefore, we must conclude that TPA is the most unlikely mechanism.

The authors of Ref. [21] discussed the possibility that the intensity-dependent absorption coefficient of GaSe may be due to two successive one-photon transitions via the exciton state. Since the transmission of the sample decayed on a time scale

comparable to the laser pulse width (about 100 fs), which is much shorter than the lifetimes of the excitons, they concluded that the effect is due to TPA and does not involve the population of an exciton state. The mechanism may be different in the present experiment using a narrow-band cw laser.

5. Conclusions

We have demonstrated that SHG Maker fringe experiments on GaSe with weak cw diode lasers are feasible. We have investigated the nonlinear blue-shifted PL of GaSe and the mixed crystal $GaSe_{0.9}S_{0.1}$ excited by a He–Ne laser.

The PL signal increases strongly when the band edge and the exciton states are shifted to longer wavelengths, i.e., toward the laser line. It reaches its maximum when the photon energy of the laser coincides with the transition of the direct exciton emitting the PL. The electric-field-induced enhancement of the PL observed in our former study [12] is due to its concomitant red shift. The latter is probably caused by the Franz–Keldysh effect, since its magnitude is consistent with this mechanism. Also slight Joule heating due to weak current flow in the electrode chip may have contributed to the spectral shift. A direct influence of the electric field on the Maker fringe signal or the nonlinear process in the PL generation can be ruled out.

The physical nature of the nonlinear mechanism has not been elucidated in the present study. Most probably it consists of two successive linear absorption processes involving the exciton state. SHG or TPA resonance-enhanced by the exciton state are less likely. Especially the enhancement factor of the TPA coefficient measured in Ref. [19] is too small to explain our data.

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