Chalcogenide Letters Vol. 18, No. 4, April 2021, p. 155 - 159

Thermal nonlinearities in GaSe

V. M. Salmanov[a,*], M. A. Jafarov[a], A. G. Guseinov[a],
R. M. Mamedov[a], A. A. Salmanova[b]
[a]*Baku State University, Baku, AZ1148 Azerbaijan*
[b]*Azerbaijan State University of Oil and Industry, Baku, Azerbaijan*

The nonlinear light absorption at the fundamental absorption edge under laser excitation in GaSe crystals has been investiqated experimentally. It is shown that at high excitation levels, the absorption coefficient shifted towards lower energies (red shift). The nonlinear refractive index is positive at frequencies below the absorption edge and negative on the high-energy side. The laser-induced negative index change is referred to as a self-defocusing optical nonlinearity. The positive $\Delta n(\omega)$ on the high-energy side to a self-focusing optical nonlinearity. The measured parameters showed that GaSe crystals exhibits strong nonlinear properties.

(Received October 13, 2020; Accepted April 1, 2021)

Keywords: Laser, GaSe crystals, Thermal nonlinearities, Influence of an external electric field

1. Introduction

When semiconductors are excited by powerful laser radiation, electron-hole pairs are generated, the concentration of which can reach ~ 10^{18}-10^{19} cm^{-3}. The recombination of these carriers mainly occurs through two channels, radiatively or nonradiatively. In semiconductors with the usual values of the band gap (1-2 eV), the intensity of radiative recombination was negligible. In radiative recombination, photon emission occurs, the energy of which corresponds to band-zone, exciton or impurity transitions. In the case of nonradiative recombination, electron-hole pairs generated by laser radiation transfer their energy to the crystal through phonon emission, which corresponds to lattice heating. In experiment, nonradiative recombination is observed in the vast majority of cases. In most semiconductor crystals, heating the sample reduces the band gap with a corresponding redshift relative to the edge of the absorption band. As a result of the influence of laser heating, the absorption coefficient and the refractive index of a substance change. The detection and investigation of thermal nonlinearity in GaSe crystals is of particular interest. Previously, optical nonlinearities of electronic origin were discovered in GaSe, such as harmonic generation [1, 2], parametric light generation [3, 4], electron-hole plasma [5-9], stimulated emission [10-14], multiphoton absorption [15, 16], etc., have been observed in these crystals.

In this paper, we present the experimental results thermal nonlinearities in GaSe under the influence of laser radiation.

2. Experimental methods

GaSe crystals were grown by the Bridgman method. Gallium selenide has a layered structure, where each layer contains two gallium and two selenium close-packed sublayers in the stacking sequence Se-Ga-Ga-Se [17]. The samples were cleaved from the ingots having thicknesses of (20-150) μm parallel to the c-axis. Our samples exhibited a p-type conductivity and had resistivities in the range 10^3-10^6 Ω·cm. The energy gap of GaSe is E_g = 2.02 eV at room temperature.

* Corresponding author: vagif_salmanov@yahoo.com
https://doi.org/10.15251/CL.2021.184.155

Two light sources were used in the experiment. The CW second harmonic Nd:YAG laser (λ=532 nm with a repetition frequency of 10 Hz, maximum power of 12 MVt/cm^2 and a pulse width of 10 ns) was used as an excitation source which increases temperature of the sample. The laser intensity was varied using calibrated neutral light filters. The second source was a halogen lamp to measure the transmission of samples excited by laser radiation. The optical absorption spectra of GaSe were studied using an M833 automated monochromator with double dispersion (spectral resolution ~ 0.024 nm at a wavelength of 600 nm), with computer control and a detector detecting radiation in the wavelength range of 350 - 2000 nm. The experimental setup is shown in Fig. 1.

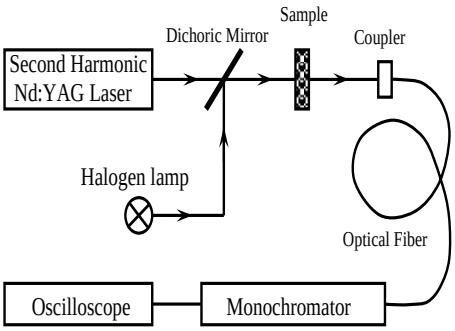

Fig. 1. Experimental setup for measurement thermal nonlinearities in GaSe.

3. Experimental results and discussion

Fig. 2 displays the effect of laser heating on the optical absorption and the index of refraction. Curve 1 is plotted for a low laser intensity (W≈0.1 MVt/cm^2), where the heating by the laser is negligible. For a larger laser intensity (W≈5 MVt/cm^2), the generated heat has caused the band edge to shift toward the red (curve 2). The change in the absorption spectrum is shown in Fig. 2,b. The shift of the absorption spectrum toward lower energies gives rise to an refractive index change.

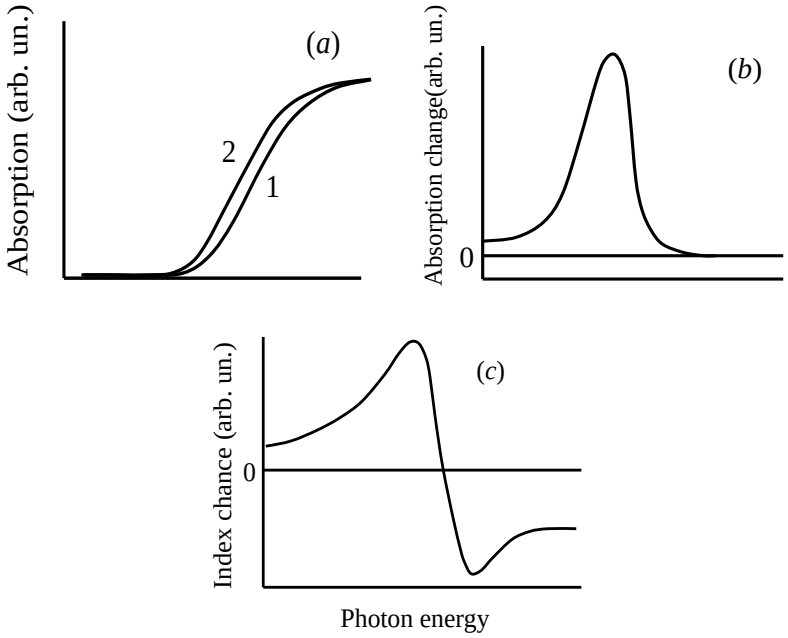

Fig. 2. Thermal optical nonlinearity in GaSe. (a) Schematics of the absorption spectra in the vicinity of the band qap for low (curve 1) and high (curve 2) laser intensities. (b) The change in the absorption coefficient. (c) The change in the refractive index.

From the Kramers-Kronig relation [18] we may write the change in refractive index at photon energy $\hbar\omega$ as:

$$\Delta n(\hbar\omega) = \frac{hc}{\pi}\int_0^{\infty} \frac{\Delta\alpha(\hbar\omega')}{(\hbar\omega')^2 - (\hbar\omega)^2} d(\hbar\omega') \tag{1}$$

Using eq. (1) to compute the index change related to the absorption change of Fig. 2, b, we obtain the result plotted in Fig. 2,c. As can be seen from this figure, in this case a thermally induced refractive index change is positive below the band edge and negative on the high-energy side. The laser-induced negative index change is referred to as a self-defocusing optical nonlinearity. The positive $\Delta n(\omega)$ on the low-energy side correspond to a self-focusing optical nonlinearity. The reason for such terminology is that the semiconductor medium behaves like a lens when a laser beam with a Gaussian spatial profile is incident on it. The red side of the band edge with $\Delta n(\omega)>0$, the medium acts as a positive lens. A laser beam with a Gaussian shape has an intensity profile such that the intensity in the center is larger than the sides. The larger intensity in the center of the beam induces a larger index of refraction in the semiconductor [$\Delta n(\omega)>0$] compared with the sides of the beam. The optical pathlength for the beam [$n(\omega)d$, where $n(\omega)$ is the index and d is the thickness] in the center is, thus, larger than the sides. The material effectively behaves like a positive lens for the Gaussian beam. As is well known, the optical pathlength is larger in the center of a positive lens.

As mentioned above, heating of the crystal lattice as a result of nonradiative recombination of electron-hole pairs generated by laser radiation leads to a shift of the edge of the absorption band towards long waves. As shown by our experimental results, in GaSe crystals, a significant shift of the edge of the absorption band is also observed under the influence of an external electric field. Fig. 3 shows the transmission spectra a GaSe sample with different applied voltages. The absorption edge moves towards longer wavelengths by increasing the applied voltage. A large shift of about 16 nm in the absorption edge corresponding to 50 meV is observed for the applied voltage of 18 V.

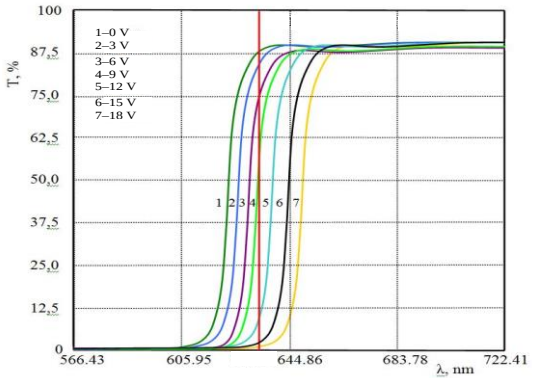

Fig. 3. Transmission spectra of GaSe for different applied voltage.

In our opinion, the redshift absorption edge in GaSe can be explained on the base of the Franz-Keldysh effect or thermal heating of the sample under the application of a continuous electric field. Franz-Keldysh predicted that the applied fied causes a broadening and low-energy shift of the band-edge absorption spectrum. The redshift of the band-edge results in an increase of optical absorption below the zero-field band gap. Our experimental results cannot be explained by the Franz-Keldysh effect. According to this model, the shift of absorption edge can be evaluated by the relation [19]:

$$h\theta = 0.0725(\frac{m_0}{\mu})^{1/3} E^{2/3} \quad (2)$$

where $\mu^{-1} = (m_e)^{-1} + (m_h)^{-1}$ is the reduced effective mass and E is the applied electric field in MW/cm. Taking $m_e = 0.3m_0$, $m_h = 0.2m_0$ and E=10^3 V/cm, the calculated value of the shift is ~1.4 meV which is much smaller than its experimental value ~50 meV.

The obtained experimental results can successfully be explained on the base of heating crystal lattice of the applied electric field. Calculation shows that, application of a continuous voltage of ~20V to the sample having a resistivity of ~10^3 Ω·cm generates a Joule effect of 1.9 W/cm^2. This heat power is sufficient enough to heat the sample by ~55-60 ^{0}C.

On the other hand, it is known that for most semiconductors, such as GaSe, a good fit to the measured thermal band qap reduction is given by [18]:

$$E_g(T) = 2020meV - \frac{0.58T^2}{T + 226K}\frac{meV}{K} \quad (3)$$

Indeed, estimates based on formula (3) show that heating a GaSe crystal by laser radiation to 50-60^{0}C can lead to a shift of the absorption edge to the long-wavelength range of ~50 meV.

Thus, our experimental results confirm the fact that there is a thermal nonlinearity effect in GaSe crystals under the action of laser radiation.

4. Conclusion

Thermal nonlinearity of the absorption coefficient and refractive index was found in GaSe crystals under the action of laser radiation. The laser-induced negative index change is referred to as a self-defocusing optical nonlinearity. The positive Δn(ω) on the low-energy side correspond to a self-focusing optical nonlinearity. The reason for such terminology is that the semiconductor medium behaves like a collecting and scattering lens. The effect of thermal nonlinearity observed in GaSe crystals under the influence of laser radiation is also evidenced by the significant shift of the edge of the absorption band that we discovered in the long-wavelength region of the spectrum under the influence of an external electric field applied to the sample. Calculation shows that, application of a continuous voltage of ~ 20 V to the sample leads to heating of the substance ~ 55-60 ^{0}C.

Thus, the experimental results presented show that a simple method can be used to detect and study the thermal nonlinearity of the optical parameters of GaSe crystals under laser excitation. Thermal nonlinearities has slow response time, determined by the time necessary to cool the crystal. This slow response helps distinguish thermally induced nonlinearities from optical nonlinearities of electronic origin.

Acknowledgements

This work was supported by the Science Development foundation under the president of the Republic of Azerbaijan – Grant № EİF/ MQM/ Elm-Tehsil -1-2016-1(26)-71/01/1.

References

[1] G. B. Abdullaev, L. A. Gulevski, A. P. Prokhorov, A. D. Saveliev, E. Yu. Salaev, V. V. Smirnov, JETP Lett. **16**, 130 (1972).

[2] G. A. Akhundov, A. A. Agaeva, V. M. Salmanov, Ju. P. Scharonov, I. D. Yarochetski, Sov.

Phys. Semicond. **7**, 1229 (1229).
[3] G. B. Abdullaev, K. R. Allakhverdiev, L. A. Gulevski, A. P. Prokhorov, E. Yu. Salaev, A. D. Saveliev, V. V. Smirnov, Quantum Electronics **2**, 1228 (1975).
[4] E. B. Beregylin, P. M. Valov, T. B. Ribakova, V. M. Salmanov, I. D. Yarochetski, Sov. Phys. Semicond. 9, 2288 (1975).
[5] R. Baltramieyunas, V. Narkevicius, E. Skaistys, J. Vaitkus, J. Viscakas, Nuovo Cimento B **38**, 603 (1977).
[6] H. M. Mammadov, M. A. Jafarov*, E. F.Nasirov, D. Piriyeva. Chalcogenide Letters, **18**, 31(2021)
[7] S. S. Yao, J. Buchert, R. R. Alfano, Phys. Rev. B **25**, 6534 (1982).
[8] V. S. Dneprovskii, A. I. Furtichev, V. I. Klimov, E. V. Nazvanova, D. K. Okorokov, U. V. Vandishev, Phys. Stat. Sol. B **146**, 341 (1988).
[9] L. Pavesi, J. L. Staehly, Phys. Rev. B **39**, 10982 (1989).
[10] R. E. Nahory, K. L. Shaklee, R. F. Leheny, J. C. De Winter, Solid State Commun. **9**, 1107(1971).
[11] I. M. Catalano, A. Cingolani, M. Ferrara, A. Minafra, Phys. Stat. Sol. B **68**, 345 (1975).
[12] X. Z. Lu, R.Rao, B. Wilman, S. Lee, A. G. Doukas, R. R. Alfano, Phys. Rev. B **36**, 1140(1987).
[13] A. I. Bobrysheva, G. P. Golubev, I. I. Dobinda, E. A. Zhukov, D. G. Luchinskii, Yu. G. Shekun, Phys. Stat. Sol. A **117**, 587 (1990).
[14] A. G. Kyazim-zade, V. M. Salmanov, A. G. Guseinov, M. A. Jafarov, R. M. Mamedov, R. M. Rzayev, A. A. Salmanova, N. D. Dashdamirova, F. SH. Ahmadova, Bandfilling effect in GaSe and InSe at high optical exchange levels, Chalcogenide Letters, **16**, 465 (2019)
[15] A. H. Kyazimzadeh, V. M. Salmanov, A. H. Mohtari. Inorganic Materials **44**(4), 1 (2008).
[16] G. A. Akhundov, V. M. Salmanov. Sov. Phys. Semicond. **6**, 405 (1972).
[17] M. Schulter, Nuovo Cimento **13B**, 313 (1973).
[18] N. Peyghambarian, S. W. Koch, A. Mysyrovicz, Introduction to semiconductor optics, Series in Solid State Physical Electronics (Pretice-Hall, New Jersey, p. 325, 1993.
[19] V. A. Tjagay, O. B. Snitko. Electroreflection in semiconductors, Naygova Dumca, Kiev, p. 47, 1980.