

Influence the cationic substitution in $\text{AgGaGe}_3\text{Se}_8$ on the electrooptical, IR optical and nonlinear properties

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In present article we present results of detailed study of the possibility adapting $\text{AgGaGe}_3\text{Se}_8$ single crystal properties to desired requirements by investigate the influence of the different cationic substitution on the physical properties: optical, nonlinear optical (NLO) — Second Harmonic Generation (SHG) and temperature dependent photoconductivity. We report results obtained for modified crystals based on $\text{AgGaGe}_3\text{Se}_8$ by cationic substitution of the elements belong to first — (Ag–Cu), third (Ga–In), and fourth (Ge–Sn) groups of the periodic system. For the convincing observation the effects of various impurities and compare results with obtained for virgin $\text{AgGaGe}_3\text{Se}_8$ crystal was conducted replacing at 5 mol. % one element by another.

Keywords: SHG, NLO, impurities.

Описаны возможности подстройки оптических, нелинейно-оптических (генерация второй гармоники), фотоэлектрических свойств $\text{AgGaGe}_3\text{Se}_8$ монокристалла к заранее заданным свойствам при помощи катионного замещения. Представлены результаты для монокристаллов твердых растворов, полученных с помощью катионного замещения первой (Ag–Cu), третьей (Ga–In) и четвертой (Ge–Sn) групп периодической системы элементов. Для возможности сравнить результаты исследованы кристаллы с 5 мол. % замещением одного элемента другим.

Вплив катіонного заміщення на фотоелектричні, ІЧ-оптичні та нелінійно-оптичні властивості монокристалу $\text{AgGaGe}_3\text{Se}_8$. *А.С.Кримусь, Г.Л.Мирончук, О.В.Парасюк, І.В.Кітик, М.П'ясецький.*

Описано можливості підстроювання оптичних, нелінійно-оптичних (генерация другої гармоніки), фотоелектричних властивостей $\text{AgGaGe}_3\text{Se}_8$ монокристалу до заздалегідь заданим властивостям за допомогою катіонного заміщення. Представлено результати для монокристалів твердих розчинів, отриманих за допомогою катіонного заміщення першої (Ag–Cu), третьої (Ga–In) і четвертої (Ge–Sn) груп періодичної системи елементів. Для можливості порівняти результати досліджено кристали з 5 мол. % заміщенням одного елемента іншим.

1. Introduction

Chalcogenide single crystal AgGaSe_2 is well known for possible application in non-linear optics and infrared technology in the spectral range of 3–18 μm [1, 2]. As one of an attempt to improve the desired properties of the AgGaSe_2 crystal was adding GeSe_2 . In [3] were presented properties of obtained quaternary phase $\text{Ag}_x\text{Ga}_x\text{Ge}_{1-x}\text{Se}_2$. The resulting solid solution has a wide range of homogeneity for $0.167 < x < 0.333$. Was found a number of important advantages for $\text{Ag}_x\text{Ga}_x\text{Ge}_{1-x}\text{Se}_2$ in comparison with triple compound: a lower melting point and a simpler process of growing [4], which leads to a reduction of crystals; greater resistance to laser irradiation [5], which is an important aspect when using compounds with powerful sources of optical radiation.

Single crystal $\text{AgGaGe}_3\text{Se}_8$ corresponds to maximum melting on the phase diagram and melts congruently [3] crystallizes in orthorhombic non-symmetrical space group $Fdd2$ with the band gap (2.17 eV) [6] as the strong defective semiconductor with a large anisotropy of physical properties [7].

Great interest by titled crystals caused by the unique its physical properties that can be used to create electro-optical [8, 9] and optical [10, 11] devices, namely a wide range of optical transmission (0.6–15 μm) [12], photosensitivity [6] nonlinear optical [10], magnetic [13] or piezoelectric properties [14].

As the efficient way to adjust the properties of the single crystal $\text{AgGaGe}_3\text{Se}_8$, in [15] was carried out doping rare-earth elements. Observed changes the electrical and optical properties of the single crystal by doping indicates the possibility tuning principal material constants of the single crystal $\text{AgGaGe}_3\text{Se}_8$ by adding impurities.

In present article we extend more detailed study of the possibility adapting single crystal properties to desired requirements by investigate the influence of cationic substitution on the structural properties and the features of the electron spectrum. We report cationic substitution of the elements belong to first — (Ag–Cu), third (Ga–In), and fourth (Ge–Sn) groups of the periodic system. To be able clearly observe the effects of various substitutions on the virgin crystal properties was conducted replacing at 5 mol. % one element by another.

2. Experimental

Measurements of the photoconductivity kinetics were performed using electrometer

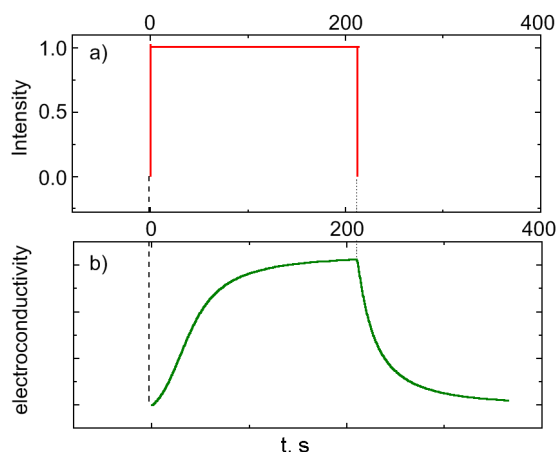


Fig. 1. Kinetics of photoconductivity relaxation (b) for monocrystalline solid solution $\text{Ag}_{0.95}\text{Cu}_{0.05}\text{GaGe}_3\text{Se}_8$ at $T = 240$ K, when the pulse of light had rectangular shape (a).

Keithley 6514. The speed of the signal registration was 500 measurements/sec. Temperature dependent studies were conducted in nitrogen cryostat with adjustable temperature in the temperature range of 77–300 K. The temperature dependences were made in the thermostat Utrecs K 41-3, with accuracy ± 0.1 K. Excitation of impurities to have opportunity observe the conductivity was created using a laser with a wavelength of 808 nm, with adjustable output power. Measurements of second harmonic generation were performed using powder method and 1064 nm laser in pulsed mode. To study the properties of absorption spectra in IR spectral range was used spectrometer Spectrum Two™ FTIR Spectrometer (PerkinElmer).

3. Results and discussion

All investigated compounds, like the initial one, are strongly compensated semiconductors with p -type conductivity.

By irradiate of the sample pulse of rectangular shape, as shown in Fig. 1a, saturated photoconductivity value is not achieved immediately saturated value, but only after a certain time after the lighting switch on (Fig. 1b). Upon termination lighting non-equilibrium conductivity also not disappear immediately, but after some time.

Generally, photo conductance stable wavelength depends on the intensity of incident like the light, and is described by the formula [16]:

$$\sigma_{\max} \sim I^b, \quad (1)$$

where σ_{\max} — maximal (saturated) conductivity; I is the intensity of the incident light.

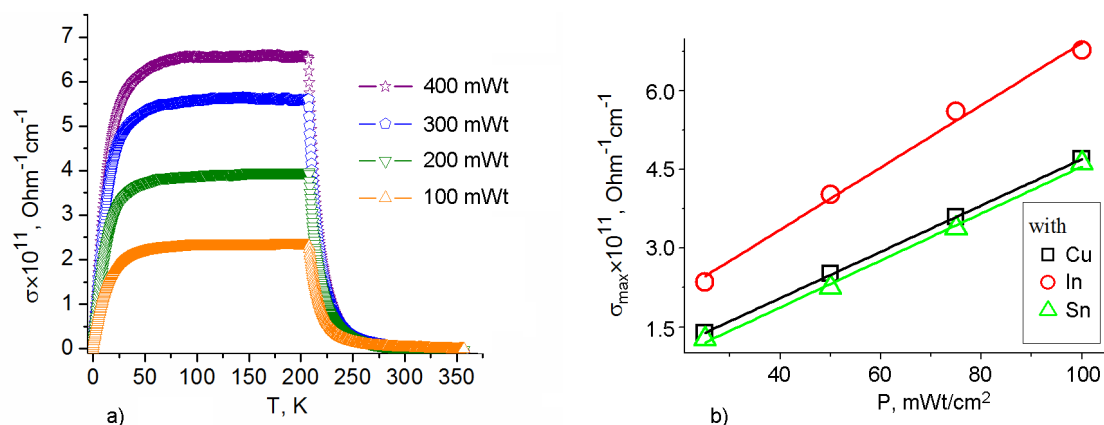


Fig. 2. The influence of intensity the incident light on the kinetics of relaxation (a), the maximum value of the conductivity (b) for the measured crystals at room temperature.

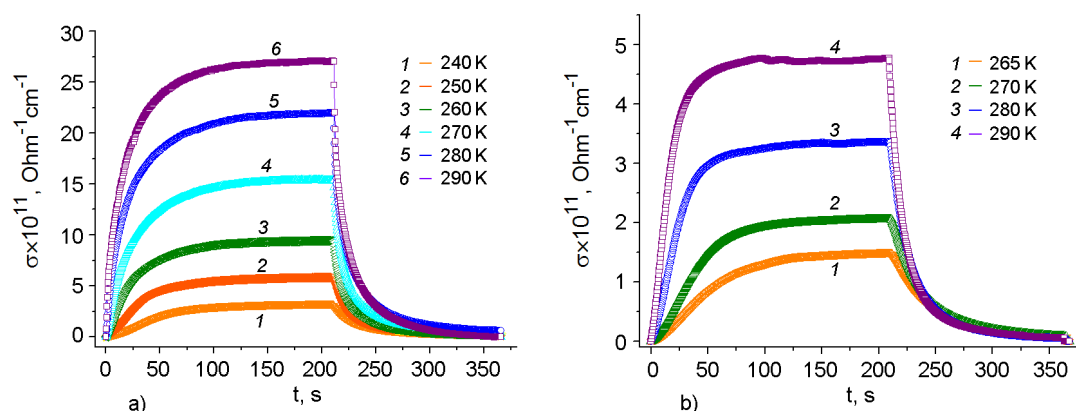


Fig. 3. Temperature dependences of relaxation kinetics for crystals (a) $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$ (b) $AgGa_{0.95}In_{0.05}Ge_3Se_8$ and (c) $AgGaGe_{2.85}Sn_{0.15}Se_8$.

When $b = 1$ in Eq. (1) photo-resistive effect referred to as linear, and $b < 1$ — as sublinear.

Figure 2 presents the kinetics of relaxation under the irradiation by the different intensities of the incident light. As can be seen from Fig. 2b, the σ_{max} (saturated photoconductivity) almost linearly increases along with the intensity of incident light, that corresponds to a linear photo-resistive effect. Similar dependences were obtained for other studied samples.

Figure 3 presents the relaxation kinetics for crystals (a) $Ag_{0.95}Cu_{0.05}GaGe_3Se_8$, (b) $AgGa_{0.95}In_{0.05}Ge_3Se_8$ and (c) $AgGaGe_{2.85}Sn_{0.15}Se_8$. From the shape of the curves, we can conclude that the kinetics of relaxation have complex dependence and its source in long-lasting effect.

Furthermore photoconductivity change with the temperature and depends from substituting ion. Currently there are two models that describe the long-term processes of relaxation kinetics [17], but separate par-

ticular mechanisms that correspond to both models seems quite a difficult task.

The long-term relaxation curves of which presents processes of arise and vanish photoconductivity may be estimated by the exponential formulas (2) and (3) [18]

$$\Delta\sigma = \Delta\sigma_{st}(1 - e^{-t/\tau_1}), \tag{2}$$

$$\Delta\sigma = \Delta\sigma_{st}(e^{-t/\tau_2}), \tag{3}$$

where τ is the time of relaxation of no equilibrium charge carriers.

It should be noted that the simultaneously occurrence the bulk relaxation kinetics and surface relaxation, which under certain conditions can undergo into bulk relaxation [19]. But in the present study we investigated specimens with a big thickness and therefore this effect can be neglected, and relaxation kinetics will be considered as the relaxation inside the volume of the sample.

Due to the absorption spectrum from [20] we decided to use the 808 wavelength

Table. The value of relaxation kinetics times at different temperatures for crystals $\text{Ag}_{0.95}\text{Cu}_{0.05}\text{GaGe}_3\text{Se}_8$, $\text{AgGa}_{0.95}\text{In}_{0.05}\text{Ge}_3\text{Se}_8$ and $\text{AgGaGe}_{2.85}\text{Sn}_{0.15}\text{Se}_8$

T, K	$\text{Ag}_{0.95}\text{Cu}_{0.05}\text{GaGe}_3\text{Se}_8$			$\text{AgGa}_{0.95}\text{In}_{0.05}\text{Ge}_3\text{Se}_8$			$\text{AgGaGe}_{2.85}\text{Sn}_{0.15}\text{Se}_8$		
	τ_1, s	τ_2, s	τ_3, s	τ_1, s	τ_2, s	τ_3, s	τ_1, s	τ_2, s	τ_3, s
240(245*)	37.84	20.95	40.07	–	–	–	52.05*	35.788*	65.05*
250	28.69	14.6	36.44	–	–	–	44.3	29.61	62.03
260(265*)	27.25	10.19	24.77	44.18*	36.30*	54.32*	27.01	19.56	32.26
270	25.22	8.4	20.46	33.93	28.77	43.44	18.63	13.38	19.63
280	23.4	5.89	14.81	21.47	18.98	25.92	16.85	9.81	16.99
290	21.84	3.77	10.16	13.42	13.22	19.93	15.86	7.14	15.93

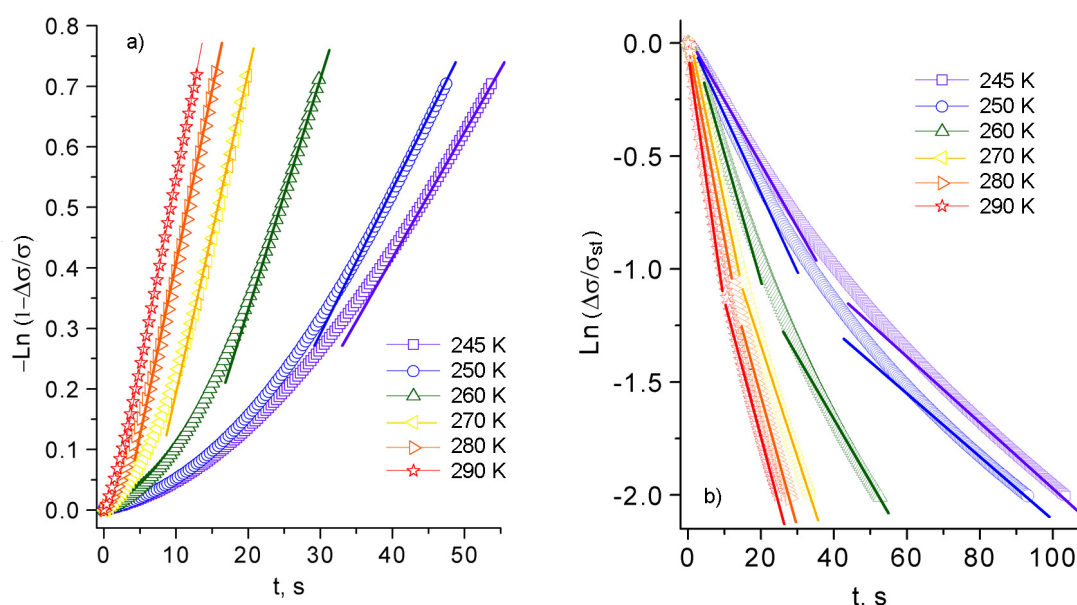


Fig. 4. Kinetics of increase (a) and vanishing (b) doping-based kinetics in solid solution $\text{AgGaGe}_{2.85}\text{Sn}_{0.15}\text{Se}_8$.

of exciting light, which corresponds to impurities conductivity. In this regard, the analysis is carried out with the use of long-term relaxation model, defined by the admittance of free charge carriers traps [21]. Fig. 4a represent the kinetics of growth of conductivity for solid solution $\text{AgGaGe}_{2.85}\text{Sn}_{0.15}\text{Se}_8$. Similar growth curves were obtained for the other investigated crystals. As you can see from the figure, at the initial phase the conductivity growth deviates from the exponential dependence that can be associated with low filling energy levels. After some time, set up the balance between the V-zone and traps (t). Further kinetics of conductivity growth is connected with the generation of no equilibrium current carriers and includes recombination via the r and s centres, what caused that in coordinates $\ln(\Delta\sigma/\Delta\sigma_{st}) - t$ is an al-

most straight line, the slope of which determine time τ_1 . The results of the computations of times τ_1 is represented in Table. Great value for τ_1 times indicate the involvement of recombination barriers or small levels of sticking in the relaxation kinetics. Reduce the time of relaxation with increasing temperature may be due to a decrease of the concentration V_{Ag} .

As we can see from Fig. 4b, after the switch off lighting the kinetics of relaxation in the coordinates $\ln(\Delta\sigma/\Delta\sigma_{st}) - t$ may be described at least by two contributions, which corresponds to two levels of recombination and can be described by two independent exponential fuinctions (4)

$$\Delta\sigma = A_1(e^{-t/\tau_2}) + A_2(e^{-t/\tau_3}), \quad (4)$$

where the constants A_1 and A_2 almost equal $\Delta\sigma_{st}$. The tangent angle of incline determine values of times τ_2 and τ_3 which are collected in the Table 1. In the presence of centers of binding relaxation kinetics time can be described from the temperature dependence [18]:

$$\tau = \tau_p \left(1 + B \exp \left(\frac{E_{tp}}{kT} \right) \right), \quad (5)$$

where τ_p — life time of free holes; E_{tp} is the distance from the tapping structure level to the top of valence band; $B = N_t/N$ is the ratio of the concentration of binding centres to an effective hole density of states in the valence band.

Assuming that $\tau > \tau_p$, which is a characteristic for impurities conduction, we can obtain the Eq. 6:

$$\tau = \tau_p \frac{N_t}{N_V} \exp \left(\frac{E_{tp}}{kT} \right). \quad (6)$$

Figure 5 presents the times of relaxation kinetics vis temperature in the $\ln(\tau)$ - $1/T$ coordinates. The dependences are located on straight lines which the tangent of slope give opportunity to determine the energy of holes. The results of the evaluation of the energy of hole traps are the following: 0.21, 0.26 and 0.22 eV for $\text{Ag}_{0.95}\text{Cu}_{0.05}\text{GaGe}_3\text{Se}_8$, $\text{AgGa}_{0.95}\text{In}_{0.05}\text{Ge}_3\text{Se}_8$ and $\text{AgGaGe}_{2.85}\text{Sn}_{0.15}\text{Se}_8$ single solid solutions, respectively.

Fig. 6a presents the spectral dependence of the absorption in the range 450–1100 cm^{-1} for the investigated crystals, renormalized to the maximum value absorption of the $\text{Ag}_{0.95}\text{Cu}_{0.05}\text{GaGe}_3\text{Se}_8$. As we can see from the picture, the peaks of absorption for all the studied compounds are on

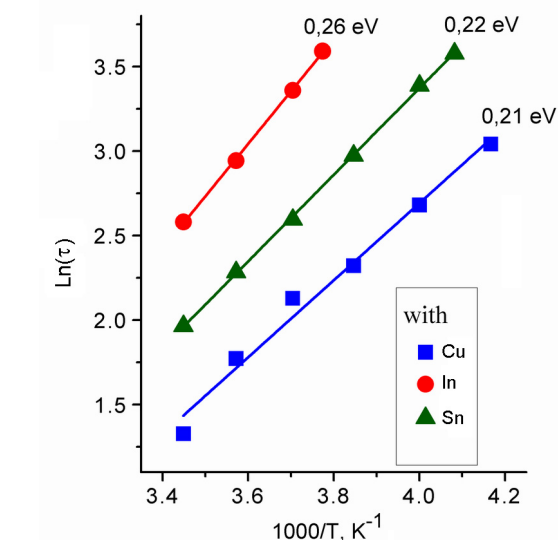
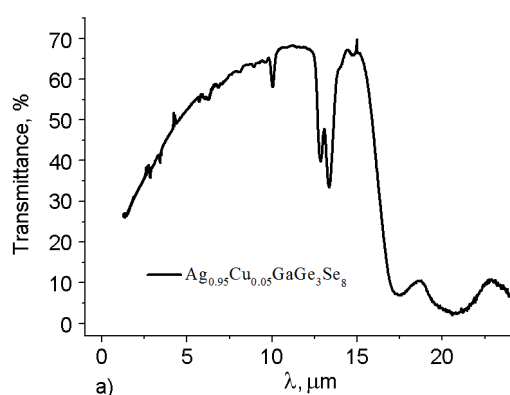


Fig. 5. Temperature dependences of the relaxation times for the studied compounds.

the same wavelengths, no new peaks of absorption does not arise.

This behavior of the transmission curve (6b) may be due to the presence of radiation scattering centers.

Fig. 7a present dependence of the magnitude of the output signal second harmonic generation (SHG) from the incident light angle to surface of sample (investigation of sample with Sn gave no results of SHG). Further were carried out at SHG measurements, at incident light angle which corresponds to the maximum of output signal: 30 and 35 degrees for the crystal of Cu and In, respectively. In Fig. 7b is represented the dependence of the intensity the SHG signal from power of incident light. As you can see from the picture, according to crystals with different composition have similar be-

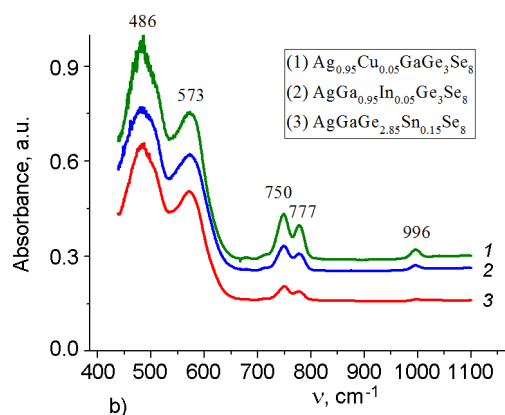


Fig. 6. The spectral dependences of the absorption coefficients for the (a) studied compounds and (b) pure $\text{AgGaGe}_3\text{Se}_8$.

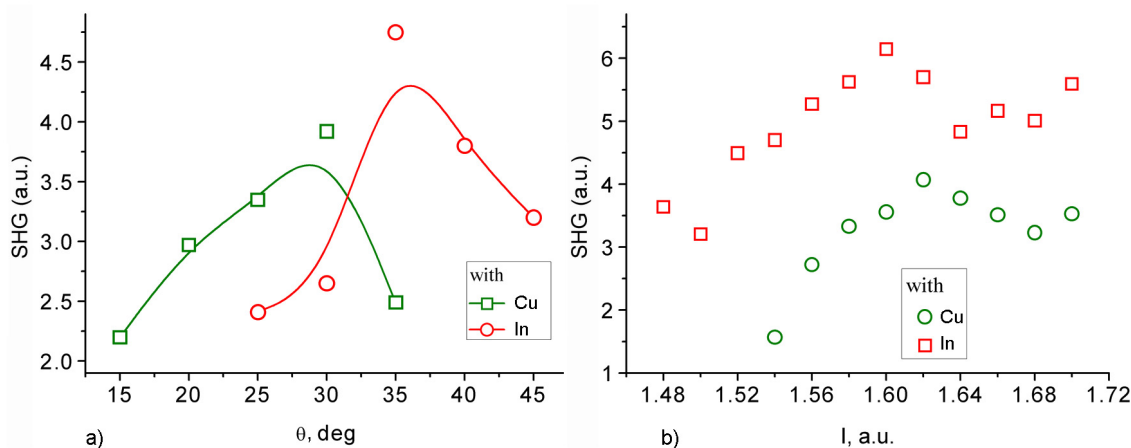


Fig. 7. Angular dependences of the second harmonics generation intensity (a), power dependences SHG (b) for investigated crystals.

havior of angle and power dependent SHG, but differ in the values.

4. Conclusions

In present work we investigated kinetics relaxation, TPA and SGH for set of doped crystal $\text{AgGaGe}_3\text{Se}_8$, modified by cationic substitution of the elements (Ag–Cu), (Ga–In), and (Ge–Sn): $\text{Ag}_{0.95}\text{Cu}_{0.05}\text{GaGe}_3\text{Se}_8$, $\text{AgGa}_{0.95}\text{In}_{0.05}\text{Ge}_3\text{Se}_8$ and $\text{AgGaGe}_{2.85}\text{Sn}_{0.15}\text{Se}_8$. Was shown the complex nature of the curves of growth and disappearance photoconductivity. Large times τ_1 indicate the participation of recombination barriers or small levels of adhesion in the relaxation of photoconductivity. We calculated temperature dependent relaxation times for the studied compounds, determined energy of the traps, which are equal 0.21 eV, 0.26 eV and 0.22 eV for crystals doped by Cu, In, Sn, respectively. We also investigated the spectral dependence of the coefficient of transmittance in the wide spectral range 1–25 μm , and show the main differences between the pure single crystal and based on it solid solutions. The resulting behavior of the transmission curve can be due to the presence of scattering centers. We presented results of the angular and energy dependence of generation of the second harmonic in the investigated compounds.

References

1. R.L.Byer, M.M.Choy, R.L.Herbst et al., *Appl. Phys. Lett.*, **24**, 65 (1974).
2. M.T.Whittaker, T.E.Stenger, D.G.Krause, D.H.Matthiesen, *J. Cryst. Growth*, **310**, 1904 (2008).
3. J.D.Olekseyuk, A.Y.Gulyak, L.Y.Sysa et al., *J. Alloys Compd.*, **241**, 187 (1996).
4. O.V.Parasyuk, A.O.Fedorchuk, G.P.Gorgut et al., *Opt. Mater.*, **35**, 65 (2012).
5. M.V.Shevchuk, V.V.Atuchin, A.V.Kityk et al., *J. Cryst. Growth*, **318**, 708 (2011).
6. G.Lakshminarayana, M.Piasecki, G.E.Davydyuk et al., *Mater. Chem. Phys.*, **135**, 837 (2012).
7. V.Badikov, K.Mitin, F.Noack et al., *Opt. Mater.*, **31**, 590 (2009).
8. V.Petrov, F.Noack, V.Badikov et al., *Appl. Opt.*, **43**, 4590 (2004).
9. G.L.Myronchuk, O.V.Zamurueva, O.V.Parasyuk et al., *J. Mater. Sci. Mater. Electron.*, **25**, 3226 (2014).
10. D.J.Knuteson, N.B.Singh, G.Kanner et al., *J. Cryst. Growth*, **312**, 1114 (2010).
11. V.Yo.Stadnyk, R.S.Brezvin, M.Ya.Rudysch et al., *Opt. Spectrosc.*, **117**, 756 (2014).
12. V.Panyutin, V.Badikov, G.Shevyrdyaeva et al., *Proc. of SPIE*, **6875**, 68750A (2008).
13. D.Adamenko, O.Parasyuk, R.Vlokh, *Ukr. J. Phys. Opt.*, **17**, 27 (2016).
14. I.Martynyuk-Lototska, M.Kushnirevych, G.L.Myronchuk et al., *Ukr. J. Phys. Opt.*, **16**, 77 (2015).
15. G.E.Davidyuk, O.N.Yurchenko, O.V.Parasyuk et al., *Inorg. Mater.*, **44**, 361 (2008).
16. K.V.Shalimova, *Physics of Semiconductors*, Mir, Moscow (2010). [in Russian]
17. M.S.Yunusov, M.Karimov, B.L.Oksengendler, *Semiconductors*, **32**, 238 (1998).
18. R.Enderlein, *Fundamentals of Semiconductor Physics and Devices*, Hardcover (1997).
19. T.S.Rao, A.K.Chaudhuri, *Bull. Mater. Sci.*, **19**, 449 (1996).
20. I.V.Kityk, G.L.Myronchuk, O.V.Parasyuk et al., *Opt. Mat.*, **63**, 197 (2017).
21. A.V.Novosad, V.V.Bozhko, H.E.Davydyuk et al., *Semiconductors*, **48**, 286 (2014).