Influence the cationic substitution in AgGaGe₃Se₈ 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 AgGaGe₃Se₈ 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 AgGaGe₃Se₈ 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 AgGaGe₃Se₈ crystal was conducted replacing at 5 mol. % one element by another.

Keywords: SHG, NLO, impurities.

Описана можливість подіління оптичних, нелінійно-оптичних (генерація другої гармоніки), фотоелектричних властивостей AgGaGe₃Se₈ монокристалу за допомогою квантового заміщення. Представлені результати для монокристалів твердих рідків, отриманих з допомогою квантового заміщення першої (Ag–Cu), третій (Ga–In) і четвертої (Ge–Sn) груп періодичної системи елементів. Для можливості порівняння результати досліджено кристи з 5 мол. % заміщення одного елемента іншим.

Вплив катіонного заміщення на фотоелектричні, ПЧ-оптичні та нелінійно-оптичні властивості монокристалів AgGaGe₃Se₈. А.С.Крымус, Г.Л.Мирончук, О.В.Парасюк, І.В.Китик, М.Писецький.

Описано можливості підтримування оптичних, нелінійно-оптичних (генерація другої гармоніки), фотоелектричних властивостей AgGaGe₃Se₈ монокристалу за допомогою катіонного заміщення. Представлено результати для монокристалів твердих рідків, отриманих за допомогою катіонного заміщення першої (Ag–Cu), третій (Ga–In) і четвертої (Ge–Sn) груп періодичної системи елементів. Для можливості порівняння результати досліджено кристи з 5 мол. % заміщення одного елемента іншим.
1. Introduction

Chalcogenide single crystal AgGaSe₂ is well known for possible application in nonlinear 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 AgGaSe₂ crystal was adding GeSe₂. In [3] were presented properties of obtained quaternary phase AgₓGa₁₋ₓGe₁₋ₓSe₂. The resulting solid solution has a wide range of homogeneity for 0.167 < x < 0.333. Was found a number of important advantages for AgₓGa₁₋ₓGe₁₋ₓSe₂ 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 AgGaGe₃Se₈ 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 AgGaGe₃Se₈, 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 AgGaGe₃Se₈ 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 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 Utrees 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]:

\[ \sigma_{\text{max}} \sim I^b, \]

where \( \sigma_{\text{max}} \) — maximal (saturated) conductivity; \( I \) is the intensity of the incident light.
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 $\sigma_{\text{max}}$ (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) $\text{AgGa}_{0.95}\text{In}_{0.05}\text{GeSe}_8$ (b) $\text{AgGa}_{0.85}\text{In}_{0.15}\text{GeSe}_8$ and (c) $\text{AgGaGe}_2\text{Sn}_{0.15}\text{Se}_8$. 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 particular 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]

$$\Delta \sigma = \Delta \sigma_{\text{eq}} \left(1 - e^{-t/\tau_1}\right),$$  \hspace{1cm} (2)

$$\Delta \sigma = \Delta \sigma_{\text{eq}} \left(e^{-t/\tau_2}\right),$$  \hspace{1cm} (3)

where $\tau$ 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
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 AgGaGe2.85Sn0.15Se8. 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 almost straight line, the slope of which determine time $\tau_1$. The results of the computations of times $\tau_1$ is represented in Table. Great value for $\tau_1$ 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 functions (4)

$$\Delta\sigma = A_1(\exp(t/\tau_1)) + A_2(\exp(t/\tau_2))$$

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Table. The value of relaxation kinetics times at different temperatures for crystals Ag0.95Cu0.05GaGe2Se8, AgGa0.95In0.05Ge3Se8 and AgGaGe2.85Sn0.15Se8

<table>
<thead>
<tr>
<th>T, K</th>
<th>$\tau_1$, s</th>
<th>$\tau_2$, s</th>
<th>$\tau_3$, s</th>
<th>$\tau_4$, s</th>
<th>$\tau_5$, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>240(245)</td>
<td>37.84</td>
<td>20.95</td>
<td>40.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>28.69</td>
<td>14.6</td>
<td>36.44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>260(265)</td>
<td>27.25</td>
<td>10.19</td>
<td>24.77</td>
<td>44.18$^a$</td>
<td>36.30$^a$</td>
</tr>
<tr>
<td>270</td>
<td>25.22</td>
<td>8.4</td>
<td>20.46</td>
<td>33.93</td>
<td>28.77</td>
</tr>
<tr>
<td>280</td>
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<td>5.89</td>
<td>14.81</td>
<td>21.47</td>
<td>18.98</td>
</tr>
<tr>
<td>290</td>
<td>21.84</td>
<td>3.77</td>
<td>10.16</td>
<td>13.42</td>
<td>13.22</td>
</tr>
</tbody>
</table>

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Fig. 4. Kinetics of increase (a) and vanishing (b) doping-based kinetics in solid solution AgGaGe2.85Sn0.15Se8.
where the constants \( A_1 \) and \( A_2 \) almost equal \( \Delta \sigma_{St} \). The tangent angle of incline determine values of times \( \tau_2 \) and \( \tau_3 \) 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]:

\[
\tau = \tau_p \left( 1 + B \exp \left( \frac{E_{tp}}{kT} \right) \right),
\]

(5)

where \( \tau_p \) — life time of free holes; \( E_{tp} \) is the distance from the taping structure level to the top of valence band; \( B = N_s / N \) 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:

\[
\tau = \frac{\tau_p N_s}{N_v} \exp \left( \frac{E_{tp}}{kT} \right).
\]

(6)

Figure 5 presents the times of relaxation kinetics vs 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 \( \text{Ag}_{0.95}\text{Cu}_{0.05}\text{Ge}_{2.86}\text{Se}_{8}, \text{AgGe}_{0.05}\text{In}_{0.05}\text{Ge}_{3.05}\text{Se}_{8} \) and \( \text{AgGaGe}_{2.86}\text{Sn}_{0.15}\text{Se}_{6} \) 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 \( \text{Ag}_{0.95}\text{Cu}_{0.05}\text{Ga}_{2.86}\text{Ge}_{3.05}\text{Se}_{8} \). As we can see from the picture, the peaks of absorption for all the studied compounds are on 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 \( \text{Sn} \) 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 \( \text{Cu} \) and \( \text{In} \), 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-

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

**Fig. 6.** The spectral dependences of the absorption coefficients for the (a) studied compounds and (b) pure \( \text{AgGaGe}_{2.86}\text{Se}_{6} \).

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behavior 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 AgGaGeSe\(_2\)S\(_3\), modified by cationic substitution of the elements (Ag–Cu), (Ge–In), and (Ge–Sn):Ag\(_{0.95}\)Cu\(_{0.05}\)Ge\(_{0.03}\)Se\(_2\), Ag\(_{0.95}\)In\(_{0.05}\)Ge\(_{0.03}\)Se\(_2\), and Ag\(_{0.95}\)Ge\(_{0.05}\)Sn\(_{0.05}\)Se\(_2\). Was shown the complex nature of the curves of growth and disappearance photoconductivity. Large times \(\tau\) 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

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