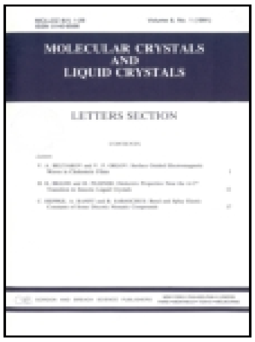
MOLECULAR CRYSTALS AND LIQUID CRYSTALS

LETTERS SECTION

Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Enhanced persistent photoconduction in $CuInS_2$–$ZnIn_2S_4$ alloys single crystals and processes of its relaxation

V. V. Bozhko, A. V. Novosad, O. V. Parasyuk, N. Vainorius, V. Vertelis, A. Nekrošius & V. Kažukauskas

To cite this article: V. V. Bozhko, A. V. Novosad, O. V. Parasyuk, N. Vainorius, V. Vertelis, A. Nekrošius & V. Kažukauskas (2016) Enhanced persistent photoconduction in $CuInS_2$–$ZnIn_2S_4$ alloys single crystals and processes of its relaxation, Molecular Crystals and Liquid Crystals, 627:1, 153-162, DOI: 10.1080/15421406.2015.1137382

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1137382

MOL. CRYST. LIQ. CRYST.
2016, VOL. 627, 153–162
http://dx.doi.org/10.1080/15421406.2015.1137382

Taylor & Francis
Taylor & Francis Group

Enhanced persistent photoconduction in $CuInS_2$–$ZnIn_2S_4$ alloys single crystals and processes of its relaxation

V. V. Bozhko[a], A. V. Novosad[a], O. V. Parasyuk[a], N. Vainorius[b], V. Vertelis[b], A. Nekrošius[b], and V. Kažukauskas[b]

[a]Lesya Ukrainka Eastern European National University 43025 Lutsk, Ukraine; [b]Semiconductor Physics Department and Institute of Applied Research, Vilnius University, Saulėtekio al. 9, bldg.3, LT-10222 Vilnius, Lithuania

ABSTRACT
Photoelectrical response in $CuInS_2$–$ZnIn_2S_4$ alloys single crystals was analysed in the low temperature region from 30 K up to 100 K. The molar ratio of $ZnIn_2S_4$ in the alloys was varied in the range 0 mol%–16 mol%. The crystals with up to 12 mol% were the single-crystalline, meanwhile those with 16 mol% were the two phase ones. We have analysed spectral distribution of their photocurrent at different temperatures and the following relaxation towards the stationary values. The photo-induced photoconductivity phenomena were identified. Moreover the long-lasting relaxations with characteristic times exceeding 1.5×10^3 sec were observed at lowest temperatures. They used to shorten exponentially with increasing temperature showing thermally activated behaviour. The main parameters of the photoconductivity kinetics and their temperature dependencies were determined. The observed behaviour was explained by the slow multicenter recombination due to the combined effect of different trapping and recombination centers. The effects of both – "fast" and "slow" recombination centers were taken into account.

KEYWORDS
$CuInS_2$–$ZnIn_2S_4$ alloys single crystals; solid solutions; semiconductors; photoconductivity; relaxation; recombination centers

1. Introduction

Compound semiconductor $CuInSe_2$ and its alloys feature the optimal combination of the optical and electronic properties, which make them perfectly suitable for applications in optoelectronics. Particularly, they are promising materials for the active absorbing layers in thin film heterojunction solar cells [1, 2, 3]. Numerous data demonstrate that the physical properties of $CuInSe_2$ compound and CuInSe-based alloys are controlled to a large extent by point defects of the crystal lattice [4, 5, 6, 7]. Thus, the in-depth studies of the behavior of defects in these semiconductors can reveal new ways of controlling the (photo-) electrical characteristics, and spectral sensitivity in particular.

The long-lasting ($\sim10^3$ sec) photoconductivity relaxations in $Cu_{1\text{-}x}Zn_xInS_2$ alloys single crystals were first reported in [8]. Semiconductors, characterized by the long-lasting relaxations of photoconductivity, are widely used as materials for the slow-relaxing photoresistors and photo-memory systems [9]. Moreover, studies of the photoconductivity and its relaxations is one of the most used methods for determining parameters of the localized states in the band gap, as well as the nonequilibrium charge carrier lifetimes [10, 11]. We have

CONTACT V. V. Bozhko ✉ bozhko@univer.lutsk.ua; V. Kažukauskas ✉ vaidotas.kazukauskas@ff.vu.lt
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

Table 1. Results of the EDX analysis of the samples.

$ZnIn_2S_4$ content, mol%	Element	Measured concentration, at.%	Batch composition, at%
4	Cu	23.12 ± 0.45	23.30
	In	25.24 ± 0.23	25.24
	Zn	–	0.97
	S	51.65 ± 0.21	50.49
8	Cu	21.79 ± 0.34	21.70
	In	25.46 ± 0,16	25.47
	Zn	1.76 ± 0.42	1.89
	S	50.99 ± 0.67	50.94
12	Cu	20.68 ± 0.54	20.17
	In	25.43 ± 0.36	25.69
	Zn	2.55 ± 0.32	2.76
	S	52.99 ± 0.77	51.38

demonstrated earlier that photoconductivity is a sensitive tool for the analysis of charge transport in defective and inhomogeneous materials as well [12, 13, 14, 15, 16, 17].

The purpose of this study is investigation of the photoconductivity spectra and its relaxation in $Cu_{1-x}Zn_xInS_2$ alloys single crystals in the temperature range from ~30 up to 100 K. Attention is paid to the influence of the cation-vacancy defects on the photoelectrical properties of crystals.

2. Samples and experiment

We have investigated $CuInS_2$-$ZnIn_2S_4$ solid solutions containing 4, 8, 12 and 16 mol% of the $ZnInS_4$. The crystal growth technology, results of their X-ray structural analysis and some physical properties are presented in our previous publications [18, 19]. The crystals with up to 12 mol% $ZnIn_2S_4$ were the single-crystalline, meanwhile those with as much as 16 mol% were the two phase ones. The composition of grown crystals was controlled by EDX analysis. The results of EDX analysis are presented in Table 1. They had confirmed that the content of the elements in the solid solutions is coinciding well with the composition of the initial charge.

To measure the (photo-) electrical properties of $CuInS_2$-$ZnIn_2S_4$ alloys the samples in the form of regular parallelepipeds of about $\sim 6\times 2\times 1$ mm^3 were fabricated. All the crystals had n-type conductivity. The relaxation processes and photoconductivity spectra were measured in the temperature regions T≈30–100 K. To avoid pre-excitation of the samples by high-energy photons, photoconductivity spectra were first measured starting from the low quanta energies of the exciting light. After that, the spectra were scanned in the opposite direction starting from the highest quanta energies. To assure the stationary measurement conditions, duration of the single scans was as long as up to 3000 s. Kinetics of the photoconductivity growth and decay were recorded after the excitation of the samples by light corresponding to the maxima of the induced photoconductivity. The energy position of these peaks was found to be 1.32 eV, 1.35 eV and 1.30 eV for the samples with 8, 12 and 16 mol% of $ZnIn_2S_4$, respectively [18]. The light excitation of the samples lasted for 3000 sec till the photocurrent saturation was reached, after that light was turned off and relaxation kinetics were measured.

3. Results and discussion

The induced impurity-related photoconductivity was observed in $Cu_{1-x}Zn_xInS_2$ single crystals, containing ~8 and ~12 mol% $ZnIn_2S_4$ at low temperature (T≈30 K) in [18]. The explanation and model of the induced impurity-related photoconductivity was first proposed in [20].

To explain the experimental results, in [18] we had proposed the two-defect-center recombination model. According to the model, the impurity and induced photoconductivity phenomena are caused by the transitions to the valence band from the acceptor levels formed by V_{Cu} and V_{In}, respectively. It was argued that V_{In} play the role of the fast recombination s-centers, and the slow recombination r-centers are formed by V_{Cu} [18, 21]. Meanwhile two donor levels, which are caused by V_S, play the role of shallow traps (t-levels). The thermal activation energies (E_D) of these levels were determined from the spectra of thermally stimulated currents in [18]. They were found to be E_{D1}: 0.016 eV and 0.023 eV, E_{D2}: 0.081 eV and 0.117 eV for the samples containing 8 and 12 mol % $ZnIn_2S_4$, respectively.

The photoconductivity spectra at different temperatures are shown in Fig. 1.

Increase in the height of the induced photoconductivity peak compared to that of the impurity photoconductivity (shortwave maximum) can be explained by the fact that upon light excitation trap levels become filled, thus more generated electrons can take part in the photoconductivity without being trapped. This means that the trapping time constant of electrons exceeds the electron lifetime.

Reduction of the difference in heights of the maxima of the impurity photoconductivity and induced photoconductivity at higher temperatures in Fig. 1 is caused by the onset of full or partial thermal activation of electrons from t-levels. This assumption is supported by the fact that the thermally stimulated conductivity maxima are observed at ~70 K and ~80 K in the samples with 8 and 12mol% $ZnIn_2S_4$, respectively [18]. Shift of the peaks of the impurity photoconductivity towards longer wavelengths with increasing temperature is presumably due to the decrease of E_g. This shift is marked by the doted straight line in Fig. 1. The thermal coefficient of the change in the position of the photoconductivity peak is $4.3\ 10^{-4}$ eV·K^{-1}, being consistent with the thermal coefficient of other chalcogenide compounds [22].

Kinetics of the photoconductivity growth and decay of $Cu_{1-x}Zn_xInS_2$ single crystals are shown in Figs. 2, 3. It can be seen that these long-lasting relaxation processes are of complex nature. In case of impurity excitation photoconductivity growth in semiconductors can be described by the expression [11, 20]:

$$\Delta\sigma = \Delta\sigma_{st} \cdot \left(1 - \exp\left(-\frac{t}{\tau_1}\right)\right) \tag{1}$$

Here τ_1 - photoconductivity relaxation time upon excitation, $\Delta\sigma_{st}$ - stationary nonequilibrium conductivity.

In the $CuInS_2$-$ZnIn_2S_4$ alloys with the lowest content of the second component (~ 4 mol% $ZnIn_2S_4$) the long-lasting photoconductivity relaxations were not observed. This is consistent with the data of Ref. [18], according to which in $CuInS_2$-$ZnIn_2S_4$ with 4 mol% $ZnIn_2S_4$ as well as in $CuInS_2$ crystals the photoconductivity peak corresponds to band-to-band optical transitions. Thus, low content of Zn atoms is the reason for such variation of photoelectrical properties.

As is known [e.g., 18], during the formation of $CuInS_2$-$ZnIn_2S_4$ solid solutions, two Cu atoms are substituted by one Zn atom in their crystallographic positions 4a. This causes formation of the tetrahedral voids and appearance of V_{Cu}. Concentration of V_{Cu} grows with increasing $ZnIn_2S_4$ content; this leads to an increase in the degree of compensation of the electrons.

Figure 2 shows photoconductivity growth of $CuInS_2$-$ZnIn_2S_4$ solid solutions containing 8, 12 and 16 mol% of $ZnIn_2S_4$. In the semi-logarithmic scaling they are well described by

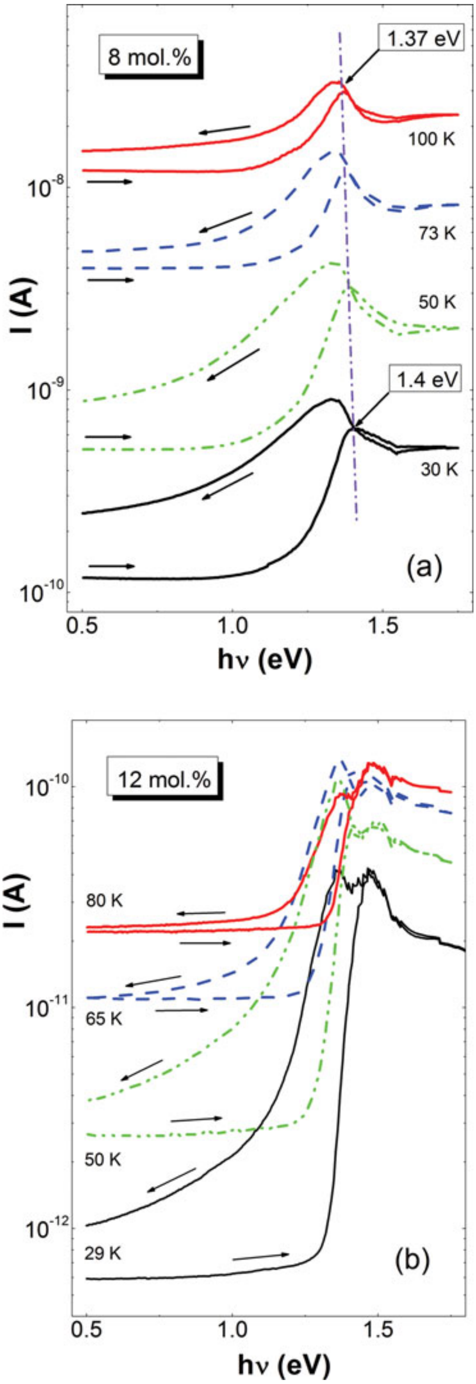

Figure 1. Photoconductivity spectra of the $CuInS_2$-$ZnIn_2S_4$ alloys containing 8 mol% (a) and 12 mol % (b) of $ZnIn_2S_4$ at different temperatures. Dash-dotted line indicates shift of the impurity photoconductivity peaks towards longer wavelengths with temperature.

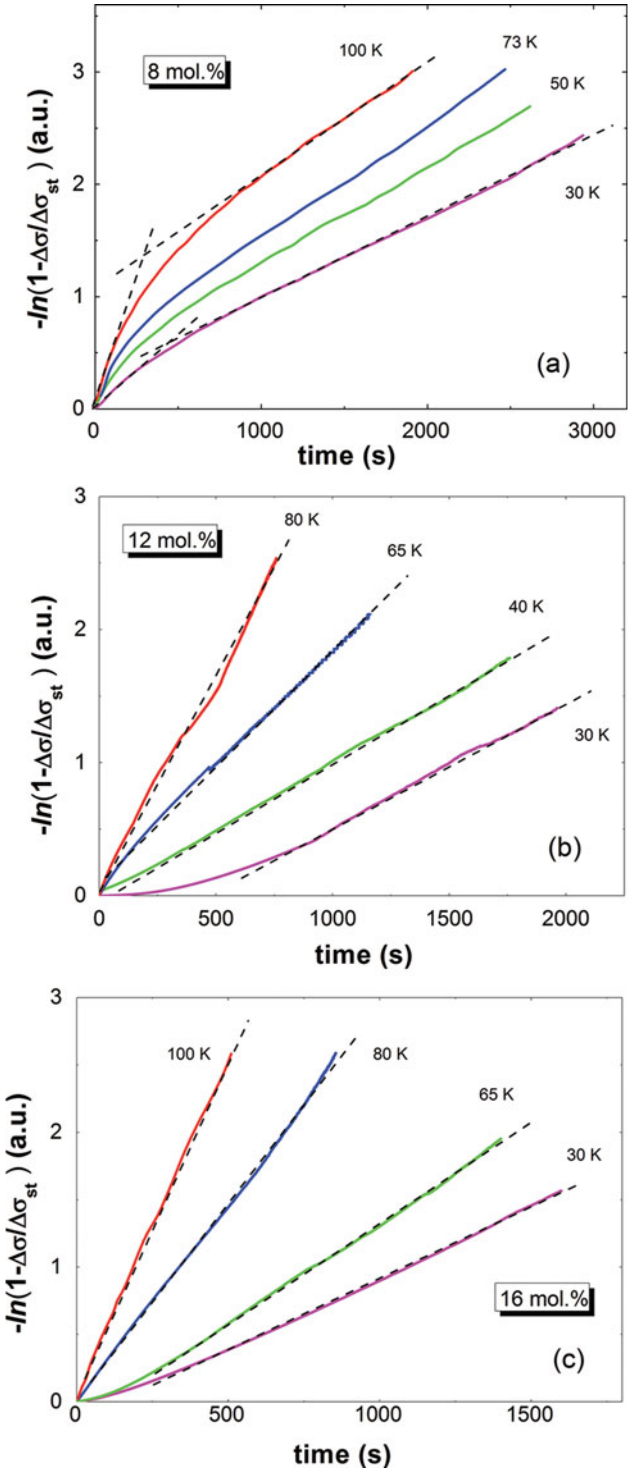

Figure 2. Kinetics of the photoconductivity growth of the $CuInS_2$-$ZnIn_2S_4$ alloys containing 8 (a), 12 (b) and 16 (c) mol % of $ZnIn_2S_4$ at different temperatures.

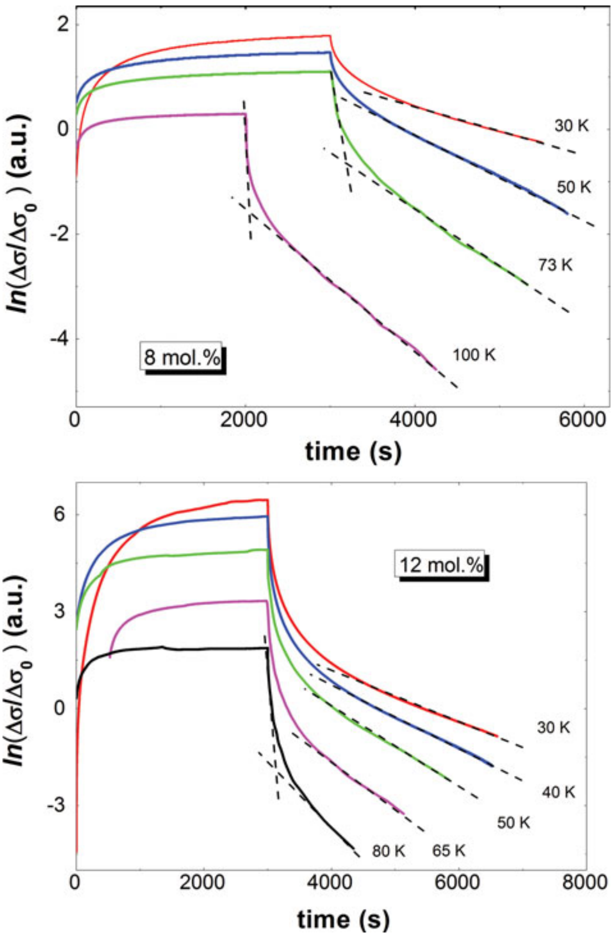

Figure 3. Kinetics of the photoconductivity decay of $CuInS_2$-$ZnIn_2S_4$ alloys containing 8 and 12 mol% of $ZnIn_2S_4$ at different temperatures.

the straight lines in a wide time interval. From the slope of these straight lines the relaxation time constants of photoconductivity τ_1 were defined (Table 2). Large values of τ_1 ($\sim 10^2$–10^3 s) indicate participation of the shallow traps (t-levels) or recombination barriers in the photoconductivity relaxation.

Presently, two major models are used to explain the long-lasting relaxation of photoconductivity. The first one is based on the representation of the capture of nonequilibrium charge carriers by the strongly localized states in the vicinity of point defects (traps) and/or impurities with deep energy levels in the band gap. In the second model electrons and holes become spatially separated by potential barriers caused by fluctuations of the band gap edges. Such

Table 2. Temporal parameters of relaxation processes in $CuInS_2$-$ZnIn_2S_4$.

8 mol. % $ZnIn_2S_4$					12 mol. % $ZnIn_2S_4$				16 mol. % $ZnIn_2S_4$			
T, K	τ_1, s	τ_2, s	τ_3, s	τ_4, s	T, K	τ_1, s	τ_3, s	τ_4, s	T, K	τ_1, s	τ_3, s	τ_4, s
30	600	1420	80	1550	30	1060	~10	1250	30	925	100	1700
50	300	1170	50	1150	40	900	~10	1000	63	600	60	820
73	200	1040	30	870	65	540	~10	660	80	320	40	610
100	140	860	15	680	80	400	~10	500	100	210	25	470

spatial fluctuations can arise in highly compensated crystals due to local inhomogeneities of doping, or around clusters of defects, or can be caused by, e.g., ionizing. Thus, in order to take part in conductivity, charge carriers have to overcome the so-called mobility barriers. In order to recombine and/or to be trapped charge carriers of different signs have to move in space to meet each other by overcoming so-called recombination barriers. In most cases, the differentiation of both relaxation mechanisms is a challenging and complex task.

As we have studied the relaxation of impurity photoconductivity induced by light quanta from the impurity region, the analysis of the experimental results based on the relaxation model due to the capture of free carriers on localized centers is more appropriate. In such case, the relaxation time constant of photoconductivity is not equal to the lifetime of the photoexcited charge carriers, and will significantly exceed it, since part of the electrons will be captured on the *t*-levels. Moreover, as compared to the band-to-band recombination, the relaxation time constants are much longer because the main recombination channels are transitions of the electrons to defect sites - the *r* or *s* recombination centers [11, 20]. Long-lasting photoconductivity relaxations in other semiconductor compounds were observed in [23, 24, 25, 26].

Characteristically, in Fig. 2(b,c) deviations from the exponential growth of the photoconductivity are seen at the initial stages in the temperature region 30–60 K in the samples with 12 and 16 mol% of $ZnIn_2S_4$. The detailed analysis showed that after the onset of excitation photoconductivity increases linearly with time. Such linear behavior is characteristic in case of nearly empty t-levels [11, 20], e.g., in highly compensated semiconductors, including $Cu_{1-x}Zn_xInS_2$ with the high content of $ZnIn_2S_4$. The reason for the linear growth is that the balance between the conduction band and the *t*-levels takes some time after the beginning of the photoexcitation. After the establishment of equilibrium between the conduction band and t-levels, alongside with the photoexcitation of electrons, they start recombining through the *r*- and *s*-centers.

In the samples with lower $ZnIn_2S_4$ content (8 mol%) two straight-line segments can be singled out in the photoconductivity growth process in $-\ln(1-\frac{\Delta\sigma}{\Delta\sigma_{st}})-t$ scaling, see Fig. 2(a). At the initial stage the increase of photoconductivity occurs with a characteristic time τ_1 (Table 2). Later on (approx. 500 seconds at 30 K) photoconductivity growth slows down and is described by the relaxation time $\tau_2>\tau_1$ (Table 2). Both τ_1 and τ_2 decrease with increasing temperature. Different photoconductivity kinetics in the samples with different $ZnIn_2S_4$ content can be due to the different concentrations of V_{Cu} resulting in a redistribution of electrons at defect levels. Similar processes were observed in Cu-doped Ge [20].

In Fig. 3 photoconductivity decay after the light excitation is switched off is presented. It is seen that the photoconductivity relaxation in crystals with 8 and 12 mol% $ZnIn_2S_4$ is characterized by the presence of at least two recombination channels. In the two-phase $Cu_{1-x}Zn_xInS_2$ alloys with 16 mol% of $ZnIn_2S_4$ the results are similar. The photoconductivity relaxation in this case is described well by the sum of two exponents:

$$\Delta\sigma = A\cdot\exp\left(-\frac{t}{\tau_3}\right)+B\cdot\exp\left(-\frac{t}{\tau_4}\right) \tag{2}$$

here $A\approx B\approx\Delta\sigma_{st}$. From the slopes of the straight lines (Fig. 3.) the relaxation time constants τ_3 and τ_4 were estimated. The fast and the slow components with characteristic relaxation times: $\tau_3\sim 10$ s and $\tau_4\sim 10^3$ s, respectively, could be singled out. Both these values decrease with increasing temperature, as can be seen from Table 2. The fast recombination

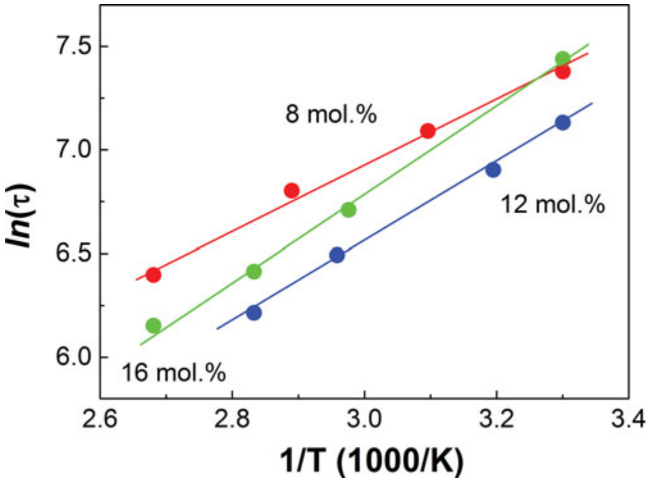

Figure 4. Dependence of the relaxation time constants of the slow relaxation component on the temperature of $CuInS_2$-$ZnIn_2S_4$ solid solutions with different $ZnIn_2S_4$ content.

channel, which is observed at the initial stages could be due to electron capture by the *s*-fast recombination centers. The slow relaxation component is given by *r*-recombination centers.

In the presence of electron trapping centers the photoconductivity relaxation time decrease with increasing temperature can be described as [11]:

$$\tau = \tau_n \cdot \left(1 + \frac{N_t}{N_c} \cdot \exp\left(\frac{E_{tn}}{kT}\right)\right), \tag{3}$$

here τ_n - nonequilibrium electron lifetimes, N_t - concentration of trapping centers, N_c - effective density of electron states in the conduction band, E_{tn} - energy distance from the electron trap level to the conduction band.

As follows from Eq.(3), the photoconductivity relaxation time decreases with increasing temperature, approaching τ_n. Thus, the lower the temperature and the higher the concentration of traps, the more the photoconductivity relaxation time constants differ from the lifetime of nonequilibrium charge carriers. The high concentration of traps in the investigated compounds is evidenced by the high induced photoconductivity. Thus, assuming that $\tau >> \tau_\mathrm{n}$ in the used temperature interval, Eq. (3) can be rewritten as:

$$\tau \approx \tau_n \cdot \frac{N_t}{N_c} \cdot \exp\left(\frac{E_{tn}}{kT}\right). \tag{4}$$

Therefore E_{tn} could be determined from the slope of the temperature dependencies of the relaxation time constants in $\ln \tau - 1/T$ scaling. The resulting τ dependencies on temperature are well described by straight lines in Fig. 4. From the slope of these lines E_{tn} values of 0.11 eV, 0.15 eV and 0.18 eV were evaluated for $CuInS_2$-$ZnIn_2S_4$ alloys with 8, 12 and 16 mol% of $ZnIn_2S_4$, respectively. These values characterizing t-trapping centers are close to those, evaluated in [18] from the thermally stimulated current spectra.

4. Conclusions

Photoconductivity spectra and photoconductivity transients were investigated in $Cu_{1-x}Zn_xInS_2$ single crystals. The photo-induced defect related enhanced photoconductivity was observed in the photoconductivity spectra. The photoconductivity relaxation kinetics at low temperatures is characterized by two types of relaxation processes: the fast and the slow ones with characteristic relaxation times of $\sim 10^1$ s and $\sim 10^3$ s, respectively. These two relaxation processes are controlled by the s-centers of fast recombination and r-centers of slow recombination. The thermal activation energies of the trapping t-levels formed by the Sulphur vacancies V_s were evaluated from the temperature dependencies of the relaxation time constants of photoconductivity.

Acknowledgments

The partial financial support from the Research Council of Lithuania (Project No TAP LU 02–2014) and the State Agency on Science, Innovations and Informatization of Ukraine (Grant no. M/106–2014) is acknowledged.

References

[1] Scheer, R., Walter, T., Schock, H. W., Fearheiley, M. L., & Lewerenz, H. J. (1993). *Appl. Phys. Lett.*, *63*, 3294–3296.

[2] Mere, A., Kijatkina, O., Rebane, H., Krustok, J., & Krunks, M. (2003). *J. Phys. Chem. of Solids*, *64*, 2025–2029.

[3] Lee, D., & Yong, K. (2014). *J. Phys. Chem. C*, *118*, 7788–7800.

[4] Verheijen, A. W., Giling, L. J., & Bloem, J. (1979). *Mater. Res. Bull.*, *14*, 237–240.

[5] Ueng, H. Y., & Hwang, H. L. (1987). *J. Appl. Phys.*, *62*, 434–438.

[6] Lahlou, N., & Massé, G. (1981). *J. Appl. Phys.*, *52*, 978–982.

[7] Garuthara, R., Wijesundara, R., & Siripala, W. (2003). *Sol. En. Mater. Sol. Cells*, *79*, 331–338.

[8] Novosad, A.V., Bozhko, V.V., Davidyuk, G. E., Kozer, V.R., Parasyuk, O.V., & Kažukauskas, V. (2012). *Proc. VI Int. Conf. On Relaxational, nonlinear and acoustooptical processes and materials. Lutsk*, Ukraine. p. 230 (In Russian).

[9] Vavilov, V.S., Euthymiou, P.C., & Zardas, G.E. (1999). *Phys. Usp.*, *42*, 199–201.

[10] Vorobjev, Yu. V., Dobrovolskij, V. N., & Stricha, V.I. (1988). *Methods of Investigation of Semiconductors*. Kiev, Vysshja Shkola, (In Russian).

[11] Serdyuk, V.V., Cheremesyuk, G.G., & Terek, M. (1982). *Phototelectrical Processes in Semiconductors*. Kiev-Odessa, Vysshja Shkola, (In Russian).

[12] Vaitkus, J., Kažukauskas, V., Kiliulis, R., & Storasta, J. (1994). *Inst. Phys. Conf. Series*, *136*, 755–760.

[13] Kažukauskas, V., & Vaitkus, J. (1994). *Zeitschrift fuer Physik B*, *94* (4), 401–407.

[14] Kiliulis, R., Kažukauskas, V., Storasta, J., & Vaitkus, J.V. (1996). *J. de Physique I.*, *6* (9), 1165–1187.

[15] Kažukauskas, V., Kuhnel, G., & Siegel, W. (1997). *Appl. Phys. Lett.*, *70* (13), 1751–1753.

[16] Kažukauskas, V. (1998). *J. Appl. Phys.*, *84* (4), 2053–2061.

[17] Affolder, A., Aleev, A., Allport, P.P. et al. (2011). *Nucl. Instrum. Meth. A*, *658* (1), 11–16.

[18] Bozhko, V.V., Novosad, A.V., Davidyuk, G.E., Kozer, V.R., Parasyuk, O.V., Vainorius, N., Janonis, V., Sakavičius, A., & Kažukauskas, V. (2013). *J. All. Comp.*, *553*, 48–52.

[19] Kozer, V. R., Bozhko, V. V., Parasyuk, O. V., Novosad, O. V., & Fedorchuk, A. O. (2014). *J. Mater. Sci: Mater. Electron.*, *25* (1), 163–167.

[20] Ryvkin, S.M. (1963). *Photoelectrical Phenomena in Semiconductors*, Fizmatgiz, Moscow, (In Russian).

[21] Ivanov, V.A., Gremenyuk, V.F., Zareckaja, E.P., Sergejeva, O.N., Viktorov, I.A., & Zalesskij, V.B. (2005). *Proc. Int. Conf. on Topical Problems of Solid State Physics.*, Minsk. pp. 426–429. (In Russian).

[22] Kazmerski, L.L., & Shieh, C.C. (1977). *Thin Solid Films*, *41* (1), 35–41.

[23] Nedeoglo, D.D., Simashkevich, A.V., & Khromov, V.I. (1980). *Phys. Stat. Sol. (a)*, *57* (1), 419–427.

[24] Yunusov, M.S., Karimov, M., & Oksengendler, B.L. (1998). *Semiconductors*, *32* (3), 238–240.

[25] Mal’khanov, S.E. (1999). *Semiconductors*, *33* (5), 529–530.

[26] Maiorova, T. L., Kluyev, V. G., & Samofalova, T. V. (2011). *Semiconductors*, *45*, 567–571.