

Characterization of defect states in $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution by photoluminescence and thermally stimulated current



N.M. Gasanly*

Department of Physics, Middle East Technical University, 06800 Ankara, Turkey
Virtual International Scientific Research Centre, Baku State University, 1148 Baku, Azerbaijan

ARTICLE INFO

Article history:

Received 19 April 2015
Received in revised form 28 April 2015
Accepted 29 April 2015
Available online 14 May 2015

Keywords:

Layered crystals
Crystal growth
Luminescence
Defects

ABSTRACT

Photoluminescence (PL) and thermally stimulated current (TSC) in $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution grown by Bridgman method have been studied in the photon energy region of 1.46–1.60 eV and in the temperature range of 10–42 K (PL) and in the temperature range of 10–100 K with heating rate of 1.0 K/s (TSC). A PL band centered at 1.53 eV was observed at $T = 10$ K. Variations of emission band has been studied as a function of excitation laser intensity in the 1.8–183.0 mW cm^{-2} range. Radiative transitions from shallow donor level located at 13 meV below the bottom of conduction band to acceptor level located at 217 meV above the top of the valence band were suggested to be responsible for the observed PL band. The analysis of the TSC data revealed the electron trap level with activation energy 12 meV. An energy level diagram showing transitions in the band gap of the crystal has been presented.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

I–III–VI ternary semiconductors with the general formula of AB_5C_8 have potential as photo absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells. AgIn_5S_8 and CuIn_5S_8 crystals are the visible-light-active materials with high-absorption coefficients, suitable band gaps, good radiation stability, and easy conversion between n- and p-type carrier types which permits a variety of potentially low-cost homo and hetero junction [1,2]. The ternary semiconductor compounds AgIn_5S_8 and CuIn_5S_8 have been confirmed as materials suitable for use in high-frequency thin films convertors, infrared detectors and various types of heterojunctions [3]. Moreover, such crystals due to their crystallochemistry structure may be of particular interest for the photovoltaics, photosensors and IR laser operated devices [4]. The solid solutions of copper and indium based ternary chalcogenide crystals are the well-established absorber materials for thin film solar cells [5].

The optical and electrical properties of AgIn_5S_8 and CuIn_5S_8 have been studied in Refs. [6–10]. The energy band gaps for the direct optical transitions of AgIn_5S_8 and CuIn_5S_8 are 1.78 and 1.51 eV at 300 K, and 1.88 and 1.57 eV at 96 K, respectively [11]. Infrared reflection and Raman scattering spectra of AgIn_5S_8 and

CuIn_5S_8 crystals have also been investigated and analyzed [12]. Earlier, photoluminescence (PL) spectra of AgIn_5S_8 crystals were investigated in the temperature range of 10–170 K [13]. The observed PL band centered at 1.65 eV was attributed to the radiative recombination of charge carriers from donor ($E_d = 0.06$ eV) to acceptor ($E_a = 0.32$ eV) states. Recently, thermally stimulated current (TSC) measurements were carried out on as-grown AgIn_5S_8 single crystals [14]. The investigations were performed in temperatures ranging from 10 to 70 K with heating rate of 0.2 K/s. The analysis of the data revealed the electron trap level with activation energy 5 meV.

The crystals of composition $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ ($x = 0.5$) may be imagined as a result of replacing in $\text{Ag}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ solid solutions (formed from AgIn_5S_8 and CuIn_5S_8 spinels) of a half of silver (copper) atoms by copper (silver) ones. In $\text{Ag}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$, the existence of continuous solid solutions ($0 \leq x \leq 1$), when substituting Ag for Cu within the spinel crystal structure, offers the possibility for creating absorber layers with tailored compositional gradients and therefore achieving the desired band gap profile [15]. Their band gap energy varies from 1.51 to 1.78 eV within the wide continuous series of solid solutions. Previously, Bodnar [16] has reported the crystal growth procedure of $\text{Ag}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ ($0 \leq x \leq 1$) solid solutions.

The influence of defects on the performance of optoelectronic devices is a well-known subject. In optoelectronic devices such as LEDs or lasers, defects may introduce non radiative recombination centers to lower the internal quantum efficiency or even

* Address: Department of Physics, Middle East Technical University, 06800 Ankara, Turkey. Fax: +90 312 210 50 99.

E-mail address: nizami@metu.edu.tr

render light generation impossible, depending on defect density. In the case of electronic devices, defects introduce scattering centers lowering carrier mobility, hence hindering high-frequency operation. Thus, it is very useful to get detailed information on energetic parameters of recombination and trapping centers in semiconductor in order to obtain high-quality devices.

In this article, we present the results of a systematic experimental analysis of the photoluminescence and thermally stimulated current measurements on $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution. The PL spectra were studied in the photon energy region of 1.46–1.60 eV and in the temperature range of 10–42 K. The TSC investigations were performed in temperatures ranging from 10 to 100 K with heating rate of 1.0 K/s. The TSC curves and the temperature and excitation intensity dependencies of PL spectra were studied in details in order to propose a model for the recombination and trapping processes of photoexcited carriers and a scheme for the defect levels in the band gap of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution.

2. Experimental details

$\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ semiconductor polycrystals were synthesized using high-purity elements taken in stoichiometric proportions. Copper (Fluka cat. No. 61,140), indium (Fluka cat. No. 57,077) and sulfur (Fluka cat. No. 84,680) were of 99.999% purity, and silver (Fluka cat. No. 85,130) was of 99.99% purity. The single crystals were grown by the Bridgman method from resultant polycrystalline ingots in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 55 cm in length) with a tip at the bottom in our crystal growth laboratory. No seed crystal was used. After evacuation and sealing off, the tube was introduced into the upper zone of a vertical two-zone growth furnace. The temperatures in the upper and lower zones were about 1130 and 840 °C. The temperature gradient between the zones was 30 °C cm^{-1} . After melt homogenization for 2 h, the tube was lowered through the gradient zone at a rate of 1.0 mm h^{-1} . Then the tube was pulled to the cold zone at the same rate, and the grown crystal was homogenized at 840 °C for 50 h. After that, the temperature of the cold zone was lowered to 600 °C and then the furnace was shut off. The resulting ingot with 8.5 mm in diameter and about 35 cm and 13 g in length and mass, respectively, was air/moister stable. The final ingot exhibited monocrystalline nature. The samples selected for the measurements were taken from the middle part of the ingot.

The crystal structure properties were identified using X-ray diffraction (XRD) experiments. Measurements were performed using “Rigaku miniflex” diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154049\text{ nm}$). The scanning speed of the diffractometer was $0.02^\circ/\text{s}$. Experiments were accomplished in the diffraction angle (2θ) range of 10–82°.

In the PL and TSC measurements, samples with a typical size of $10 \times 6 \times 3\text{ mm}^3$ were used. The electrical conductivity of the studied samples was n-type as determined by the hot probe method. The green line ($\lambda = 532\text{ nm}$) of a continuous frequency-doubled YAG:Nd³⁺ laser was used as the excitation light source. PL experiments were carried out by collecting the light from the laser-illuminated face of the sample. A “CTI-Cryogenics M-22” closed-cycle helium cryostat was used to cool the sample from room temperature down to 10 K, and the temperature was controlled within an accuracy of $\pm 0.5\text{ K}$. The PL spectra of the sample in the energy region of 1.46–1.60 eV were analyzed using a “Oriel MS-257” grating monochromator and “Hamamatsu S7031” FFT-CCD Image Sensor with single stage electric cooler. Sets of neutral density filters were used to adjust the exciting laser intensity from 1.8 to 183.0 mW cm^{-2} . All of the PL spectra have been corrected for the spectral response of the optical apparatus.

For TSC experiments, two electrodes were made on the sample using silver paste according to sandwich geometry: one was on the

front as a small droplet to allow illumination and the other one was at the back covering the whole surface of the sample to maintain electrical and thermal conductivity. Thin copper wires were used to attach to the electrodes for circuit connection. The copper holder was mounted on the cold finger of the cryostat and the back side was grounded through the sample holder. The TSC measurements were carried out in the temperature range of 10–100 K using a closed cycle helium cryostat. A Lake-Shore 331 temperature controller was utilized to provide constant heating rate of 1.0 K/s. A Keithley 228 A voltage/current source and a Keithley 6435 picoammeter were employed for TSC measurements. At low temperatures, carriers were excited by a light emitting diode, generating light at a maximum peak of 2.6 eV.

3. Results and discussion

XRD technique was used to obtain the structural parameters of the $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution. The crystal system, Miller indices of the diffraction peaks and lattice parameters were evaluated using a least-squares computer program “DICVOL 04”. Fig. 1 shows the X-ray diffractogram of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$. The sharp diffraction peaks are the indication of the well crystallinity of the sample. Miller indices (hkl) are shown on the diffraction peaks. The lattice parameter of the cubic unit cell was found to be $a = 1.0758\text{ nm}$. This parameter value is well correlates with those reported for AgIn_5S_8 (1.0825 nm) and CuIn_5S_8 (1.0687 nm) [17].

Fig. 2 presents the PL spectra of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution in 10–42 K temperatures range at constant laser excitation intensity $L = 183.0\text{ mW cm}^{-2}$. The observed emission band has asymmetrical Gaussian line shape and centered at $E_p = 1.53\text{ eV}$ at $T = 10\text{ K}$. As seen from Fig. 2, emission band changes its peak position and intensity as a function of the sample temperature: the peak position shows several degrees of red shift and the peak intensity decreases as temperature is increased. Inset of Fig. 3 illustrates the shift of the peak energy to lower energies with increasing temperature. It is well known that the donor–acceptor pair transition energy decreases along with the band gap energy when the temperature is increased [18].

The experimental data for the temperature dependence of PL band intensity can be fitted by the following expression [19]

$$I(T) = \frac{I_0}{1 + \sigma_1 T^{3/2} + \sigma_2 T^{3/2} \exp(-E_t/kT)}, \quad (1)$$

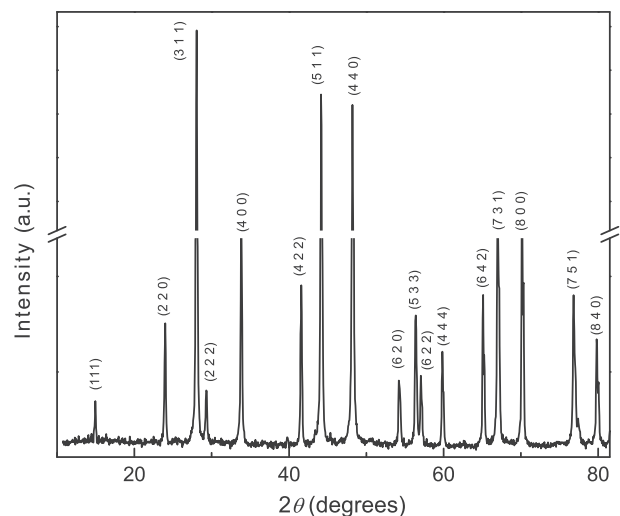


Fig. 1. X-ray diffraction pattern of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ powder sample.

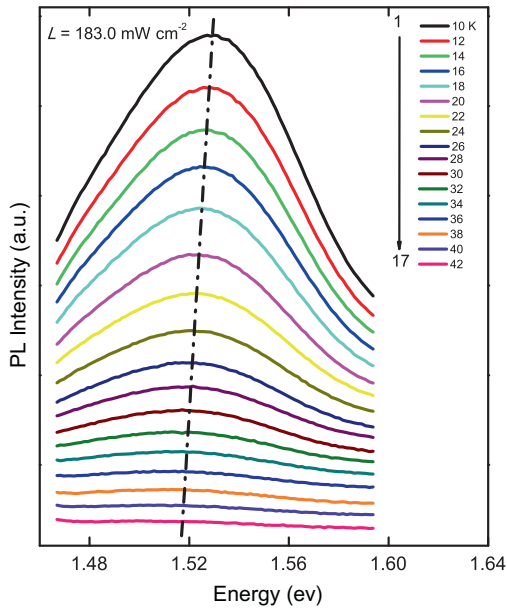


Fig. 2. Temperature dependence of PL spectra from $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution at excitation laser intensity $L = 183.0 \text{ mW cm}^{-2}$.

where I_0 is a proportionality constant, E_t the thermal activation energy, k the Boltzmann's constant, σ_1 and σ_2 are the fitting parameters associated with the temperature dependence of the capture cross sections of the donor and acceptor levels. Fig. 3 shows the temperature dependence of the emission band maximum intensity as a function of the reciprocal temperature in the 10–42 K range. After a nonlinear least squares fit, the quenching activation energy for emission band is found to be 13 meV. Since $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution is an n-type semiconductor, we believe that this level is shallow donor level located at $E_d = 13 \text{ meV}$ below the bottom of the conduction band. This shallow level can be considered as originating from the deviations in the stoichiometry (i.e., sulfur vacancies) [20–22]. From electrical resistivity and Hall effect measurements on CuIn_5S_8 crystals, the activation energy of a similar donor level was found to be 17 meV [20] and 16 meV [21]. Moreover, the donor level with activation energy (16 meV) was revealed from temperature dependence of photoconductivity in AgIn_5S_8 crystals [22].

The laser excitation intensity dependence of PL spectra also provides valuable information on the recombination mechanism

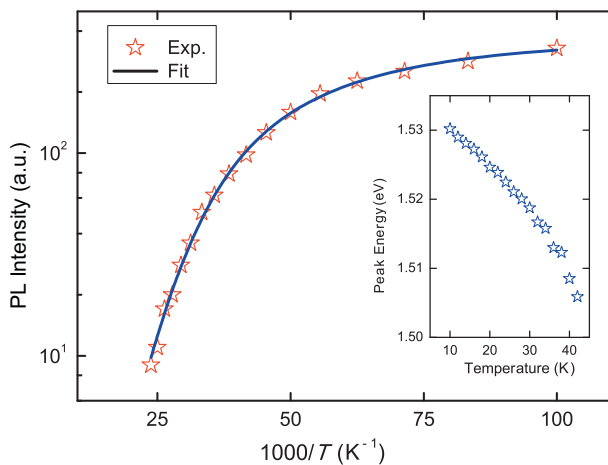


Fig. 3. Temperature dependencies of PL band intensity for $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution. Stars are the experimental data. Solid curve shows the theoretical fit using Eq. (1). Inset: Temperature dependence of emission band peak energy.

responsible for the observed luminescence. Fig. 4 presents the PL spectra for 17 different laser intensities at $T = 10 \text{ K}$. From analysis of the spectra, we obtained the information about the peak energy position and intensity for emission band at different laser excitation intensities. Our analysis reveals that the peak energy position does not shift with increasing laser excitation intensity. In contrast with in homogeneously distributed donor–acceptor pairs where increasing laser intensity excites more pairs that are closely spaced leading to blue shift of the peak energy of the observed bands [18], this result suggests that the donor–acceptor pairs are located at only closely spaced sites and are distributed homogeneously.

In PL spectra of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution, the increase in the band peak intensity with increase in the laser excitation intensity was observed. The logarithmic plot of PL intensity versus laser excitation intensity is given in Fig. 5. Experimental data can be fitted by a simple power law of the form

$$I \propto L^\gamma, \tag{2}$$

where I corresponds to the PL intensity, L corresponds to excitation laser intensity and γ is a dimensionless constant. We find that PL intensity at the emission band maximum increases sublinearly with increase of excitation laser intensity with the value of $\gamma = 0.95$. It is well known that for excitation laser photon energy exceeding the band gap energy E_g , the exponent γ is generally $1 < \gamma < 2$ for free and bound exciton emission, whereas $0 < \gamma \leq 1$ is typical for free-to-bound and donor–acceptor pair recombination [23,24]. Thus, the obtained value of $\gamma < 1$ for the observed band is further evidence that the observed emission is due to donor–acceptor pair recombination.

The analysis of the PL spectra as a function of temperature and excitation laser intensity allows one to obtain a possible scheme for the states located in the forbidden energy gap of the $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution $T = 10 \text{ K}$ (inset of Fig. 5). In the proposed scheme, shallow donor level d is located at $E_d = 13 \text{ meV}$ below the bottom of the conduction band. Here, it is necessary to recall the general expression for emission energy of donor–acceptor pair as [18]

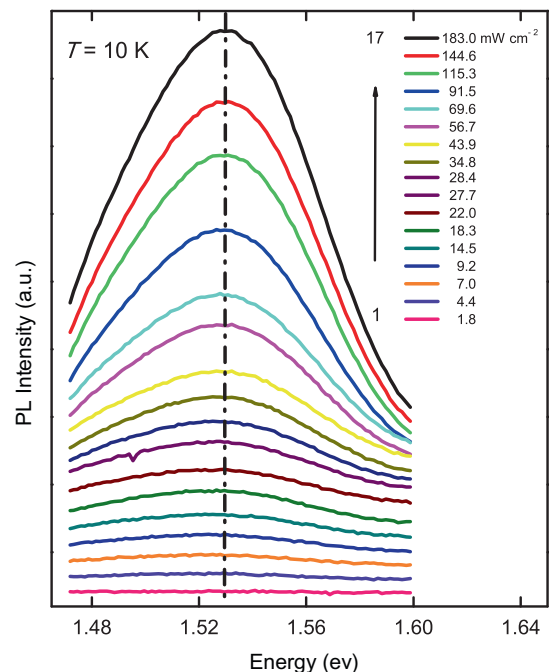


Fig. 4. PL spectra of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution as a function of excitation laser intensity at $T = 10 \text{ K}$.

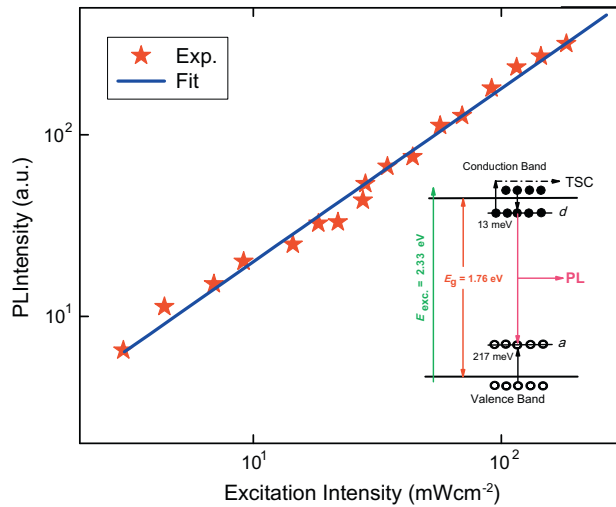


Fig. 5. Dependence of PL intensity at the emission band maximums versus excitation laser. Intensity at $T = 10$ K. The solid line shows the theoretical fit using Eq. (2). Inset: Energy level diagram of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution at $T = 10$ K.

$$E_p = E_g - E_d - E_a, \quad (3)$$

where E_g is the band gap energy of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution, E_d and E_a are the donor and acceptor level energies, respectively. A simple calculation with Eq. (3) for emission band by using the values of $E_g = 1.76$ eV [15], $E_p = 1.53$ eV and $E_d = 13$ meV gives us the energy of the moderately deep acceptor level as $E_a = 217$ meV (inset of Fig. 5). Taking into account the above considerations, the observed emission band in the PL spectra has been attributed to the radiative transitions from the donor level d to the acceptor level a . Since the studied crystals were not intentionally doped, we propose the presence of structural vacancies in the cation sublattice as the origin of moderately deep acceptor level a located above the valence band in $n\text{-Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution, by analogy with the isostructural $n\text{-CdIn}_2\text{S}_4$ [25] and $n\text{-AgIn}_5\text{S}_8$ [26] crystals where the relatively deep acceptor levels with activation energies 200 and 224 meV were assigned to similar vacancies, respectively. It should be noted, that in the chalcogenide compounds the top of valence band is formed prevalingly by the p-chalcogenic delocalized states and the bottom of conduction band is originated from the s- and d-cationic states [27,28].

Fig. 6 presents the TSC curve of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution registered with the heating rate of 1.0 K/s. When the front surface of the sample is illuminated, both types of carriers are created in this region. Only one type of carriers will be driven along the whole field zone, while the second type is collected very quickly depending on the bias voltage. Only the former can be trapped. It was revealed, that if the polarity of the illuminated surface is negative, the intensity of the TSC peak was highest. It means that the electrons are distributed in the crystal and then trapped. Therefore, the peak appearing in the TSC spectra of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution can be assigned to electron traps.

There are several methods to evaluate the trapping parameters from the experimental TSC curve [29]. We have used the initial rise method for the analysis of the present data. This method is independent of the order of kinetics and therefore can be applied to the TSC curve without considering the retrapping process. As the trapped charge carriers are excited to the non-localized states from trap levels through heating, the initial tail of the TSC curve must arise as proportional to $\exp(E_t/kT)$ [24]. Then, the logarithmic plot of the TSC current as a function of the reciprocal of temperature yields a straight line with slope of $(-E_t/k)$ (inset of Fig. 6). The accuracy of the fitting by the straight line was $R^2 = 0.9984$. We

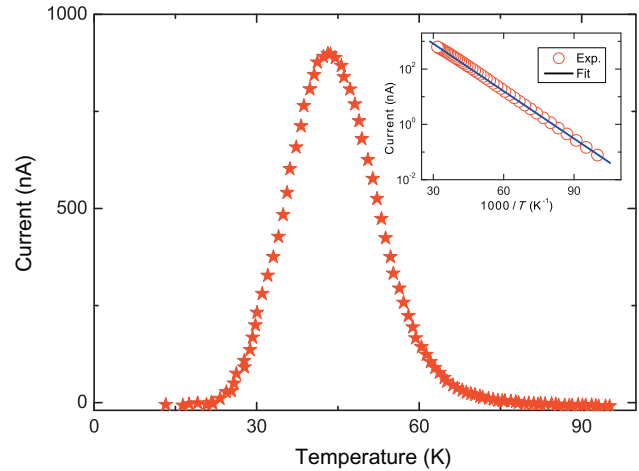


Fig. 6. Experimental TSC curve of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution with heating rate of 1.0 K/s. Inset: Thermally stimulated current versus $1000/T$. Circles are experimental data. Solid line is the theoretical fit using initial rise method.

evaluated the experimental error in the determination of activation energy as $E_t = (12 \pm 1)$ meV.

At this point, it is worthwhile to give an insight into the transitions in the forbidden band gap of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution by combining the results of PL and TSC studies (inset of Fig. 5). The present result of PL experiment in the 10–42 K temperature range showed the existence of one electron trap with activation energy 13 meV. Taking into account the possible errors (about 5%), the obtained energies of 13 and 12 meV in the PL and TSC studies, respectively, may possibly be assigned to the same level. This level is thought to be partially compensated allowing for both PL emission and thermally stimulated current.

4. Conclusions

The PL spectra of $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution as a function of temperature and excitation laser intensity were studied. An emission band centered at 1.53 eV was observed in the PL spectra at $T = 10$ K. The variation of the spectra with laser excitation intensity and temperature suggested that the transitions between the donor ($E_d = 13$ meV) and acceptor ($E_a = 217$ meV) levels can be responsible for the observed emission band. The analysis of the thermally stimulated current data in $\text{Ag}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ solid solution established the electron trap level with activation energy $E_d = 12$ meV. The revealed donor level is thought to be partially compensated allowing for both PL emission and thermally stimulated current. As the studied crystals were not intentionally doped, the revealed centers are thought to originate from anion and cation vacancies caused by nonstoichiometry, created during crystal growth.

Acknowledgements

The author is grateful to Dr. A. Seyhan and Dr. T. Yildirim for their assistance.

References

- [1] M. Gannouni, M. Kanzari, J. Alloys Compd. 509 (2011) 6004.
- [2] M. Gannouni, M. Kanzari, Appl. Surface Sci. 257 (2011) 10338.
- [3] I.V. Bodnar, Semiconductors 46 (2012) 602.
- [4] G.P. Gorgut, A.O. Fedorchuk, I.V. Kityk, V.P. Sachanyuk, I.D. Olekseyuk, O.V. Parasyuk, J. Cryst. Growth 324 (2011) 212.
- [5] Y.E. Romanyuk, L.P. Marushko, L.V. Piskach, I.V. Kityk, A.O. Fedorchuk, V.I. Pekhnyo, O.V. Parasyuk, Cryst. Eng. Commun. 145 (2013) 4838.
- [6] M. Gannouni, I. Ben Assaker, R. Chtourou, Mat. Res. Bull. 61 (2015) 519.
- [7] N. Hemiri, M. Kanzari, Solid State Commun. 160 (2013) 32.

- [8] M. Gannouni, I. Ben Assaker, R.J. Chtourou, J. Electroch. Soc. 160 (2013) H446.
- [9] L. Makhova, R. Szargan, I. Konovalov, Thin Solid Films 472 (2005) 157.
- [10] L. Makhova, I. Konovalov, Thin Solid Films 515 (2007) 5938.
- [11] N.S. Orlova, I.V. Bodnar, E.A. Kudritskaya, Cryst. Res. Technol. 33 (1998) 37.
- [12] N.M. Gasanly, A.Z. Magomedov, N.N. Melnik, Phys. Status Solidi (b) 117 (1993) K31.
- [13] N.M. Gasanly, A. Serpenguzel, A. Aydinli, O. Gurlu, I. Yilmaz, J. Appl. Phys. 85 (1999) 31999.
- [14] T. Yildirim, N.M. Gasanly, Cryst. Res. Technol. 44 (2009) 1267.
- [15] I.V. Bodnar, E.A. Kudritskaya, I.K. Polushina, V.Yu. Rud, Yu.V. Rud, Semiconductors 32 (1998) 933.
- [16] I.V. Bodnar, Inorg. Mater. 36 (2000) 660.
- [17] M. Robbins, M.A. Miksovsky, Mat. Res. Bull. 6 (1971) 359.
- [18] P.Y. Yu, M. Cardona, Fundamentals of Semiconductors, Springer, Berlin, 1995.
- [19] J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, New Jersey, 1971.
- [20] S. Kitamura, S. Endo, T. Irie, J. Phys. Chem. Solids 46 (1985) 881.
- [21] A.F. Qasrawi, N.M. Gasanly, Cryst. Res. Technol. 36 (2001) 1399.
- [22] A.F. Qasrawi, T.S. Kayed, I. Ercan, J. Alloys Compd. 508 (2010) 380.
- [23] T. Schmidt, K. Lischka, W. Zulehner, Phys. Rev. B 45 (1992) 8989.
- [24] A. Bauknecht, S. Siebentritt, J. Albert, M.C. Lux-Steiner, J. Appl. Phys. 89 (2001) 4391.
- [25] E. Grilli, M. Guzzi, P. Cappeletti, A.V. Moskalonov, Phys. Status Solidi (b) 59 (1980) 755.
- [26] A.F. Qasrawi, T.S. Kayed, I. Ercan, Mat. Sci. Eng. B 113 (2004) 73.
- [27] A.H. Reshak, I.V. Kityk, O.V. Parasyuk, H. Kamarudin, S. Auluck, J. Phys. Chem. 117 (2013) 2545.
- [28] A.O. Fedorchuk, G.P. Gorgut, O.V. Parasyuk, G. Lakshminarayana, I.V. Kityk, M. Piasecki, J. Phys. Chem. Solids 72 (2011) 1354.
- [29] R. Chen, S.W.S. Mckeever, Theory of Thermoluminescence and Related Phenomena, Word Scientific, Singapore, 1997.