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Near-infrared photoluminescence and thermally stimulated current in $Cu_3Ga_5Se_9$ layered crystals: A comparative study

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HIGHLIGHTS

- Defect states in $Cu_3Ga_5Se_9$ layered crystals were studied by IR photoluminescence.
- The observed infrared PL band was assigned to donor–acceptor pair recombination.
- Trapping center with energy 22 meV was revealed from thermally stimulated current.
- Established defect states are supposed originating from anion and cation vacancies.

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ABSTRACT

Near-infrared photoluminescence (PL) and thermally stimulated current (TSC) spectra of $Cu_3Ga_5Se_9$ layered crystals grown by Bridgman method have been studied in the photon energy region of 1.35–1.46 eV and the temperature range of 15–115 K (PL) and 10–170 K (TSC). An infrared PL band centered at 1.42 eV was revealed at $T = 15$ K. Radiative transitions from shallow donor level placed at 20 meV to moderately deep acceptor level at 310 meV were suggested to be the reason of the observed PL band. TSC curve of $Cu_3Ga_5Se_9$ crystal exhibited one broad peak at nearly 88 K. The thermal activation energy of traps was found to be 22 meV. An energy level diagram demonstrating the transitions in the crystal band gap was plotted taking account of results of PL and TSC experiments conducted below room temperature.
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1. Introduction

$Cu_3Ga_5Se_9$ semiconductor is the representative of materials with general formula $A_3B_5C_9$, where A = Cu, Ag, Au; B = Ga, In; C = S, Se, Te. The possibility of formation of $A_3B_5C_9$-type ternary compounds has been revealed on the basis of physicochemical analysis and the state diagram of ABC_2–B_2C_3 systems [1]. Optical and photoelectrical properties of these crystals have been studied previously [2–7]. The detailed state diagram of the $CuGaSe_2$–Ga_2Se_3 system has been examined in Ref. [8]. It has been found that at 25 mol% Ga_2Se_3, the $Cu_3Ga_5Se_9$ compound is formed with melting temperature of 1088 °C. The authors have reported that $Cu_3Ga_5Se_9$ crystals had a layered structure and were crystallized in orthorhombic structure with the parameters $a = 0.3977$, $b = 0.5581$ and $c = 2.1947$ nm. The cathode- and photoluminescence spectra of $Cu_3Ga_5Se_9$ crystals have been measured at various excitation intensities and temperatures [9]. The results indicated that the radiative recombination of nonequilibrium charge carriers occurs primarily through impurity levels due to anion and cation vacancies. The fabrication of detectors based on $Cu_3Ga_5Se_9$ single crystals for high-intensity radiation was suggested. The band gap for optical transitions was found to be 1.74 eV at room temperature. Infrared reflection spectra of $Cu_3Ga_5Se_9$ crystals have been studied in Ref. [10]. The analysis of spectra carried out by Kramers–Kronig method permitted to calculate the spectral dependence of imaginary part of dielectric constant from the maximum positions of which the frequencies of five optical modes have been obtained (191, 201, 219, 246 and 276 cm^{-1}).

In this paper we report the results of variation of near-infrared PL spectra intensity in $Cu_3Ga_5Se_9$ crystals in 15–115 K temperature range. The analysis of data presents the evidence that the radiative transitions arise from recombination of charge carriers between donor and acceptor states. In addition, we established in thermally stimulated current (TSC) curve of $Cu_3Ga_5Se_9$ one broad peak. The thermal activation energy of trap level was found to be 22 meV.

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2. Experimental details

$Cu_3Ga_5Se_9$ polycrystals were synthesized from particular elements taken in stoichiometric proportions. Usually, the synthesis of binary and ternary chalcogenide compounds are characterized by high pressure of the chalcogenide vapors, the endothermal reactions leading to a sharp increase in temperature and by strong interaction of the above compounds with the oxygen (especially, at high temperatures). Therefore, a special method has been developed for the synthesis of compounds with high volatile compounds. The single crystals were grown from polycrystals by Bridgman method in our crystal growth laboratory (Middle East Technical University). The ampoule was lowered inside of vertical furnace through a thermal gradient of 30 °C/cm at a rate of 1.0 mm/h. The resulting ingot occurred gray in color. The chemical composition of $Cu_3Ga_5Se_9$ crystals was determined by energy dispersive spectroscopic analysis (Fig. 1). The composition of samples under study was found to be 17.9(Cu):29.6(Ga):52.5(Se). The electrical conductivity of the studied sample was established as n-type.

Samples suitable for PL experiments had typical dimensions of $13 \times 6 \times 2$ mm^3. The green line ($\lambda = 532$ nm) of a continuous frequency-doubled YAG:Nd^{3+} laser was used as the excitation source. A closed-cycle helium cryostat was employed to cool the sample down to 15 K. The measured infrared PL spectra in the region 1.35–1.46 eV have been corrected for the spectral response of the optical apparatus. The TSC measurements were conducted in the range of 10–170 K. A temperature controller was operated to arrange heating rate of 0.8 K/s. The carriers were excited by a LED, generating light at a maximum peak of 2.6 eV. The details of employed in our experiments PL and TSC techniques were reported in our previous papers [11,12].

3. Results and discussion

Fig. 2 demonstrates the infrared PL spectra of $Cu_3Ga_5Se_9$ crystals in 15–115 K temperature range at constant excitation intensity $L = 183.0$ mW/cm^2. We detected at $T = 15$ K the emission band centered at 1.42 eV and having asymmetrical Gaussian line shape with low- and high-energy side half-widths of 29 and 19 meV, respectively. As seen from Fig. 2, the peak intensity diminishes as the temperature is elevated and the peak position displays several degrees of red shift (about 3 meV) with increasing temperature. Inset of Fig. 3 depicts the shift of the peak energy toward lower

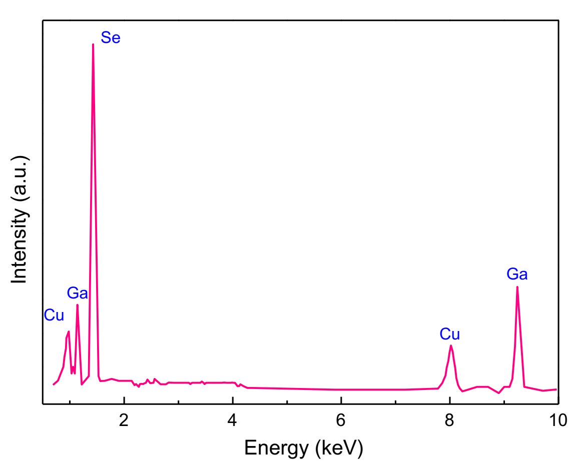

Fig. 1. Energy-dispersive spectroscopic analysis of $Cu_3Ga_5Se_9$ crystal.

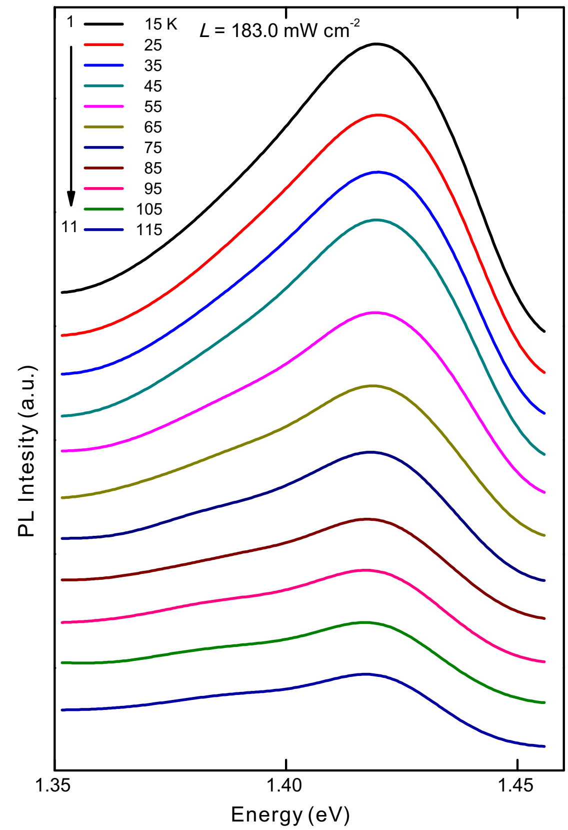

Fig. 2. Temperature dependence of PL spectra from $Cu_3Ga_5Se_9$ crystals at excitation intensity $L = 183.0$ mW cm^{-2}.

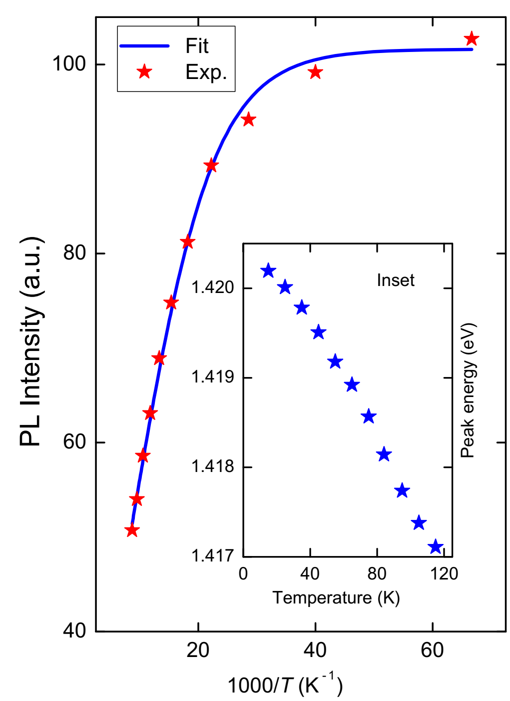

Fig. 3. Temperature dependency of PL band intensity. Stars are the experimental data. Solid curve shows the theoretical fit using Eq. (1). Inset: Temperature dependence of emission band peak energy.

energies with rising temperature. It is well-known that the donor–acceptor pair transition energy decreases along with the gap energy as the temperature is elevated [13].

The temperature dependence of PL band intensity can be analyzed by means of following relation [14]

$$I(T) = \frac{I_0}{1 + \alpha \exp(-E_t/kT)}, \quad (1)$$

where I_0 is a proportionality constant, E_t is the activation energy and α is the recombination process rate parameter. Fig. 3 displays the temperature dependence of the emission band maximum intensity versus the reciprocal temperature in the 15–115 K range. The best fit employing Eq. (1), presented by the solid curve in Fig. 3, has been accomplished with the quenching activation energy $E_t = 20$ meV. As $Cu_3Ga_5Se_9$ crystal is an n-type semiconductor, we consider this level as shallow donor level placed at 20 meV below the conduction band bottom. This level may be supposed as arising from the deviations in the stoichiometry (i.e., selenium vacancies) [15,16].

Fig. 4 demonstrates the suggested scheme for the states placed in the energy gap of the $Cu_3Ga_5Se_9$ crystal at $T = 15$ K. In this scheme, shallow donor level ***d*** is located at $E_d = 20$ meV below the bottom of conduction band. Here, we recall the expression for radiative emission energy of donor–acceptor pair as following [13]

$$E_p = E_g - E_d - E_a, \quad (2)$$

where E_g is the energy band gap of $Cu_3Ga_5Se_9$ crystal, E_d and E_a are the energies of donor and acceptor levels, respectively. Employing the values of $E_g = 1.75$ eV, $E_p = 1.42$ eV and $E_d = 20$ meV gives us the energy of the moderately deep acceptor level as $E_a = 310$ meV (Fig. 4). The emission band in the infrared PL spectra has been assigned to the transitions between the donor ***d*** and acceptor level ***a***. As the crystals under study were unintentionally doped, these centers are implied to arise from anion and cation vacancies and/or stacking faults, quite possible to exist in layered $Cu_3Ga_5Se_9$ due to the weakness of the van der Waals forces between the layers [17].

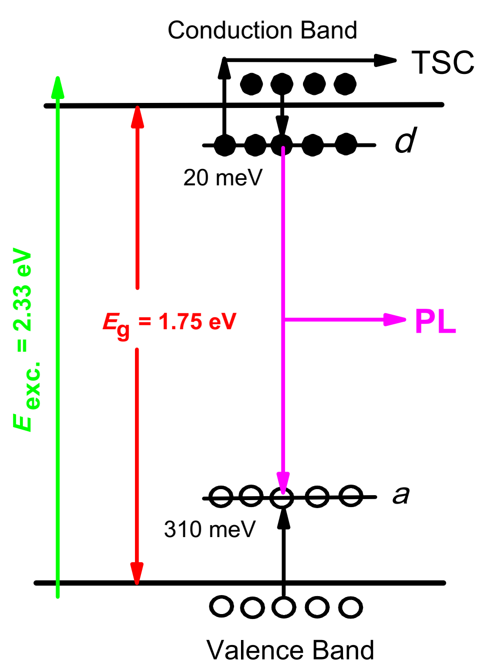

Fig. 4. Energy level diagram of $Cu_3Ga_5Se_9$ crystal at $T = 15$ K.

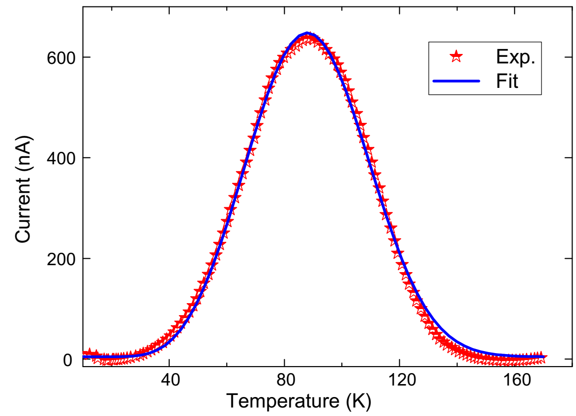

Fig. 5. TSC curve of $Cu_3Ga_5Se_9$ crystal with heating rate of 0.8 K/s. Stars are experimental data. Solid line is the theoretical fit employing the curve fitting method.

Fig. 5 shows the TSC curve of $Cu_3Ga_5Se_9$ crystal registered employing the constant heating rate 0.8 K/s. In our experiments we observed that the intensity of TSC peak was highest when the polarity of the illuminated surface of the sample was negative. One may reach a conclusion that the electrons are distributed in the crystal and then trapped [12]. Thus, the peak observing in the TSC spectra of $Cu_3Ga_5Se_9$ crystal can be associated with the electron traps.

Several methods are available for evaluating the trapping parameters from measurements of TSC spectra [18]. We have used the curve fitting method for analyzing the experimental data. It is well-known that thermally stimulated current is described by the expression [11]

$$I(T) = A\left[-\frac{E_t}{kT} - \int_{T_0}^{T} \frac{s}{\beta} \exp\left(-\frac{E_t}{kT}\right) dT\right]. \quad (3)$$

Here, I is the thermally stimulated current, A is a constant number that depends on the experimental conditions and properties of the crystal, E_t is the activation energy, β is the heating rate and T_0 is the temperature at which heating begins. The experimental TSC data could be fitted to Eq. (3) (solid line in Fig. 5). As seen from this figure, good agreement has been obtained between the experimental and theoretical curves. As a result, the activation energy of the revealed trap level was established as 22 meV.

Finally, we would like to compare the obtained experimental results of PL and TSC investigations (Fig. 4). The present PL study on $Cu_3Ga_5Se_9$ crystal in the temperature range of 15–115 K established the occurrence of a donor level with activation energy $E_t = 20$ meV. Taking into consideration the possible miscalculation (about 5%), the reveled energies of 20 and 22 meV in the PL and TSC studies, respectively, may be attributed to the same level. This revealed level is implied to be partially compensated permitting both PL emission and thermally stimulated current.

4. Conclusions

The near-infrared PL spectra of $Cu_3Ga_5Se_9$ crystals versus temperature were studied. A broad emission band centered at 1.42 eV was observed in infrared PL spectra at $T = 15$ K. The variation of the spectra with temperature supposed that the transitions from donor ($E_d = 20$ meV) to acceptor ($E_a = 310$ meV) levels may be responsible for the detected band. The analysis of the TSC data in $Cu_3Ga_5Se_9$ crystals established the electron trap level with energy depth 22 meV. The revealed energy level is thought to be partially compensated permitting both PL emission and thermally stimulated current. Since the crystals under study were unintentionally doped, these centers are implied to arise from anion and cation vacancies and/or stacking faults, created during crystal growth process.

Conflict of interest

There is no conflict of interest.

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References

[1] V.I. Tagirov, N.F. Gakhramanov, A.G. Guseinov, F.M. Aliev, G.G. Guseinov, A new class of ternary semiconductive compounds of type $A_3B_5C_9$, Sov. Phys. Crystallogr. 25 (1980) 237–239.

[2] M. Kaleli, M. Parlak, C. Ercelebi, Studies on device properties of an n-$AgIn_5Se_8$/p-Si heterojunction diode, Semicond. Sci. Technol. 26 (2011) 105013(1)–105013(7).

[3] A. Guseinov, V.I. Tagirov, M.B. Dzhafarov, Stimulation of low-frequency oscillations of the current in $Ag_3In_5Se_9$ by IR radiation and an electric field, Sov. Phys. Tech. Phys. 35 (1990) 1229–1230.

[4] M. Parlak, C. Ercelebi, I. Gunal, H. Ozkan, N.M. Gasanly, A. Culfaz, Crystal data, electrical resistivity and mobility in $Cu_3In_5Se_9$ and $Cu_3In_5Te_9$ single crystals, Cryst. Res. Technol. 32 (1997) 395–400.

[5] M. Parlak, C. Erccelebi, I. Gunal, H. Ozkan, N.M. Gasanly, Structural and electrical characterization of $Ag_3Ga_5Te_9$ and $Ag_3In_5Se_9$ crystals, Cryst. Res. Technol. 33 (1998) 923–928.

[6] N.F. Gakhramanov, B.Sh. Barkhalov, Yu.G. Nurullayev, Current oscillations in Ag3In5Se9 stimulated by electric field and IR-irradiation, in: Proc. SPIE 6636, 19th International Conference on Photoelectronics and Night Vision Devices, 2007. 66360V(1)–66360V(4).

[7] T. Colakoglu, M. Parlak, Structural characterization of polycrystalline Ag–In–Se thin films deposited by e-beam technique, Appl. Surface Sci. 254 (2008) 1569–1577.

[8] H. Ozkan, N. Gasanly, I. Yilmaz, A. Culfaz, V. Nagiev, Crystal data for $A_3B_5C_9$-type ternary compounds, Turk. J. Phys. 22 (1998) 519–524.

[9] A. Guseinov, Cathodo- and photoluminescence of $Cu_3Ga_5Se_9$ single crystals, Inorg. Mater. 47 (2011) 1049–1052.

[10] N.M. Gasanly, A.G. Guseinov, E.A. Aslanov, S.A. El-Hamid, Infrared reflection spectra of $Cu_3B_5C_9$ single crystals, Phys. Status Solidi (b) 158 (1990) K85–K88.

[11] I. Guler, K. Goksen, N.M. Gasanly, R. Turan, Low-temperature visible photoluminescence and optical absorption in $Tl_2In_2Se_3S$ semiconductor, Physica B 395 (2007) 116–120.

[12] N.A.P. Mogaddam, N.S. Yuksek, N.M. Gasanly, H. Ozkan, Determination of trapping center parameters of Tl_2InGaS_4 layered crystals by thermally stimulated current measurements, J. Alloys Compd. 417 (2006) 23–28.

[13] P.Y. Yu, M. Cardona, Fundamentals of Semiconductors, Springer, Berlin, 1995.

[14] J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, New Jersey, 1971.

[15] S. Kitamura, S. Endo, T. Irie, Semiconducting properties of $CuIn_5S_8$ single crystals. I. Electrical properties, J. Phys. Chem. Solids 46 (1985) 881–885.

[16] A.F. Qasrawi, N.M. Gasanly, Crystal data, photoconductivity and carrier scattering mechanisms in $CuIn_5S_8$ single crystals, Cryst. Res. Technol. 36 (2001) 1399–1410.

[17] V. Capozzi, Kinetics of radiative recombinations in GaSe and influence of Cu dopping on the luminescence spectra, Phys. Rev. B 28 (1983) 4620–4627.

[18] R. Chen, S.W.S. Mckeever, Theory of Thermoluminescence and Related Phenomena, Word Scientific, Singapore, 1997.