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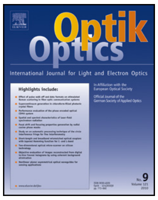

Combined low-temperature photoluminescence and thermally stimulated current studies in $Cu_3In_5S_9$ layered single crystals

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ABSTRACT

Photoluminescence (PL) and thermally stimulated current (TSC) spectra of $Cu_3In_5S_9$ layered crystals grown by Bridgman method have been studied in the photon energy region of 1.20–1.65 eV and the temperature range of 15–70 K (PL) and in the temperature region of 10–130 K (TSC). A broad PL band centered at 1.484 eV was observed at $T = 15$ K. Radiative transitions from shallow donor level located at 16 meV to moderately deep acceptor level located at 120 meV were suggested to be responsible for the observed PL band. TSC curve of $Cu_3In_5S_9$ crystal exhibited one broad peak at about 60 K. The activation energy of trap level was found to be 17 meV. An energy level diagram showing transitions in the band gap of the crystal was plotted taking into account the results of PL and TSC measurements carried out below room temperature. Moreover, the absorption edge of $Cu_3In_5S_9$ crystals have been studied through transmission and reflection measurements in the photon energy range 1.13–1.85 eV. The band gap energy was determined as 1.61 eV.

1. Introduction

Compound $Cu_3In_5S_9$ is one of the representatives of a class 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 semiconductor compounds has been revealed based on a physicochemical analysis and the state diagram of ABC_2–B_2C_3 quasi-binary systems [1]. Optical and photoelectrical properties of these crystals have been studied previously [2–7]. The cathode- and photo-luminescence spectra of $Cu_3Ga_5Se_9$ single crystals have been measured at different excitation intensities and temperatures [8]. The results indicate 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 detailed state diagram of the $CuInS_2$–In_2S_3 system has been investigated in Ref. [9]. It has been found that at 25 mol% In_2S_3, the $Cu_3In_5S_9$ compound, melting congruently at 1085 °C, is formed. The authors reported that $Cu_3In_5S_9$ single crystals had a layered structure and were crystallized in a monoclinic structure with the parameters $a = 0.660$ nm, $b = 0.691$ nm, $c = 0.812$ nm and $\beta = 89^\circ$. Ito and Ryo [10] reported the fabrication of superstrate-structured solar cells by the deposition of $Cu_3In_5S_9$ films under air by spray pyrolysis. The cells had an open-circuit voltage of 0.551 V, a photocurrent density of 9.5 mA cm^{-2}, a fill factor of 0.45, and a conversion efficiency of 2.14%. Infrared reflection and Raman scattering spectra of $Cu_3In_5S_9$ crystals have also been studied and analyzed in Refs. [11,12]. The frequencies of 18 IR-active and 23 Raman-active optical modes have been obtained.

One of the determining factors in the eventual device performance of semiconductors is the presence of impurity and/or defect centers in the crystal. Thus, it is very useful to get detailed information on energetic parameters of recombination centers in semiconductor in order to obtain high-quality devices. In the present paper we report the intensity variation of the PL spectra in the temperature range of 15–70 K in $Cu_3In_5S_9$ crystals. The analysis of the data suggests that the radiative transitions originate from recombination of charge carriers from donor to acceptor states. Moreover, we established in thermally stimulated current (TSC) curve of $Cu_3In_5S_9$ crystal one broad peak. The activation energy of trap level was found to be 17 meV.

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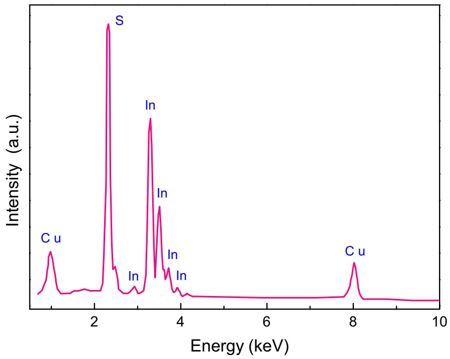

Fig. 1. Energy-dispersive spectroscopic analysis of $Cu_3In_5S_9$ crystal.

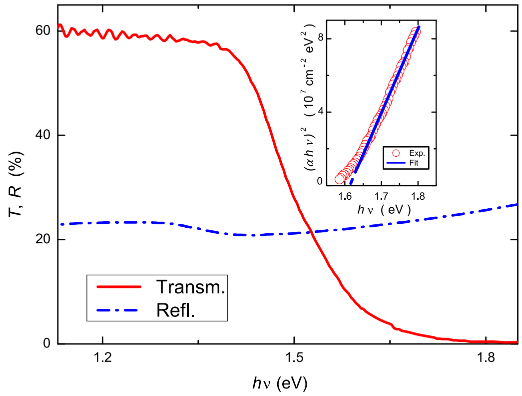

Fig. 2. Spectral dependencies of reflection and transmission for $Cu_3In_5S_9$ crystals. Inset: plot of $(\alpha h\nu)^2$ versus $h\nu$ for $Cu_3In_5S_9$ crystals.

2. Experimental details

$Cu_3In_5S_9$ semiconductor polycrystals were synthesized using high-purity 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 synthesis was carried out in quartz ampoules evacuated to 10^{-5} Torr. The single crystals were grown from obtained polycrystals by the Bridgman method in silica tubes (10 mm in diameter and about 15 cm in length) with a tip at the bottom in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C cm^{-1} at a rate of 1.0 mm h^{-1}. The resulting ingot appeared gray in color and the freshly cleaved surfaces were mirror-like. The chemical composition of $Cu_3In_5S_9$ crystals was determined by energy dispersive spectroscopic analysis using JSM-6400 electron microscope (Fig. 1). The atomic composition of the studied samples (Cu:In:S) was found to be 17.9:29.7:52.4, respectively. The electrical conductivity of the studied sample was n-type as determined by the hot probe method.

Crystals suitable for PL measurements had typical sample dimensions of $12 \times 5 \times 1$ mm^3. The green line ($\lambda = 532$ nm) of a continuous frequency-doubled YAG:Nd^{3+} laser was used as the excitation light source. A "CTI-Cryogenics M-22" closed-cycle helium cryostat was used to cool the sample from room temperature down to 15 K. PL spectra of the sample in the region 1.20–1.65 eV were analyzed using a "Oriel MS-257" grating monochromator and "Hamamatsu S7031" FFT-CCD Image Sensor. All of the PL spectra have been corrected for the spectral response of the optical apparatus.

The transmission and reflection measurements were carried out in the 1.13–2.00 eV photon energy region with a "Shimadzu" UV-1201 model spectrophotometer. The transmission measurements were done under the normal incidence of light. For reflection experiments, the specular reflectance attachment with 5° incident angle was used.

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 side. The TSC measurements were carried out with heating rate of 0.10 K s^{-1} in the temperature range of 10–130 K. 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

Fig. 2 presents the transmission (T) and reflection (R) spectra of $Cu_3In_5S_9$ crystals registered in the photon energy range from 1.13 to 2.00 eV. The reflection measurements were carried out using the specimens with natural cleavage planes. The sample thickness was then reduced until it was convenient for measuring the transmission spectra. The thickness of the thin sample was determined using transmission interference fringes at photon energy slightly lower than the intrinsic absorption edge, i.e., in a region with relatively high transmission (Fig. 2). We evaluated the thickness of the samples (about 10 μm) by measuring the wavelengths at which two adjacent transmission maxima occur [13]

$$d = \frac{\lambda_1 \lambda_2}{2n(\lambda_2 - \lambda_1)}. \qquad (1)$$

The absorption coefficient α was calculated using the following relation [13]

$$\alpha = \frac{1}{d} \ln \left\{ \frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2 \right]^{1/2} \right\} \qquad (2)$$

The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions was carried out to obtain the information about the energy band gap. The absorption coefficient α and photon energy $h\nu$ can be related by [13]

$$\alpha(h\nu) = A\left(h\nu - E_g\right)^p. \qquad (3)$$

In this equation, A is a constant that depends on the transition probability and p is an index that characterizes the optical absorption process and it theoretically equals to 2 and 1/2 for indirect and direct allowed transitions, respectively. From the analysis of the experimental data, it was revealed that the absorption coefficient α is proportional to $(h\nu - E_g)^p$ with $p = 1/2$. Inset of Fig. 2 displays the dependence of $(\alpha h\nu)^2$ versus $h\nu$ for $Cu_3In_5S_9$ crystals. The circles show the experimental data. They were fitted to a linear equation (the solid lines) to find the energy band gap. This suggests the realization of direct allowed transitions for $Cu_3In_5S_9$ crystal with the energy band gap of $E_{gd} = 1.61$ eV.

Fig. 3 presents the PL spectra of $Cu_3In_5S_9$ crystals in 15–70 K temperatures range at laser excitation intensity $L = 430.4$ mW cm^{-2}. We observed that, at $T = 15$ K the emission band was centered at 1.484 eV and has asymmetrical Gaussian line shape with low- and high-energy side half-widths of 0.150 and 0.090 eV, respectively. As seen from Fig. 3, the peak intensity decreases as the temperature is elevated. The peak position shows several degrees of red shift (about 0.03 eV) with increasing temperature (inset 1 of Fig. 3). It is well known that the donor–acceptor pair transition energy

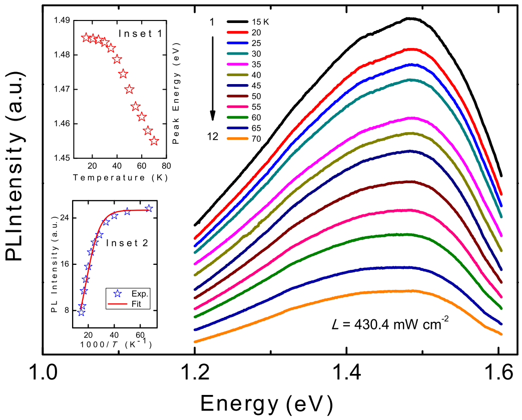

Fig. 3. Temperature dependence of PL spectra from $Cu_3In_5S_9$ crystals at excitation laser intensity $L = 430.4\,mW\,cm^{-2}$. Inset 1: temperature dependence of emission band peak energy. Inset 2: temperature dependence of PL band intensity. Stars are the experimental data. Solid curve shows the theoretical fit using Eq. (4) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

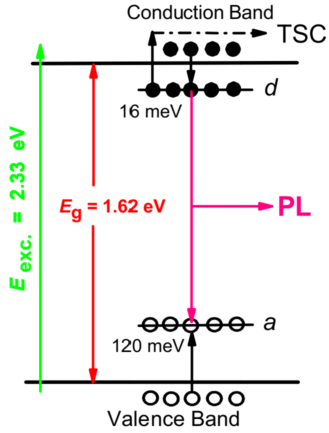

Fig. 4. Energy level diagram of $Cu_3In_5S_9$ crystal at $T = 15\,K$.

decreases along with the band gap energy when the temperature is increased [14].

The experimental data for the temperature dependence of PL band intensity can be fitted by the following expression [13]

$$I(T) = \frac{I_0}{1 + \alpha \exp\left(-E_t/kT\right)}, \tag{4}$$

where I_0 is a proportionality constant, E_t is the thermal activation energy, k is the Boltzmann's constant and α is the recombination process rate parameter. Inset 2 of Fig. 3 shows the temperature dependence of the emission band maximum intensity as a function of the reciprocal temperature in the 15–70 K range. The best fit using Eq. (4), demonstrated by the solid curve in inset 2 of Fig. 3, has been achieved with the quenching activation energy for emission band $E_t = 16\,meV$. Since $Cu_3In_5S_9$ crystal is an n-type semiconductor, we believe that this level is shallow donor level located at 16 meV below the bottom of conduction band. This level can be considered as originating from the deviations in the stoichiometry (i.e., sulfur vacancies) [15–17].

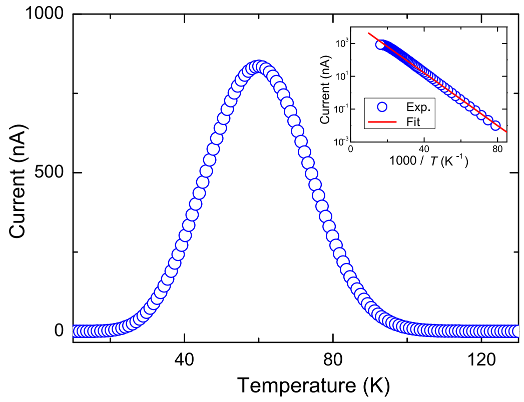

Fig. 5. Experimental TSC curve of $Cu_3In_5S_9$ crystal with heating rate of $0.10\,K\,s^{-1}$. Inset: thermally stimulated current versus $1000/T$. Circles are experimental data. Solid line is the theoretical fit using initial rise method.

Fig. 4 presents the possible scheme for the states located in the energy gap of the $Cu_3In_5S_9$ crystal $T = 15\,K$. In this scheme, shallow donor level 'd' is located at $E_d = 16\,meV$ below the bottom of conduction band. Here, it is needed to recall the general expression for emission energy of donor–acceptor pair as [14]

$$E_p = E_g - E_d - E_a, \tag{5}$$

where E_g is the band gap energy of $Cu_3In_5S_9$ crystal, E_d and E_a are the donor and acceptor level energies, respectively. A simple calculation with Eq. (5) for emission band by using the values of $E_g = 1.62\,eV$, $E_p = 1.484\,eV$ and $E_d = 16\,meV$ gives us the energy of the moderately deep acceptor level as $E_a = 120\,meV$ (Fig. 4). The observed emission band in the PL spectra has been assigned to the radiative transitions from the donor level 'd' to the acceptor level 'a'. Since the studied crystals were not intentionally doped, these centers are thought to originate from anion and cation vacancies and/or stacking faults, quite possible to exist in layered $Cu_3In_5S_9$ due to the weakness of the van der Waals forces between the layers [18].

Fig. 5 presents the TSC curve of $Cu_3In_5S_9$ crystal registered with the heating rate of $0.10\,K\,s^{-1}$. 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 $Cu_3In_5S_9$ crystal can be assigned to electron traps.

There are several methods to evaluate the trapping parameters from the experimental TSC spectra [19]. 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 initial tail of the TSC curve arises proportional to $\exp(-E_t/kT)$ [19], the logarithmic plot of the thermally stimulated current as a function of the reciprocal of temperature yields a straight line with slope of $(-E_t/k)$. Inset of Fig. 5 shows this plot giving the activation energy of the revealed trap level as 17 meV.

At this point, it is worthwhile to give an insight into the transitions in the band gap of $Cu_3In_5S_9$ crystal by combining the results of PL and TSC studies (Fig. 4). The present result of PL experiment in the 15–70 K temperature range showed the existence of one electron trap with activation energy 16 meV. Taking into account the possible errors (about 5%), the obtained energies of 16 and 17 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 $Cu_3In_5S_9$ crystals as a function of temperature were studied. A broad emission band centered at 1.484 eV was observed in the PL spectra at $T = 15\,K$. The variation of the spectra with temperature suggested that the transitions between the donor

($E_d = 16$ meV) and acceptor ($E_a = 120$ meV) levels can be responsible for the observed emission band. The analysis of the thermally stimulated current data in $Cu_3In_5S_9$ established the electron trap level with activation energy $E_d = 17$ meV. The revealed energy level is thought to be partially compensated allowing for both PL emission and thermally stimulated current. As the studied crystals were not intentionally doped, these centers are thought to originate from anion and cation vacancies and/or stacking faults, created during crystal growth. Moreover, through transmission and reflection measurements in the photon energy range 1.13–1.85 eV, the band gap energy of $Cu_3In_5S_9$ crystals was established as 1.61 eV.

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