Donor-acceptor pair recombination in AgIn5S8 single crystals

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Donor-acceptor pair recombination in $AgIn_5S_8$ single crystals

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Photoluminescence (PL) spectra of $AgIn_5S_8$ single crystals were investigated in the 1.44–1.91 eV energy region and in the 10–170 K temperature range. The PL band was observed to be centered at 1.65 eV at 10 K and an excitation intensity of 0.97 $W\,cm^{-2}$. The redshift of this band with increasing temperature and with decreasing excitation intensity was observed. To explain the observed PL behavior, we propose that the emission is due to radiative recombination of a donor-acceptor pair, with an electron occupying a donor level located at 0.06 eV below the conduction band, and a hole occupying an acceptor level located at 0.32 eV above the valence band. © *1999 American Institute of Physics.* [S0021-8979(99)03706-8]

I. INTRODUCTION

The ternary semiconducting compound $AgIn_5S_8$ has the same cubic spinel structure as $CdIn_2S_4$.[1] $AgIn_5S_8$ crystal can be derived from the $CdIn_2S_4$, if the divalent cadmium cation is replaced by the univalent silver cation and the trivalent indium cation, according to $CdIn_2S_4 => [Ag_{1/2}In_{1/2}]_t[In_2]_oS_4 => Ag_{1/2}In_{5/2}S_4 => AgIn_5S_8$. Thus, in a $AgIn_5S_8$ crystal 1/5 of the indium atoms have tetrahedral (t) and 4/5 of the indium atoms have octahedral (o) coordinations. In the tetrahedral sublattice of $AgIn_5S_8$ crystal the ratio of structural vacancies to the cations (Ag and In) is 1:3. Hence, $AgIn_5S_8$ crystal is a defect semiconductor with a 25% vacancy concentration in the cation sublattice. The optical and electrical properties of $AgIn_5S_8$ have been studied for photovoltaic applications.[2,3] The energy band gaps of $AgIn_5S_8$ for the indirect optical transitions are 1.80 eV at 300 K and 1.90 eV at 96 K. These energy band gaps can be used in photovoltaic solar cell applications. Infrared (IR) reflection and Raman scattering spectra of $AgIn_5S_8$ have also been investigated and analyzed.[4–6]

In this article, we present the results of a systematic experimental analysis of the photoluminescence (PL) of $AgIn_5S_8$ single crystals in the 1.44–1.91 eV energy region and in the 10–170 K temperature range. The PL spectra and their temperature and excitation intensity dependencies were studied in detail in order to propose a model for the recombination process of photoexcited carriers and a scheme for the impurity levels.

II. EXPERIMENTAL DETAILS

$AgIn_5S_8$ polycrystals were synthesized from particular high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals of $AgIn_5S_8$ were grown by the modified Bridgman method. The x-ray diffraction patterns of $AgIn_5S_8$ revealed a single phase of cubic spinel structure. The obtained lattice constant $a = 1.08286(8)$ nm was in good agreement with those reported by several workers.[1,2] In the PL measurements, samples with a typical size of $8\times8\times4$ mm^3 were used. The electrical conductivity of the studied samples were *n* type as determined by the hot probe method. The PL, excited by the 488 nm (2.54 eV) line of a Spectra-Physics argon ion laser, was observed from the excitation laser illuminated surface of the samples in a direction close to the surface normal. A CTI-Cryogenics M-22 closed-cycle helium cryostat was used to cool the crystals down to 10 K. The temperature was controlled within an accuracy of 0.5 K. The PL spectra in the 650–860 nm wavelength range were analyzed using a U-1000 Jobin-Yvon double grating spectrometer and a cooled GaAs photomultiplier supplied with the necessary photon counting electronics. The PL spectra have been corrected for the spectral response of the optical apparatus. A set of neutral-density filters changed the excitation laser intensity from 0.02 to 0.97 $W\,cm^{-2}$.

III. RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of $AgIn_5S_8$ single crystals measured in the 1.44–1.91 eV energy region and in the 10–170 K temperature range at a constant excitation laser intensity of 0.97 $W\,cm^{-2}$. We observed one broad band centered at $E_p = 1.65$ eV in the PL spectrum at 10 K. The emission band has a full width at half maximum (FWHM) of about 0.21 eV and has a slightly asymmetrical Gaussian line shape. These features are typical of emission bands due to donor-acceptor pair transitions observed in ternary semiconductors.[7] We also note that the peak energy position and the emission band intensity change with temperature.

In Fig. 2 we present the peak energy position, which shifts towards lower energies with increasing temperature.

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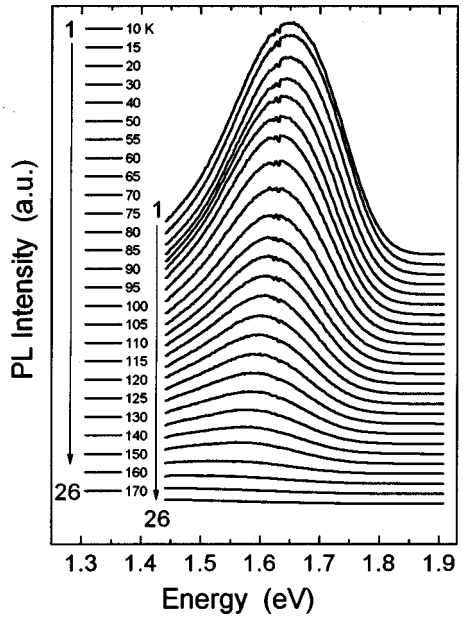

FIG. 1. PL spectra of $AgIn_5S_8$ in the 10–170 K temperature range.

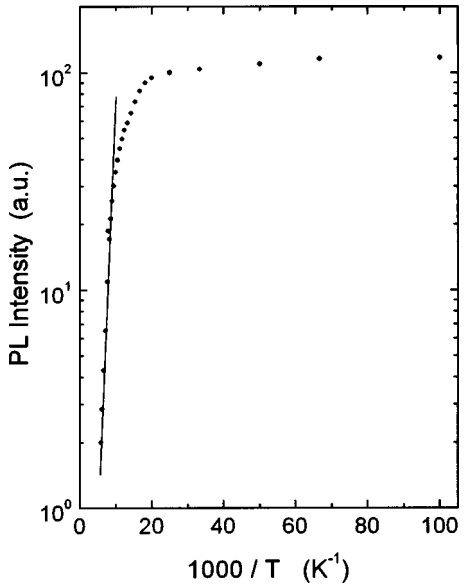

FIG. 3. Temperature dependence of the PL intensity at the emission band maximum for $AgIn_5S_8$.

Here, we also show the band gap energy at three different temperatures. Since the temperature coefficient of the band gap energy of the $AgIn_5S_8$ crystals is negative (i.e., $dE_g/dT = -4.9\times10^{-4}$ eV/K^2), the peak energy due to the donor-acceptor transition should decrease with band gap energy as the temperature increases.[8] The observed shift of the peak energy position towards lower energies satisfies the temperature dependence expected for the donor-acceptor pair recombination.

From Fig. 1 it can be seen that the emission band intensity decreases with increasing temperature. A rapid thermal quenching of the PL band is observed above $T = 100$ K. The experimental data for the temperature dependence of the PL intensity at the emission band maximum (I) can be fitted by the following expression:

$$I(T) = I_0 \exp\left(\frac{\Delta E}{kT}\right), \tag{1}$$

where I_o is a proportionality constant, ΔE the thermal activation energy, and k the Boltzmann constant. Figure 3 shows the temperature dependence of the emission band maximum intensity as a function of the reciprocal temperature in the 10–170 K range. The semilog plot of the emission band intensity as a function of the reciprocal temperature gives a straight line in the 100–170 K high-temperature region. An activation energy ($E_d = 0.06$ eV) for the emission band is derived from the slope of the straight line fit. Since the $AgIn_5S_8$ crystal is an n-type semiconductor, we consider that the impurity level is a donor level located at 0.06 eV below the bottom of the conduction band. A shallow donor level ***d*** in undoped $AgIn_5S_8$ crystal may be originated from the variations in the stoichiometry (i.e., sulphur vacancies). From the electrical resistivity and Hall effect measurements of isostructural n-$CuIn_5S_8$ crystal, in the 80–300 K temperature range, the activation energy of a similar donor level was found to be 0.09 eV.[9] This donor level has also been assigned to sulphur vacancies.

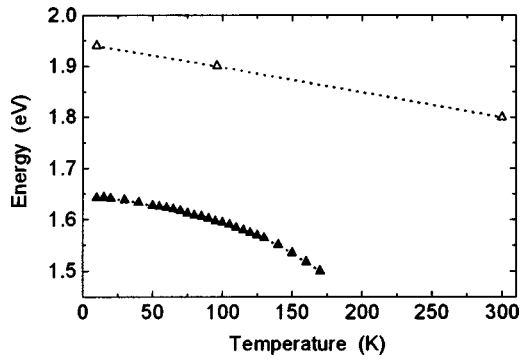

FIG. 2. Temperature dependencies of the emission band peak energy (solid triangles) and the band gap energy (open triangles) for $AgIn_5S_8$.

Figure 4 presents the PL spectra for 14 different laser excitation intensity levels at 10 K. The observed PL band slightly shifts towards higher energies with increasing excitation intensities, which is also a characteristic of the donor-acceptor pair recombination.[10] The highest energies agree with transitions between closest pairs, while the lowest energies correspond to pairs with a large separation. The blue-shift, observed with increasing excitation laser intensities, originates from the fact that the more distant pairs, with long decay times, are saturated more quickly than the closer pairs, owing to their greater transition probability.

The semilog plot in Fig. 5 shows the excitation laser intensity (L) as a function of the emission band peak energy (E_p) at 10 K. The experimental data in Fig. 5 are then fitted by the following expression:

$$L(E_p) = L_o \frac{(E_p - E_\infty)^3}{(E_B + E_\infty - 2E_p)} \exp\left(-\frac{2(E_B - E_\infty)}{E_p - E_\infty}\right), \tag{2}$$

where L_o is a proportionality constant, E_B the emitted photon energy of a close donor-acceptor pair separated by a shallow impurity Bohr radius (R_B), and E_∞ the emitted photon energy of an infinitely distant donor-acceptor pair.[11] From a

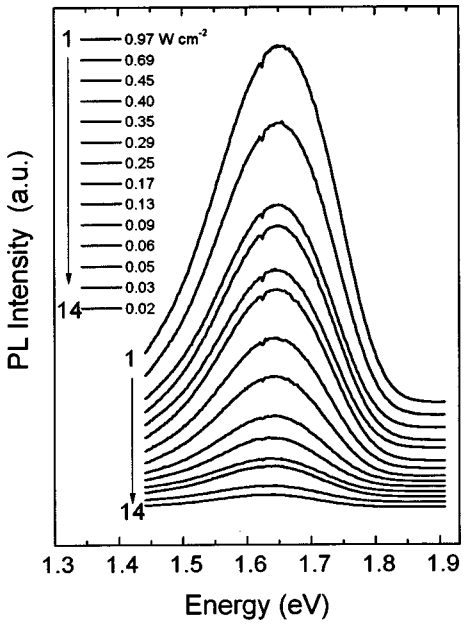

FIG. 4. Photoluminescence spectra of $AgIn_5S_8$ for different excitation laser intensities at $T=10$ K.

nonlinear least square fit to the experimental data, the photon energy values for an infinitely distant donor-acceptor pair and a close donor-acceptor pair separated by R_B are found to be $E_\infty=1.56$ eV and $E_B=1.74$ eV, respectively. These limiting photon energy values are in good agreement with the band gap energy ($E_g=1.94$ eV) and the observed values of the peak energy position (i.e., $E_\infty<1.62$ eV $<E_p<1.65$ eV $<E_B$) at 10 K.

Since the obtained value of E_d is smaller than the energy difference between the band gap energy of $AgIn_5S_8$ ($E_g=1.94$ eV at 10 K) and the spectral position of emission peak ($E_p=1.65$ eV at 10 K), i.e., $E_g-E_p=0.29$ eV $>E_d=0.06$ eV, we state that the observed emission band arises from a donor-acceptor pair recombination. We propose the presence of structural vacancies in the cation sublattice as the origin of a deep acceptor level ***a*** located above the valence band in the n-$AgIn_5S_8$ crystal, by analogy with the isostructural n-$CdIn_2S_4$ crystal where a relatively deep acceptor level ($E_a=0.20$ eV) was assigned to similar vacancies.[12]

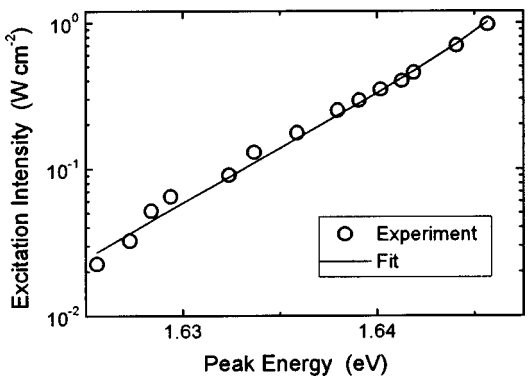

FIG. 5. Excitation intensity vs emission band peak energy at $T=10$ K.

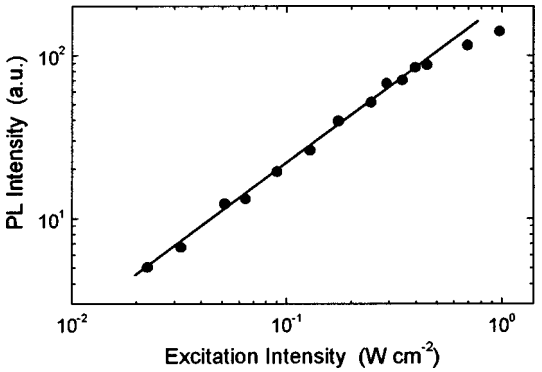

FIG. 6. Dependence of the PL intensity at the emission band maximum vs excitation intensity at $T=10$ K.

We have also analyzed the variation of the emission band intensity versus the excitation laser intensity (see Fig. 4). The experimental data can be fitted by the simple power law $I\propto L^\gamma$, where I is the PL intensity, L is the excitation laser intensity, and γ is a dimensionless exponent. It was found that the PL intensity at the emission band maximum increases sublinearly (i.e., $\gamma=0.98$) with respect to the excitation intensity (Fig. 6). Saturation starts at $L>0.4$ W cm^{-2}. For an excitation laser photon with an energy exceeding the band gap energy E_g, the coefficient γ is generally $1<\gamma<2$ for the free- and bound-exciton emission, and $\gamma\leqslant 1$ for free-to-bound and donor-acceptor pair recombinations.[13] Thus, the obtained value of $\gamma=0.98$ is in line with our previous assignment of the observed PL band in $AgIn_5S_8$ spectra 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 donor-acceptor levels located in the forbidden energy gap of the $AgIn_5S_8$ crystal. These donor-acceptor levels are involved in the radiative recombination of the photoexcited carriers observed in this work (Fig. 7). In the proposed scheme, a shallow donor level ***d*** is located at 0.06 eV below the bottom of the conduction band. From the nonlinear least square fitted value of the photon energy for an infinitely distant donor-acceptor pair $E_\infty=E_g-(E_d+E_a)=1.56$ eV,[11] an acceptor level ***a***, located at 0.32 eV above the top of the valence band, is introduced into the forbidden energy gap of $AgIn_5S_8$. Taking into account the above assignments, the observed PL emission band has been attrib-

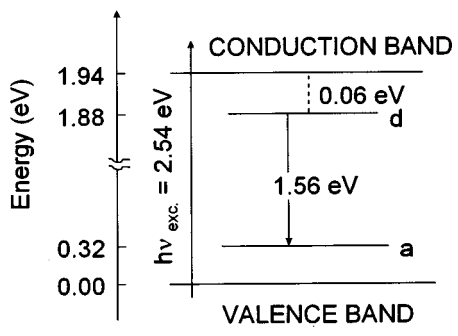

FIG. 7. Proposed energy level diagram of $AgIn_5S_8$ at $T=10$ K.

uted to the radiative recombination of an electron occupying a donor level ***d*** ($E_{\mathbf{d}}=0.06$ eV) and a hole occupying an acceptor level ***a*** ($E_{\mathbf{a}}=0.32$ eV).

IV. SUMMARY AND CONCLUSIONS

The results obtained from the photoluminescence study of $AgIn_5S_8$ single crystals in the 1.44–1.91 eV energy region and in the 10–170 K temperature range, show that the PL intensity decreases with increasing temperature. A rapid thermal quenching of the PL band is observed above $T=100$ K. This behavior was understood by introducing a donor level located at 0.06 eV below the conduction band and a deep acceptor level located at 0.32 eV above the valence band in the $AgIn_5S_8$ crystal. The blueshift of the emission band peak energy with increasing excitation laser intensity is explained using the inhomogeneously spaced donor-acceptor pair model. Also, the PL intensity increases sublinearly with respect to the excitation laser intensity, which is in accordance with our assignment that the observed PL in $AgIn_5S_8$ is due to donor-acceptor pair recombination.

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