

Photoluminescence Spectra of Tm-Doped CuAlS₂ Crystals

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Photoluminescence spectra were studied for the first time in Tm-doped CuAlS₂ crystals grown by the chemical vapor transport technique. Two sharp emission peaks at 1.55 eV (infrared) and 2.60 eV (blue) superposed on an orange broad emission band related to the host material were observed. The sharp emission lines were assigned to the f–f transitions in Tm³⁺ ions. The infrared line was found to be prominent at room temperature, the blue line at low temperatures. Both lines share the same excitation peak at 3.1 eV, which was tentatively attributed to the charge transfer transition. The temperature dependence was explained on the basis of the configurational-coordinate diagram of the luminescent center formed by the substitutional Tm³⁺ ion.

KEYWORDS: CuAlS₂ ternary semiconductor, Tm rare-earth impurity, f–f transition, photoluminescence spectrum, photoluminescence excitation spectrum

1. Introduction

Doping of semiconductors with rare-earth (RE) elements is of considerable interest due to the sharp radiative transitions between the L–S coupling terms of the RE ions, which make RE-doped semiconductors promising materials for full-color electroluminescent device realization.¹⁾

The CuAlS₂ compound is the widest band-gap member of the I–III–VI₂-type chalcopyrite semiconductors with a direct energy gap of 3.55 eV,²⁾ which is wide enough to accommodate the RE-originated luminescent centers emitting in the visible spectral region. Since CuAlS₂ contains both monovalent and trivalent cations in contrast to its binary analog ZnS in which only the divalent cation exists, there is a possibility of accommodating trivalent RE ions without breaking the charge neutrality condition. In our previous studies,^{3,4)} we established that Tb can be introduced into a CuAlS₂ crystal, occupying the Al site as a trivalent ion, and becomes a luminescent center showing two sharp emission lines at 2.278 eV and 2.532 eV attributed to f–f transitions in the 4f⁸ manifold at room temperature.

There has been strong anticipation for studies of Tm doping in CuAlS₂, aiming at realization of blue electroluminescent devices,⁵⁾ since the Tm³⁺ ion is known to become a blue emitting center when doped in ZnS.⁶⁾ We therefore carried out crystal growth experiments of Tm-doped CuAlS₂ and studied photoluminescence (PL) spectra in the crystals obtained. This paper describes the results of these studies.

2. Experimental

Tm-doped CuAlS₂ single crystals were grown by the iodine chemical vapor transport (CVT) method. Starting materials for the transport were the constituent elements at a molar ratio of Cu:Al:Tm:S = 1:0.95:0.05:2. These materials were sealed into a silica ampoule evacuated to about 10⁻⁶ Torr together with 10 mg/cm³

of iodine. The ampoule was placed in a two-zone furnace, the transport being carried out for seven days with the temperature of the source zone being 900°C and that of the growth zone being 750°C. The resulting crystals were blue in color and had a well-developed {112} plane, and the typical size was 2 mm × 2 mm × 1 mm. The resulting Tm content in the crystals was found by EPMA analysis to be 0.25 mol%, instead of the starting molar ratio of 5.0 mol%. This may be explained by the relatively large ionic radius of Tm³⁺ (~0.87 Å⁷⁾ compared with that of the Al ion (~0.54 Å⁷⁾ in the chalcopyrite structure.

PL spectra were measured under excitation by the 365 nm line of a superhigh-pressure Hg lamp, the samples being placed in an Oxford Instruments CF1104 continuous flow cryostat. The emitted light was dispersed by a JASCO CT-25C monochromator with a grating of 1200 groove/mm blazed at 750 nm and detected by a Hamamatsu R928 photomultiplier. For PL excitation (PLE) measurements, a 150 W Xe lamp combined with a JASCO CT-25C monochromator was used as an excitation source. The emitted light was again dispersed by a JASCO CT-25A monochromator with a grating of 1200 groove/mm blazed at 750 nm. All spectra were corrected for the spectral response of the detection system.

3. Results and Discussion

3.1 Photoluminescence spectra

The typical PL spectra of the Tm-doped CuAlS₂ crystals taken at different temperatures in the range 70–300 K are shown in Fig. 1. The spectrum at room temperature consists of a broad band peaking at 1.8 eV and a sharp infrared (IR) line at 1.55 eV (800 nm). The former shows a blue shift when the temperature is lowered. With the decrease of temperature, a blue (B) line at 2.60 eV (477 nm) appears and becomes stronger, while the IR line loses its intensity. We could not observe any shift of peak energies for either the B or IR line within the accuracy of our experimental system. Both B and IR emissions show fine structures consisting of several sharp lines with a half-width of about 15 cm⁻¹, which are shown in the inset of Fig. 1.

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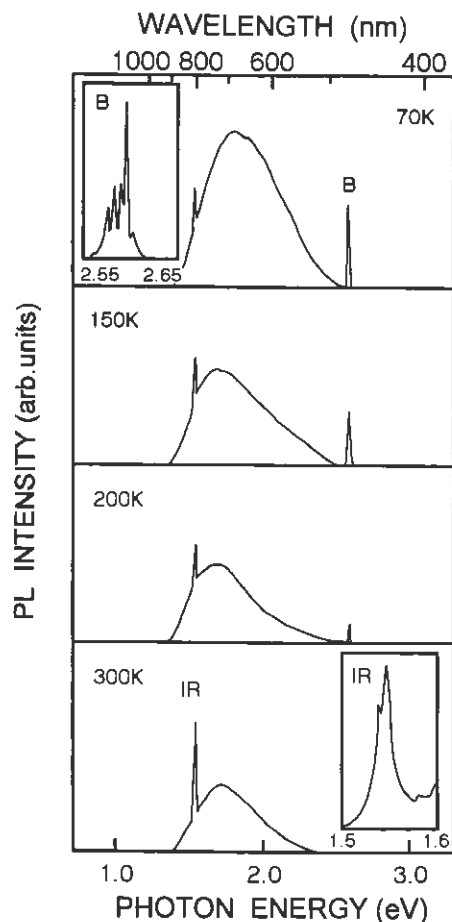


Fig. 1. Photoluminescence spectra of Tm-doped CuAlS₂ single crystal taken at different temperatures. In the insets the fine structures of the B and IR emissions are shown.

3.2 Assignments of emissions

The broad emission band has been attributed to the centers related to the host material because undoped CuAlS₂ usually shows a similar orange luminescence band peaking around 2.0 eV, which has been ascribed to the D-A pair recombination.³¹ However, the broad emission in Fig. 1 shows a considerable shift to higher energies with decrease of temperature. Such a shift has not been observed in either undoped or Tb-doped crystals of CuAlS₂ but is found to be peculiar to the Tm-doped crystals. These results suggest that Tm-related centers of some kind are involved in the formation of the broad D-A band.

Now let us consider the sharp B and IR emissions in detail. Since the spectral positions of both emissions were found to be close to the energy separation between some of the L-S coupling terms of the free trivalent Tm ion described in the Dieke diagram,⁸¹ these emissions were attributed to the electric-dipole transitions between the orbitals originating from the 4f shell of the Tm³⁺ impurity.

Strictly speaking, the electric-dipole transitions between the 4f energy levels of RE ions are parity-forbidden (Laporte's selection rule). However, the parity prohibition can be lifted due to the influence of the odd terms of the crystal field, resulting in mixing of the 4f¹² configuration of Tm³⁺ with the levels of opposite parity

such as charge transferred states 4fⁿ⁺¹3p⁻¹ or orbital promotion states 4fⁿ⁻¹5d¹.

Taking into account the spectral positions of the Tm³⁺-related emission lines, it should be noted that the assignment of the observed emission lines to the f-f transitions between energy levels in the Dieke diagram is not unique. The IR emission at 1.55 eV can be assigned either to ¹G₄→³H₅ or to ³F₄→³H₆ (ground state) f-f transitions, while the B emission at 2.60 eV may originate from either ¹G₄→³H₆ or ¹D₂→³H₅ transitions in the 4f¹² manifold of the Tm³⁺ ion.⁸¹ However, the assignment of the B emission to ¹D₂→³H₅ transitions can be ruled out since the ¹D₂ state is buried in the conduction band of the host crystal and the energy position of this state is higher than that of the excitation band found in the PLE spectra described in §3.3. Therefore, the B emission can be safely assigned to ¹G₄→³H₆ transitions. The spin prohibition for this transition is not strict because of a slight admixture of the ¹G₄ state into the ³H₆ ground state, caused by spin-orbit coupling.

Furthermore, since the IR emission shows a temperature dependence which is completely different from that of the B emission as will be shown in §3.4, the possibility of assignment of the excited state involved in the IR emission to ¹G₄ (the same excited state as for the B emission) may also be excluded. Therefore, the IR emission has been attributed to ³F₄→³H₆ electronic transitions.

The fine structures of the B and IR emissions, shown in the insets of Fig. 1, are similar to those observed in Tm-doped ZnS.⁶¹ They have been attributed to the crystal field splitting of the L-S coupling terms of Tm³⁺ involved in the emission process. From group theory, it is known that in a tetrahedral crystal field the ³H₆ ground term and the excited terms of ³F₄ and ¹G₄ symmetry split into several singlet, doublet and triplet states, the doublet and triplet terms being further split by a tetragonal component of the crystal field in the CuAlS₂ host lattice.⁹¹ Therefore, a large number of transitions should be observed at low temperatures, these transitions being subject to selection rules.

Due to the screening of the 4f shell by diffuse outer electron shells, the interaction of the 4f electrons with the ligand field is weak, leading to the splitting energy of the order 200 cm⁻¹ between the lowest and the highest sublevels, split from the same L-S coupling term by the crystal field. These considerations agree well with the observed total width of the fine structures of the B and IR emissions, the width of the B emission being 350 cm⁻¹ and that of the IR emission being 160 cm⁻¹.

3.3 Photoluminescence excitation (PLE) spectra

We found that considerably weak B and IR emission lines could be observed under He-Cd laser irradiation, although Hg lamp irradiation gave rise to strong sharp emission lines, leading us to measure photoluminescence excitation (PLE) spectra for the B and IR emissions at 70 K and room temperature, respectively. The resulting PLE spectra are shown in Fig. 2. It is found that both emissions share the same excitation band

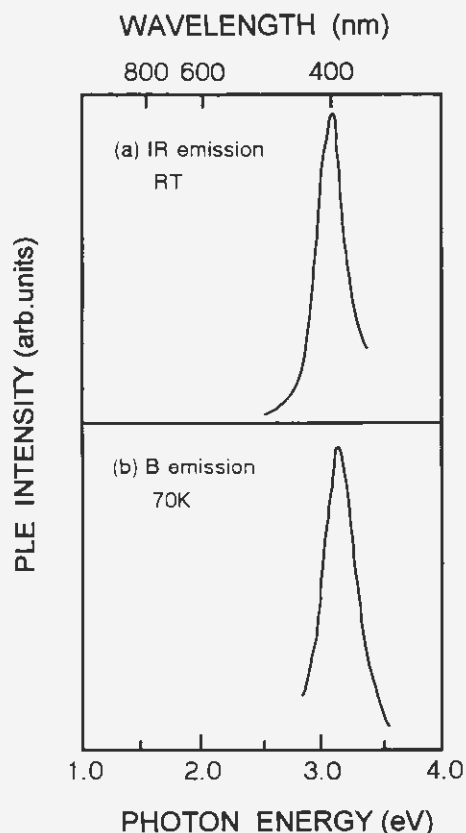


Fig. 2. PLE spectra for the IR emission at room temperature (a) and for the B emission at 70 K (b).

peaking at 3.1 eV (400 nm), suggesting both emissions originate from the same center.

However, since no levels corresponding to the energy separation of 3.1 eV from the ground state can be found in the Dieke diagram⁸⁾ for the Tm^{3+} ion ($4f^{12}$ electronic configuration), the origin of the 3.1 eV absorption peak should be sought in the other valence states of the Tm ion.

There are two possible ways of changing the valence state of the RE ion under excitation.

- 1) One of the 4f electrons is raised to the higher 5d orbitals, which can be described as $4f^n \rightarrow 4f^{n-1}5d^1$.
- 2) One of the electrons belonging to the ligands is promoted to the 4f orbitals of the central RE ion, i.e., $4f^n \rightarrow 4f^{n+1}3p^{-1}$, this process being called the "charge transfer" process.

The answer to the question as to whether the energetically lowest band corresponds to the $4f^{n-1}5d^1$ state or to the charge transfer state is related to the filling of the 4f shell in a specific RE ion. The ion under consideration, Tm^{3+} , has twelve electrons in its 4f shell, which means that it lacks only two electrons to fill the 4f shell completely. Since the state of a completely filled electron shell is very stable, we believe that for the Tm^{3+} ion, the probability of accepting an electron from ligands is higher than that of releasing an electron to the 5d shell. In other words, we believe that the energetically lowest absorption band, unrelated to the transitions in the 4f shell of Tm^{3+} , is the charge transfer band. Therefore, the PLE band peaking at 3.1 eV can be tentatively attributed to the charge transfer transi-

tions of the type $Tm^{3+} + e \rightarrow Tm^{2+}$.

3.4 Temperature dependence of intensities of B and IR emissions

The temperature dependence of intensities of the B and IR emissions are shown in Fig. 3. It can be seen from this figure that while the B emission shows only the usual thermal quenching behavior, the IR emission exhibits a peculiar feature, i.e., the increase of intensity with increase of temperature, in the range 120–240 K, which will be called "negative" thermal quenching. The temperature dependence of the intensity of the B and IR emissions can be fitted to the well-known relationship

$$I(T) = [1 + C \exp(-E_a/kT)]^{-1} \quad (1)$$

where $I(T)$ is the intensity at temperature T , k Boltzmann's constant, C a constant, and E_a the activation energy for nonradiative recombination. From Fig. 3, the value of the activation energy for the B emission is found to be $E_{a1} = 100 \pm 10$ meV. It is also found from Fig. 3 that the negative activation energy E_{a1}^- for the IR emission has the same absolute value as the activation energy E_{a1} for the B emission, which implies a thermally induced redistribution of electrons between the 1G_4 and 3F_4 levels involved in these emissions (to be discussed below). At temperatures higher than 240 K, the thermal quenching of the IR emission begins, with the activation energy being $E_{a2} = 300 \pm 20$ meV.

3.5 Interpretation of PL behavior in terms of configurational-coordinate model

In order to discuss the origin of the sharp emissions, and the observed dependence of these emissions on temperature, as well as the PLE spectra, we propose an energy level diagram based on the configurational-coordinate model shown in Fig. 4, where the lowest L-

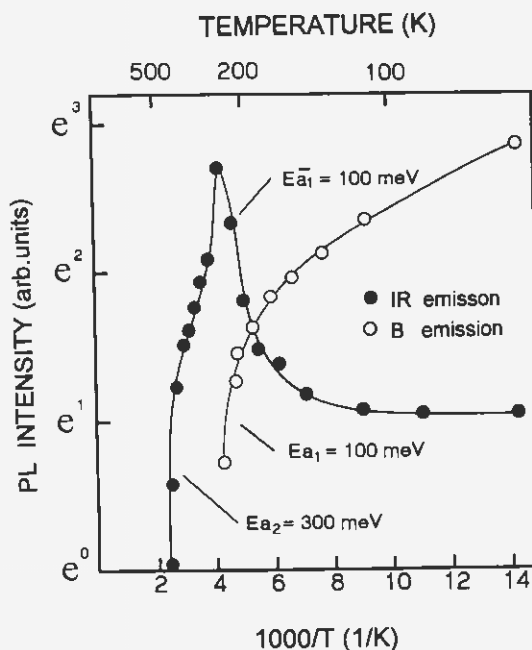


Fig. 3. Temperature dependence of intensities of the B and IR emissions.

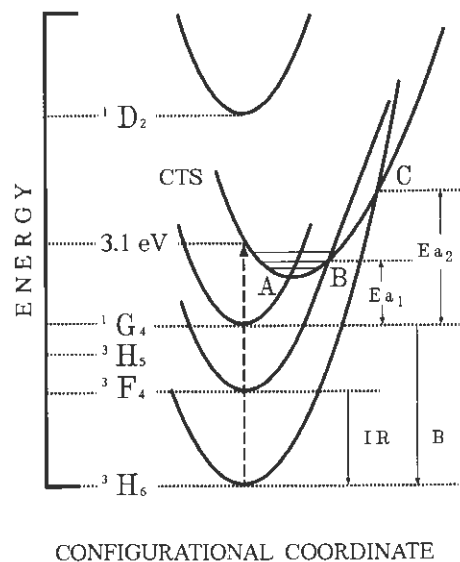


Fig. 4. Configurational coordinate model proposed for Tm^{3+} in the CuAlS_2 host. CTS—charge transfer state. E_{a1} and E_{a2} are the activation energies for CTS \rightarrow $^3\text{F}_4$ and CTS \rightarrow $^3\text{H}_6$ nonradiative electronic transitions.

S coupling terms of the Tm^{3+} ion are shown together with what is believed to be the charge transfer state (marked as CTS).

Since electrons of the 4f shell are, to a large extent "inner" electrons screened by outer electron shells from the surrounding ligands, their interaction with phonons or localized vibration modes is believed to be very weak. Therefore, the displacement of the locations of the minima of the excited states of the $4f^{12}$ manifold of the Tm^{3+} ion in relation to the ground state in the configurational coordinate is very small, which, in fact, is proven by the observation of the sharp Tm^{3+} -related emissions (if the above said displacement had been large, broad emissions should have been observed). Hence, all terms of the Tm^{3+} ion in Fig. 4 have been plotted as having minimum potential energy at the same configurational coordinate.

The important feature of the proposed diagram is that the minimum of the CTS lies at a different position in the configurational coordinate at a relatively low energy. As a result, crossovers from CTS to the Tm^{3+} terms of $^1\text{G}_4$, $^3\text{F}_4$ and $^3\text{H}_6$ symmetry are possible, the dominant crossover being determined by the temperature.

Now, the observed features of the B and IR emissions can be explained as follows.

- 1) Due to the absorption of radiation with the energy of 3.1 eV, the Tm^{3+} center captures an electron from the ligands and becomes Tm^{2+} (CTS).
- 2) Once in an excited state, the center will relax towards the equilibrium state (of the excited term) by dissipating heat. Since the intersection point A of the two potential curves representing the CTS and $^1\text{G}_4$ states lies below the vibrational level reached after excitation, the center nonradiatively relaxes to the minimum of the $^1\text{G}_4$ state, which then radiatively relaxes to the ground state, giving rise to the B emission.

- 3) As we increase the temperature, electrons on the CTS level occupy higher vibrational states, represented in Fig. 4 by horizontal lines. At a high enough temperature, electrons are thermally excited up to the B intersection and then nonradiatively relax to the minimum of the $^3\text{F}_4$ state. The subsequent radiative relaxation of these electrons to the ground state gives rise to the IR emission. Hence, the activation energy E_{a1} for quenching of the B emission and the activation energy E_{a1}^- for strengthening of the IR emission take the same value ($E_a=100$ meV) which represents the potential barrier between the minimum of the $^1\text{G}_4$ and the B intersection point of the CTS and the $^3\text{F}_4$ states.

- 4) As the temperature is further increased, electrons in the CTS are thermally excited up to the C intersection ($E_{a2}=300\pm 20$ meV) of the CTS and $^3\text{H}_6$ ground state, and nonradiatively relax to the ground term, causing the observed quenching of the IR emission at high temperatures.

4. Conclusions

The PL spectrum of Tm-doped CuAlS_2 showed two Tm^{3+} -related emission lines: one at 1.55 eV and the other at 2.60 eV, the former dominating the spectrum at room temperature, and the latter gaining intensity at low temperatures. These emission lines have been assigned to transitions from the excited states $^3\text{F}_4$ and $^1\text{G}_4$ to the $^3\text{H}_6$ ground state of the Tm^{3+} ion, respectively. Both lines share the same excitation band peaking at 3.1 eV, which is attributed to the $\text{Tm}^{3+}\rightarrow\text{Tm}^{2+}$ charge transfer transitions. The temperature dependence of the intensities of B and IR emissions have been interpreted taking into account the crossover between $4f^{12}$ terms and the CTS states in the configurational-coordinate diagram.

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- 1) T. Suyama, N. Sawara, K. Okamoto and Y. Hamakawa: *Proc. 13th Int. Conf. Solid State Devices, Tokyo, 1981*, Jpn. J. Appl. Phys. **21** (1982) Suppl. 21-1, p. 383.
- 2) S. Shirakata, I. Aksenov, K. Sato and S. Isomura: Jpn. J. Appl. Phys. **31** (1992) L1071.
- 3) Y. Kudo, N. Kojima, Y. Takada, I. Aksenov and K. Sato: Jpn. J. Appl. Phys. **31** (1992) L663.
- 4) I. Aksenov, Y. Kudo and K. Sato: Jpn. J. Appl. Phys. **31** (1992) L1009.
- 5) S. Kobayashi: *Oyo Buturi* **62** (1993) 120 [in Japanese].
- 6) W. W. Anderson, S. Razi and D. J. Walsh: *J. Chem. Phys.* **4** (1965) 1153.
- 7) *Rikagaku Jiten* (Iwanami's Dictionary of Physics and Chemistry) (Iwanami, Tokyo, 1987) 4th ed., p. 814, p. 50 [in Japanese].
- 8) G. H. Dieke and H. M. Crosswhite: *Appl. Opt.* **2** (1963) 675.
- 9) W. Low: *Paramagnetic Resonance in Solids* (Academic Press, New York, London, 1960) Solid State Physics, Suppl. 2, p. 34.