

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/260557209>

# Single Crystals of $\text{CuAlS}_2$ Doped with Rare-Earth Ions

Article in *Japanese Journal of Applied Physics* · January 1993

DOI: 10.7567/JJAPS.32S3.608

---

CITATION

1

READS

13

3 authors, including:



**Katsuaki Sato**

Tokyo University of Agriculture and Technology

287 PUBLICATIONS 3,557 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Materials and Processes for Next Generation Innovative Devices [View project](#)



Grant-in-Aid for Scientific Research from MEXT (Category No. 08455009) "Characterization of Interfaces in Artificial Superlattice by Means of Nonlinear Magneto-Optical Effect" [View project](#)

## Single Crystals of $\text{CuAlS}_2$ Doped with Rare-Earth Ions

Tsuyoshi OHGOH, Yuki KUDO\*<sup>1</sup> and Katsuaki SATO\*<sup>2</sup>

Faculty of Technology, Tokyo University of Agriculture  
and Technology, Koganei, Tokyo 184, Japan

(Received June 3, 1993)

Photoluminescence spectra have been studied in  $\text{CuAlS}_2$  single crystals doped with a series of rare-earth ions grown by the chemical vapor transport technique. Several sharp emissions originated from electronic transitions between the L-S coupling terms of 4f-shell originated multiplets have been observed for  $\text{Tb}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  ions in  $\text{CuAlS}_2$  host, whereas the spectra of Ce- and Sm-doped crystals showed no significant difference from the undoped crystals.

**KEYWORDS:**  $\text{CuAlS}_2$  ternary semiconductor, rare-earth ions, f-f transition, photoluminescence spectrum

The chalcopyrite type semiconductor  $\text{CuAlS}_2$  has a direct energy gap  $E_g = 3.55$  eV,<sup>1)</sup> wide enough to accommodate visible emitting centers such as transition metal ions and rare-earth ions. A typical photoluminescence (PL) spectrum of undoped  $\text{CuAlS}_2$  under the excitation by the 365 nm line ( $3.40$  eV  $< E_g$ ) of a superhigh-pressure Hg-lamp usually shows orange luminescence peaked at 1.9 eV. On the other hand, under the excitation by the 325 nm ( $3.81$  eV  $> E_g$ ) of He-Cd laser, it exhibits the same orange emission, as well as a purple emission peaked at 3.0 eV at low temperatures, those emissions being attributed to the radiative donor-acceptor (D-A) pair recombination.<sup>2)</sup> In this paper, we report the studies of PL properties of the  $\text{CuAlS}_2$  single crystals doped with rare-earth ions.

The single crystals were grown by the iodine chemical vapor transport method from the constituent elements with appropriate amount ( $\sim 5.0$  mol%) of rare-earth elements which were supposed to occupy the Al-site. However, the analyzed concentration of the rare-earth, in the case of Tb-doping was found to be less than 0.05 mol%, instead of the starting molar ratio of 4.5 mol%. Similar situation occurred in the case of the Tm-doped crystal, in which EPMA analysis revealed that the Tm concentration incorporated into the crystal was only 0.25 mol%. Thus the same situation is expected for other rare-earth dopants.

The starting materials were sealed in evacuated (about  $10^{-6}$  Torr) silica ampoule (13 mm inner in diameter and 200 mm in length) with  $10$  mg/cm<sup>3</sup> of iodine. The ampoule was placed in a two-zone furnace, the transport being carried out for seven days with the temperature of source-zone being  $900^\circ\text{C}$  and that of the growth-zone being  $750^\circ\text{C}$ . The resulting crystals had a well-developed {112} plane of the chalcopyrite structure. The size of the crystal is apparently dependent on ionic radius of rare-earth ions. The size of the crystals doped with rare-earth having smaller ionic radii (e.g. Ho or Tm) were smaller than those doped with larger size ions (e.g. Ce or Sm). Smaller radius ions seems to be more easily incorporated

into the crystals than larger rare-earths. This occurs the crystallinity becomes inferior to undoped crystals, because of the large ionic radii of the incorporated rare-earth ions compared with that of the Al in the chalcopyrite structure. On the other hand, the larger rare-earths can scarcely be involved into the lattice, thus resulting in relatively good crystallinity and larger size of crystals.

The obtained Tb-doped  $\text{CuAlS}_2$  crystals were colorless, although undoped  $\text{CuAlS}_2$  crystals are usually dark blue or green in color. The Tb-doped crystals showed a bright yellow emission at room temperature under the Hg-lamp excitation. A typical PL spectrum, shown in Fig. 1, consists of a yellow broad emission band peaked at about 2.0 eV, and sharp emission lines at 2.278 eV and 2.532 eV.<sup>3)</sup> The sharp emission lines have been assigned to the multiplet transitions from the common excited state  $^5\text{D}_4$  to the ground states  $^7\text{F}_5$  and  $^7\text{F}_6$ , respectively. Another sharp line at 2.262 eV is located on the low-energy side of the 2.278 eV-line at an energy separation of about  $200$  cm<sup>-1</sup> and may be assigned to a phonon replica of the 2.278 eV-line, since the phonon energy of  $216$  cm<sup>-1</sup> has been reported for  $\text{CuAlS}_2$ .<sup>4)</sup> As for the broad emission band around 2.0 eV, the time-resolved measurements showed that the peak position of the yellow band shifted towards lower energies with time, indicating that this band results from the D-A pair recombination. A

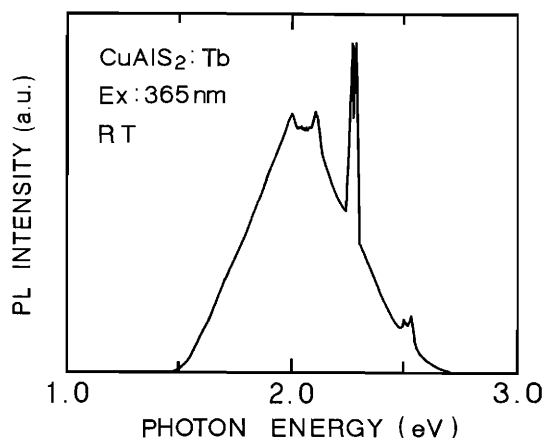


Fig. 1. PL spectrum of Tb-doped  $\text{CuAlS}_2$ .

\*<sup>1</sup>Present address: R & D center, Toshiba Corporation, Kawasaki, Kanagawa 211, Japan.

\*<sup>2</sup>To whom reprint requests should be addressed.

PL-excitation (PLE) spectrum for the sharp line at 2.278 eV shows only a broad peak at about 3.43 eV which is just below the absorption edge of CuAlS<sub>2</sub> host. No excitation was observed at 3.26 eV which is supposed to be the energy position of the excited state <sup>5</sup>D<sub>3</sub> of the Tb<sup>3+</sup> ion. Therefore, we may consider that the observed Tb-related luminescence is not caused by the direct excitation of Tb<sup>3+</sup> center but by the energy transfer from the electronic states related to the host material.

The Tm-doped CuAlS<sub>2</sub> crystals were blue in color. As shown in Fig. 2, the PL spectrum under the 365 nm line excitation consists of a broad emission band at 1.8 eV and two sharp emission lines peaked at 1.55 eV (infrared) and 2.60 eV (blue), originated from transitions between the L-S coupling terms of Tm<sup>3+</sup> ion.<sup>5)</sup> Both emission lines show fine structures consisting of several sharp lines with the half-width of about 15 cm<sup>-1</sup>. They have been attributed to the crystal field splitting of the L-S coupling terms of Tm<sup>3+</sup> involved in the emission process. From group theory it is known that in a tetrahedral crystal field the <sup>3</sup>H<sub>6</sub> ground term and the excited terms of <sup>3</sup>F<sub>4</sub> and <sup>1</sup>G<sub>4</sub> 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 CuAlS<sub>2</sub> host lattice. The spectral features of the sharp emissions were found to be strongly dependent on the temperature, the blue emission being strengthened and, to the contrary, the infrared emission being quenched with the decrease in the temperature. Since PLE spectra for the Tm<sup>3+</sup>-related two sharp emissions share the same excitation band with a peak at 3.1 eV, it is evident that they are originating from the same center. Taking into account the spectral position of the Tm<sup>3+</sup>-related blue and infrared emission lines, as well as that of the band of the excitation spectra, we assigned the blue and infrared emissions to <sup>1</sup>G<sub>4</sub>→<sup>3</sup>H<sub>6</sub> and <sup>3</sup>F<sub>4</sub>→<sup>3</sup>H<sub>6</sub> transitions in the 4f<sup>12</sup> manifold of Tm<sup>3+</sup> ion, respectively. However, since no levels corresponding to the energy separation of 3.1 eV from the ground state can be found in the Dieke diagram<sup>6)</sup> for Tm<sup>3+</sup> ion, the origin of the 3.1 eV absorption peak should be searched in the other valence states of Tm ion such as a charge transfer state.

A typical PL spectrum from a Ho doped CuAlS<sub>2</sub> is shown in Fig. 3. The spectrum consists of an orange band and two sharp lines at 1.89 eV and 2.25 eV. Such sharp emission lines were observed in electroluminescence (EL) of Ho-doped ZnS<sup>7)</sup> and were assigned to the f-f transitions in Ho<sup>3+</sup>. The sharp emission lines may be assigned to <sup>5</sup>F<sub>3</sub>→<sup>5</sup>I<sub>7</sub> and <sup>5</sup>S<sub>2</sub>→<sup>5</sup>I<sub>8</sub> transition in the 4f<sup>10</sup> manifold of Ho<sup>3+</sup>, respectively.

We have also made an attempt to dope CuAlS<sub>2</sub> with Ce and Sm rare-earth ions, but we could not observe any emissions which can be directly related to rare-earth ions under excitation by either 365 nm or 325 nm wavelengths. The Ce- and Sm-doped crystals have been found to exhibit only the host related purple emission at 3.0 eV under the He-Cd laser excitation, the intensity of this emission, however, being much higher as compared

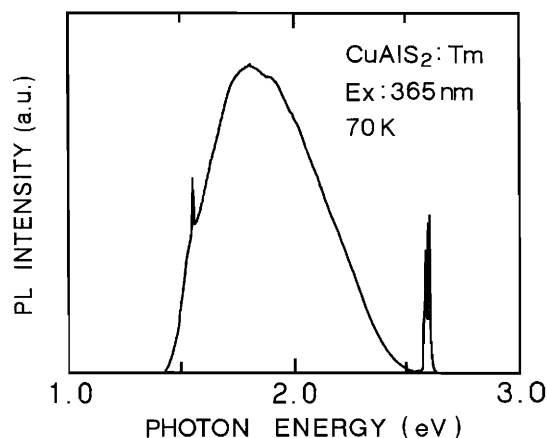


Fig. 2. PL spectrum of Tm-doped CuAlS<sub>2</sub>.

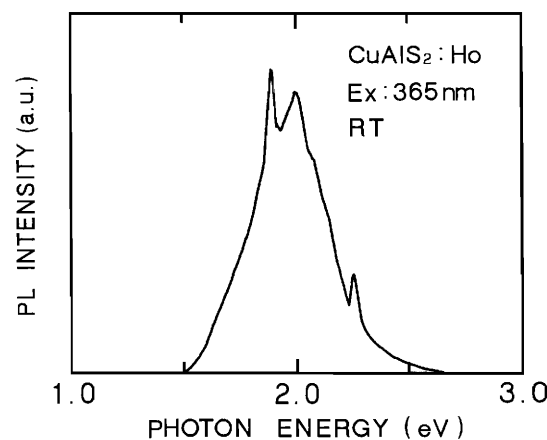


Fig. 3. PL spectrum of Ho-doped CuAlS<sub>2</sub>.

with the undoped crystals. The last result have been tentatively explained by the decrease in the concentration of lattice defects, involved in quenching mechanism of the purple emission, due to the substitution of these defects by the rare-earths.

In conclusion, we have shown that the CuAlS<sub>2</sub> crystals doped with Tb, Tm and Ho rare-earth elements exhibit several sharp emission lines in the visible spectral region originated from the internal f-f transitions, whereas those doped with Ce and Sm ions in CuAlS<sub>2</sub> have not exhibited any characteristic sharp emissions.

## References

- 1) S. Shirakata, I. Aksenov, K. Sato and S. Isomura: Jpn. J. Appl. Phys. **31** (1992) L1071.
- 2) N. Yamamoto: Jpn. J. Appl. Phys **19** (1980) 95.
- 3) Y. Kudo, N. Kojima, Y. Takada, I. Aksenov and K. Sato: Jpn. J. Appl. Phys. **31** (1992) L663.
- 4) W. H. Koschel and M. Bettini: Phys. Status Solidi b **72** (1975) 729.
- 5) T. Ohgoh, I. Aksenov, K. Kudo and K. Sato: Jpn. J. Appl. Phys. (submitted).
- 6) G. H. Dieke and H. M. Crosswhite: Appl. Opt. **2** (1963) 675.
- 7) E. W. Chase, R. T. Hepplewhite, D. C. Krupka and D. Kahng: J. Appl. Phys. **40** (1969) 2512.