

Photoluminescence in Tb-Doped CuAlS₂ Single Crystals

Yuki KUDO, Nobuaki KOJIMA*, Yasushi TAKADA,
Igor AKSENOV** and Katsuaki SATO***

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

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Single crystals of CuAlS₂ doped with Tb were prepared by the iodine vapor transport technique. These crystals showed bright yellow photoluminescence at room temperature when excited by the 365 nm line of a Hg lamp. The photoluminescence spectrum consists of a yellow broad band at 2.0 eV and sharp emission lines at 2.278 eV and 2.532 eV which are tentatively assigned to Tb³⁺ ion.

KEYWORDS: Tb-doped CuAlS₂, chalcopyrite-type semiconductor, photoluminescence, f-f transition

§1. Introduction

The CuAlS₂ ternary compound is one of the I-III-VI₂-type chalcopyrite semiconductors and is considered to be a possible candidate for visible light emitting device application since it has a sufficiently wide direct gap of 3.49 eV at room temperature and emits strong purple luminescence.¹⁾ However, only a few studies have been carried out on using this material as a host for luminescence materials. It is known that Mn impurity causes a red photoluminescence (PL) in CuAlS₂ single crystals,^{2,3)} this red PL being assigned to ligand-field transition from the lowest excited state ⁴T₁ to ground state ⁶A₁ in the 3d⁵ manifold of the Mn²⁺ ion just like the orange luminescence in ZnS:Mn. Mn-doped CuAlS₂ also showed red electroluminescence (EL), the spectrum being identical to that of PL.⁴⁾ These results suggest the possibility of realizing visible EL devices by using the CuAlS₂ compound doped with appropriate elements, such as rare earth atoms, as emission centers.

In this investigation, we prepared CuAlS₂ single crystals doped with Tb. This element was expected to show green light emission and has been known as the brightest EL center of all the rare earth elements in ZnS.⁵⁾

§2. Experimental

Tb-doped CuAlS₂ single crystals were prepared by iodine chemical vapor transport. The starting materials were CuS powder prepared by sintering appropriate amounts of Cu and S, as well as the elements of Al, S, and Tb. The molar ratio of constituent elements in the starting materials was as follows. Cu:Al:Tb:S = 1:0.955:0.045:2. These materials were sealed in vacuo in a fused silica ampoule with an inner diameter of 13 mm and length of 200 mm together with iodine, the concentration of iodine being 10 mg/cm³ of the inner volume of the ampoule. Chemical transport was carried out for seven days in a two-zone furnace, the temperature of the

source-zone being 900°C and that of the growth-zone being 750°C. The crystals obtained had a well-developed {112} plane and a typical size of 3 × 1 × 0.3 mm³. Incorporation of the Tb ions in crystals obtained was confirmed by electron spin resonance (ESR) measurements. Details will be published elsewhere.^{****} In this report the crystals are referred to as CuAl_{0.955}Tb_{0.045}S₂, although the value is only nominal since no chemical analyses were performed.

The optical absorption spectrum was measured at room temperature using a Hitachi U-3410 spectrophotometer in polished crystals having the thickness of about 200 μm. For PL measurements, the 365 nm-line of a superhigh-pressure Hg-lamp was used as an excitation source. The emitted light was dispersed by a JASCO CT-50C monochromator (focal length of 50 cm) with a 1200 groove/mm grating blazed at 500 nm, and detected by a Hamamatsu R928 photomultiplier. For PL-excitation (PLE) spectrum measurements, a 150 W Xe-lamp combined with a Ritsu MC-10N monochromator was used as an excitation source. The emitted light was again dispersed by the JASCO CT-25C (focal length of 25 cm) with a 1200 grooves/mm grating blazed at 750 nm. Obtained PLE spectra were not corrected for the spectral distribution of the light source and the monochromator used.

§3. Results and Discussion

The Tb-doped CuAlS₂ crystals obtained were colorless, although undoped CuAlS₂ crystals prepared by iodine vapor transport are usually dark blue or green in color. Optical absorption spectra of the undoped and Tb-doped CuAlS₂ single crystals are shown in Fig. 1. It can be seen that two absorption peaks at 1.3 eV and 1.9 eV observed in undoped CuAlS₂ disappear in Tb-doped CuAlS₂. These two peaks have been attributed to the charge transfer transitions related to Fe³⁺ on the Al-site.^{2,6)} The observed elimination of Fe³⁺-related absorption bands in Tb-doped crystals indicates that the valency of the Fe ion, substituting the Al-site, has been reduced

*Present address: Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152.

**On leave from Institute of Physics of Solids and Semiconductors, Academy of Sciences of Belarus, Minsk.

***To whom reprint requests should be addressed.

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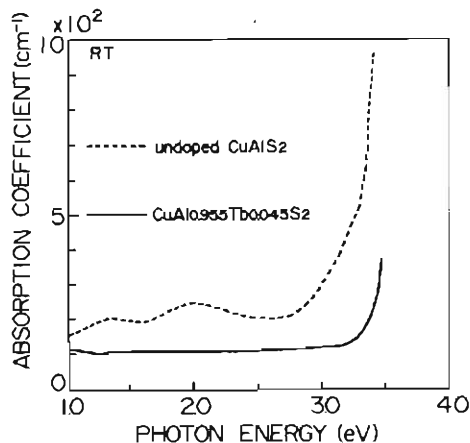


Fig. 1. Optical absorption spectra in undoped and Tb-doped CuAlS₂ single crystals measured at room temperature.

from Fe³⁺ to Fe²⁺ by Tb-doping. Such a reduction of the Fe-ion valency would not have occurred if Tb³⁺ had occupied the Al³⁺-site, since no changes in valency occur in such a case. This leads to the conclusion that the Tb³⁺ ion substitutes the Cu-site, contrary to our initial idea that Tb might occupy the Al-site. Then the charge-neutrality condition would require the introduction of some defects such as the copper vacancy V_{Cu}, or the antisite defect Cu_{Al}. Such defect chemistry is the subject of a future study.

The Tb-doped crystals showed a bright yellow emission at room temperature when excited by the 365-nm-line of the Hg-lamp. A typical PL spectrum from a Tb-doped CuAlS₂ is shown in Fig. 2(a). The spectrum

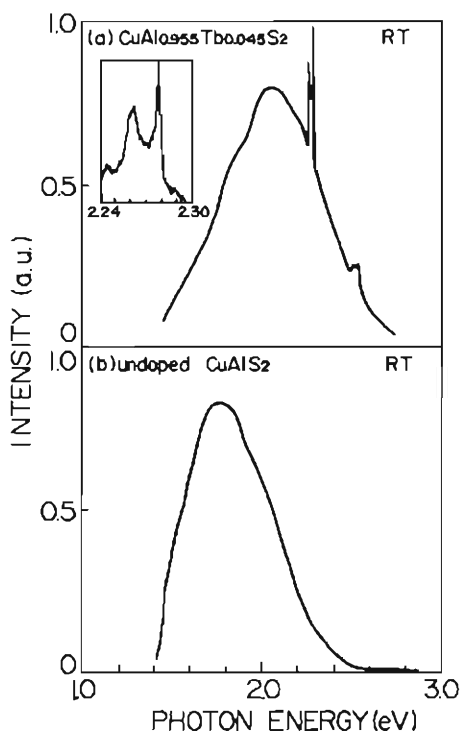


Fig. 2. Photoluminescence spectra of (a) Tb-doped and (b) undoped single crystals of CuAlS₂ measured at room temperature. In the inset of (a), detailed spectrum between 2.24 and 2.3 eV is also shown.

consists of a yellow broad band at about 2.0 eV, and sharp emission lines at 2.278 eV and 2.532 eV. In the inset of Fig. 2 the detailed spectrum between 2.24 and 2.30 eV is illustrated. Such sharp emission lines were observed in Tb-doped ZnS crystals⁷⁾ and were assigned to the f-f transitions in the Tb³⁺ ion. Since the energy positions of the observed lines are identical to those reported on ZnS:Tb, we interpret these sharp lines as originating from the multiplet transitions in the 4f⁸ manifold of the Tb³⁺ ion. The sharp emission lines may be assigned to the transitions from the common excited state ⁵D₄ to the ground states ⁷F₅ and ⁷F₆, respectively, as illustrated in Fig. 3.⁸⁾ As shown in the inset of Fig. 2, another sharp line was observed at 2.262 eV. This line is located on the low-energy side of the 2.278 eV-line at an energy separation of about 200 cm⁻¹ and may be assigned to a phonon replica of the 2.278 eV-line, since the phonon energy of 216 cm⁻¹ has been reported for CuAlS₂.⁹⁾

Next we discuss the broad PL band around 2.0 eV. For comparison, a typical PL spectrum of undoped CuAlS₂ is shown in Fig. 2(b). The undoped CuAlS₂ usually shows orange luminescence with a peak at 1.8 eV, which has been tentatively assigned to deep donor levels¹⁰⁾ or Fe impurities.²⁾

Our time-resolved measurements showed that the peak position of the orange band in undoped CuAlS₂ shifted towards lower energies with time, indicating that this band results from the donor-acceptor (D-A) pair recombination.¹¹⁾ The same low-energy shift was observed for Tb-doped crystals, suggesting that this emission is also due to the D-A-type recombination. The difference in the peak energy of the broad band between undoped and Tb-doped CuAlS₂ crystals may be explained under the assumption that the different donor species are involved in the D-A pairs forming the broad band. Lowering of the temperature down to 77 K strengthens the broad emission band, the peak energy position of this band being shifted towards lower energies. However, no significant change in the intensities of Tb-originated lines has been observed.

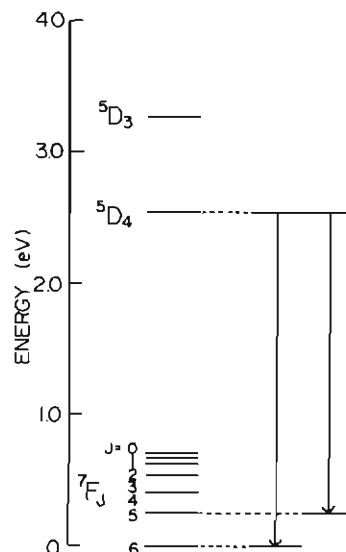


Fig. 3. Schematic energy level diagram of Tb³⁺ ion.

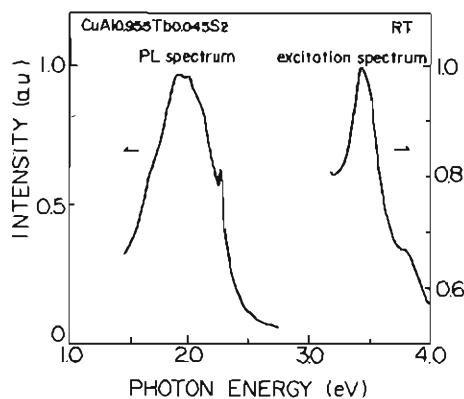


Fig. 4. Photoluminescence excitation (PLE) spectrum of 2.278 eV emission at room temperature. Photoluminescence spectrum measured with excitation energy of 3.43 eV (PLE peak) is also shown.

A PLE spectrum for the sharp line at 2.278 eV is shown in Fig. 4, together with the PL spectrum taken with the excitation energy fixed at the energy of the peak of the PLE spectrum (3.43 eV). The PLE spectrum shows only a broad peak at about 3.43 eV which is just below the absorption edge shown in Fig. 1. The PL spectrum shown in Fig. 4 is quite similar to that shown in Fig. 2(a) which was taken under Hg-lamp 365-nm-line excitation. No excitation was observed at 3.26 eV which is supposed to be the energy position of the excited state 5D_3 of the Tb^{3+} ion. Therefore, we may consider that the observed Tb-related luminescence is not caused by the direct excitation of the Tb^{3+} center but by the energy transfer from the electronic states related to the host material.

§4. Conclusions

$CuAlS_2$ crystals doped with Tb emit bright yellow luminescence at room temperature. The emission spec-

trum has been found to consist of a broad band centered at about 2.0 eV and sharp Tb-related lines at 2.278 eV and 2.532 eV superposed on the higher-energy edge of the broad band. An energy transfer mechanism between the host lattice and the Tb-ion orbitals for excitation of the Tb-related photoluminescence has been proposed, taking into account the observed PLE spectrum. Detailed studies are planned to obtain further information on the electronic structure of Tb-introduced energy levels in $CuAlS_2$.

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References

- 1) N. Yamamoto: *Proc. 4th Int. Conf. Ternary and Multinary Compounds, Tokyo, 1980*, Jpn. J. Appl. Phys. **19** (1980) Suppl. 19-3, p. 95.
- 2) P. C. Donohue, J. D. Bierlein, J. E. Hanlon and H. S. Jarrett: *J. Electrochem. Soc.* **121** (1974) 829.
- 3) K. Sato, S. Okamoto, M. Morita, A. Morita, T. Kambara and H. Takenoshita: *Prog. Cryst. Growth & Char.* **10** (1984) 311.
- 4) K. Sato, K. Ishii, S. Matsuda and S. Mizukawa: *Electroluminescence*, eds. S. Shionoya and H. Kobayashi (Springer, Berlin, 1989) p. 390.
- 5) T. Suyama, N. Sawara, K. Okamoto and Y. Hamakawa: *Proc. 13th Conf. Solid State Devices, Tokyo, 1981*, Jpn. J. Appl. Phys. **21** (1981) Suppl. 21-1, p. 383.
- 6) T. Teranishi, K. Sato and K. Kondo: *J. Phys. Soc. Jpn.* **36** (1974) 1618.
- 7) W. W. Anderson: *Phys. Rev.* **136** (1964) A556.
- 8) S. Kuboniwa and T. Hoshina: *J. Phys. Soc. Jpn.* **32** (1972) 1059.
- 9) W. H. Koschel and M. Bettini: *Phys. Status Solidi (b)* **72** (1975) 729.
- 10) N. Yamamoto: *Jpn. J. Appl. Phys.* **15** (1976) 1909.
- 11) K. Sato, K. Ishii, K. Watanabe and K. Ohe: *Jpn. J. Appl. Phys.* **30** (1991) 307.