Cryst. Res. Technol.	31	1996	S	713–716

K. SATO, Y. KIMURA, K. SHIMIZU*, T. OHGOH**
and Y. KUDO***

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

PHOTOLUMINESCENCE SPECTRA IN SINGLE CRYSTALS OF $CuAlS_2$ DOPED WITH RARE-EARTH ELEMENTS

Photoluminescence (PL) studies in single crystals of $CuAlS_2$ doped with a series of rare-earth (RE) elements have been studied. Heavy RE ions were successfully incorporated showing PL spectra characteristic of f-f transitions of trivalent RE ions.

1. INTRODUCTION

Among the series of ternary chalcopyrite type materials, $CuAlS_2$ is the only one stable material that has a band gap in the ultraviolet region (E_g=3.49 eV at room temperature). This means that $CuAlS_2$ is capable of being a host material for visible luminescence centers like ZnS whose band gap is 3.68 eV. Indeed $CuAlS_2$: Mn has been known to emit a red emission band either by optical or by electric-field excitation (SATO et al. 1984; SATO et al. 1988, SATO et al. 1991)

We have also carried out researches on the ternary material doped with RE elements aiming at realizing visible phosphors with higher brightness. Contrary to II-VI compounds the charge neutrality condition seems automatically satisfied in $CuAlS_2$ compound, since the I-III-VI_2 compound has a trivalent cation as its constituent element. We therefore performed crystal growth of $CuAlS_2$ doped with a series of RE elements. PL spectra have been measured in crystals obtained, part of the studies having been published elsewhere(KUDO et al.; OHGOH et al. 1993; OHGOH et al. 1994). Here we summarize the results and discuss the overall view on doping of RE ions.

2. EXPERIMENTAL

Single crystals of $CuAlS_2$ doped with a series of RE elements (Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb) have been prepared by chemical transport using iodine as transporting agent. Transparent single crystals with well-developed {112} planes, typical dimension being $2\times2\times1$ mm^3 were obtained. Chemical analysis revealed that the RE composition is no more than 0.25 mol%. PL spectra have been measured in these crystals between 20 K and room temperature (RT).

---

*Present address: Alps Electric Co., Ltd.

**Present address: Fuji Photo Film Co., Ltd., Kaiseimachi, Kanagawa 258, Japan

***Present address: R&D Center, Toshiba Corp., Kawasaki 210, Japan

3. RESULTS AND DISCUSSION

$CuAlS_2$ crystals doped with light RE elements (Ce, Pr, Nd, Sm and Eu) showed a yellow PL band as well as several blue or purple emissions. Both of these emissions have been observed also in undoped crystals and ascribed to so-called self-activated (SA) emission in undoped crystals. No sharp lines due to f-f transitions nor broad emission bands characteristic of d-f transitions were detected. We therefore concluded that these light RE ions could not be incorporated in $CuAlS_2$ crystals.

On the other hand, in crystals doped with heavy RE elements were observed sharp PL lines superposed on the broad yellow band. In Fig. 1 are illustrated PL spectra for wavelengths below 900nm observed in crystals doped with Tb, Dy, Ho, Er and Tm. In Fig. 2 is shown the infrared PL spectrum observed in Yb at 20 K. The PL lines observed in Figs.1 and 2 have been assigned to intracenter f-f transitions as summarized in Table 1.

We will give brief discussion for each RE ion in the order of the filling of 4f-shell.

$Tb^{3+}(4f^8)$

Several lines were observed superposed on the yellow SA band. All the sharp lines have been assigned to f-f transitions from a common excited state $^5D_4$ to several L-S coupling sublevels (J=6, 5, 4, 3) split from the ground multiplet ^5F. The most intensive line at 548 nm is regarded as a phonon-replica of $^5D_4 \rightarrow {}^5F_5$ zero-phonon-line. The excitation spectra for these levels showed a common peak at 380 nm (3.26 eV), which can be assigned to the transition from the lowest ground level to higher excited state $^5D_3$. These Tb-originated luminescence were hardly excited by across-the-gap transition. (KUDO et al.)

$Dy^{3+}(4f^9)$

Only one sharp line was observed in the Dy-doped sample at 580 nm, which can be assigned to the transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$. We failed to measure an excitation spectrum for this line emission due to weakness of the emission intensity.

$Ho^{3+}(4f^{10})$

Several lines superposed on the SA emission were observed in Ho-doped crystals. Lines observed at 656 nm, 635 nm, 620 nm, 590 nm and 551 nm can be assigned to $^5F_3 \rightarrow {}^5I_7$, $^5F_2 \rightarrow {}^5I_7$, $^3K_8 \rightarrow {}^5I_7$, $^5F_1 \rightarrow {}^5I_7$, $^5S_2 \rightarrow {}^5I_8$ intracenter transitions.

$Er^{3+}(4f^{11})$

Three distinct PL structures at 670 nm, 549 nm and 530 nm superposed on the broad SA emission band were observed and were assigned to f-f transitions $^4F_{9/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$. The color of the emission was yellow due to the presence of the strong SA emission. The broad band could be suppressed by doping very small amount of Fe impurity. In this case the emission was pure green in color at room temperature. PLE spectra for these PL lines showed a common peak at 383 nm, which has been assigned to the transition from the ground state $^4I_{15/2}$ to the higher excited state $^4G_{11/2}$.

$Tm^{3+}(4f^{12})$

At room temperature only one line is seen at 800 nm overlapped on the broad SA emission band. As temperature was decreased a blue emission line appeared at 477 nm. These emissions were excited by the broad PLE band at 400 nm, which have been tentatively ascribed to the charge-transfer transition from the ligand p-orbitals to 4f orbitals. (OHGOH et al. 1994)

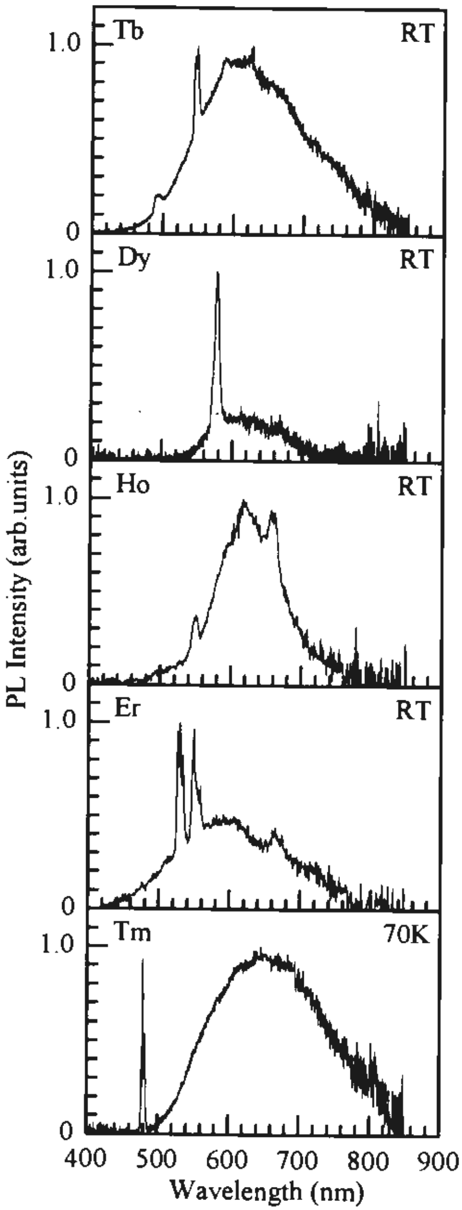

Fig. 1 PL spectra of $CuAlS_2$ single crystals doped with Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} ions.

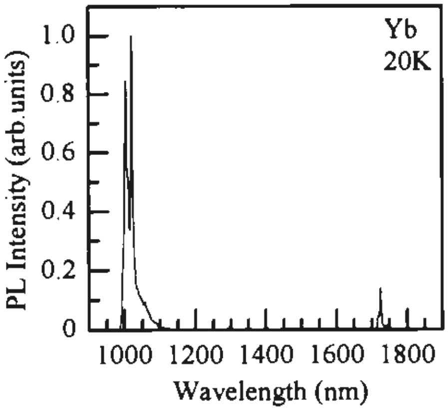

Fig. 2 PL spectra of Yb-doped $CuAlS_2$.

$Yb^{3+}(4f^{13})$

As seen in Fig. 2, Yb-doped sample showed a double-peaked emission, which was attributed to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, the only one f-f transition in Yb^{3+} ion. The fine structure may be origined from the spin-orbit splitting. In Fig. 2, another sharp infrared emission line was found at 1720 nm, which had been assigned to the crystal-field transition $^4T_1 \rightarrow {}^6A_1$ associated with the Fe^{3+} ion substituting the Cu atom (SATO et al.1990).

We tabulate relationship between PL and the ionic radii for RE ions investigated in the present study in Table 2. Ionic radii of RE ions decrease with atomic number, this phenomenon being well known as lantanide contraction. It seems that there is a certain critical radius of RE ios to be incorporated into the $CuAlS_2$ crystal lattice. Since tetrahedral covalent bond radius of Al (1.26 Å) is smaller than Cu(1.35 Å), (PHILLIPS) we believe RE ions prefer to substitute Cu atom, charge neutrality being satisfied either by an introduction of cation vacancy or by a reduction in valency of impurity Fe ion at Al site from trivalent to divalent. Thus critical size may be determined by the covalent radius of Cu.

Table 1 Photoluminescence in RE-doped $CuAlS_2$

Rare Earth	Emission line position		Assignments	PLE peak(eV) Assignment
	Energy(eV)	Wavelength(nm)		
Tb^{3+}	1.99	621	$^5D_4 \rightarrow {}^7F_3$	3.26 $^7F_6 \rightarrow {}^5D_3$
	2.11	587	$^5D_4 \rightarrow {}^7F_4$	
	2.262	548	$^5D_4 \rightarrow {}^7F_5$(Phonon replica)	
	2.278	544	$^5D_4 \rightarrow {}^7F_5$	
	2.532	490	$^5D_4 \rightarrow {}^7F_6$	
Dy^{3+}	2.14	580	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	
Ho^{3+}	1.89	656	$^5F_3 \rightarrow {}^5I_7$	
	1.95	635	$^5F_2 \rightarrow {}^5I_7$	
	2.00	620	$^3K_8 \rightarrow {}^5I_7$	
	2.10	590	$^5F_1 \rightarrow {}^5I_7$	
	2.25	551	$^5S_2 \rightarrow {}^5I_8$	
Er^{3+}	1.85	670	$^4F_{9/2} \rightarrow {}^4I_{15/2}$	3.24 $^4I_{15/2} \rightarrow {}^4G_{11/2}$
	2.26	549	$^4S_{3/2} \rightarrow {}^4I_{15/2}$	
	2.34	530	$^2H_{11/2} \rightarrow {}^4I_{15/2}$	
Tm^{3+}	1.55	800 (RT)	$^3F_4 \rightarrow {}^3H_6$	3.10 Charge Transfer State
	2.60	477 (70K)	$^1G_4 \rightarrow {}^3H_6$	
Yb^{3+}	1.21	1025	$^2F_{5/2} \rightarrow {}^2F_{7/2}$	
	1.23	1008		

Table 2 Observation / nonobservation of PL in RE-doped $CuAlS_2$

RE ions	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
n iin $4f^n$	1	2	3	4	5	6	7	8	9	10	11	12	13
Ionic radii (Å)	1.15	1.13	1.123	1.11	1.098	1.087	1.15	1.063	1.052	1.041	1.033	1.020	1.008
Emission	No	No	No	—	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes

4. CONCLUSIONS

Single crystals of $CuAlS_2$ doped with a series of RE elements were investigated. It is found light RE elements were difficult to be accommodated in the crystal, while heavy RE elements could be successfully incorporated leading to PL emissions characteristic of f-f transitions in the RE ions.

References

KUDO, Y., KOJIMA, A., TAKADA, Y. and SATO, K.: Jpn. J. Appl. Phys. **31** Part 2 [6A] (1992) L663.

OHGOH, T., KUDO, Y. and SATO, K.: *Proc. 9th Int. Conf. Ternary & Multinary Compounds*, Jpn. J. Appl. Phys. **32** (1993) Suppl. 32-3, pp. 608.

OHGOH. T., AKSENOV, I., KUDO, Y. and SATO, K.: Jpn. J. Appl. Phys. **33** (1994) 962.

PHILLIPS, J.C.: *Valence Theory of Semiconductors* (Academic Press, New York, 1973)

SATO, K., MORITA, M., OKAMOTO, S., MORITA, S., KAMBARA, T., GONDAIRA, K.I. and TAKENOSHITA, H.: *Proc. 6th Int. Conf. Ternary and Multinary Compounds, Caracas, 1984*, Prog. Cryst. Growth & Charact. **10** (1984) 311.

SATO, K., ISHII, K. and TANAKA, K.: *Proc. Int. Workshop on Electroluminescence, Tottori, 1988*, pp.390.

SATO, K., TANAKA, K.,ISHII, K. and MATSUDA, S.: J. Cryst. Growth 99 (1990) 772.

SATO, K., ISHII, K., WATANABE, K. and OHE, K.: Jpn. J. Appl. Phys. **30** [2] (1991) 307.