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## Near-Infrared Photoluminescence in Mo-Doped Single Crystals of $\text{CuAlS}_2$

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Near-infrared photoluminescence (PL) spectra were measured at 6 K in single crystals of  $\text{CuAlS}_2$  doped with different amounts of Mo. A fine-structure PL emission was observed around 1,600 nm (0.775 eV) in both lightly and heavily doped crystals. The emission was tentatively assigned to the ligand-field transition in  $4d^3$ -manifold of  $\text{Mo}^{3+}$  ions taking into account the reported PL spectrum in  $\text{Nb}^{2+}$  ( $4d^3$ )-doped GaAs. On the other hand, a broad emission band around 1,500 nm (0.826 eV) was only observed in heavily-doped crystals and was tentatively assigned to an intra-center transition of the  $\text{Mo}^{2+}$ -X complex.

KEYWORDS: molybdenum-doped copper aluminum disulfide, chalcopyrite type crystal, photoluminescence spectrum, ligand-field transition

Molybdenum is a metallic species commonly used as a back-electrode material for solar cells based on chalcopyrite-type compounds, such as  $\text{CuInSe}_2$ . Recent investigations have revealed that Mo forms  $\text{MoSe}_2$  during the formation process of chalcopyrite-type compounds.<sup>1)</sup> This finding suggests the possibility of incorporation of Mo metal in the semiconductor. No investigations have been reported to date on the optical properties and electronic structures of any 4d transition atoms in chalcopyrite-type semiconductors, although the optical spectra of Mo and other 4d-series transition atoms in III–V semiconductors are available.<sup>2,3)</sup> On the other hand, for 3d transition elements in chalcopyrite materials, there is a considerable compilation of optical and ESR data available.<sup>4)</sup> This situation prompted us to investigate the 4d-series elements in chalcopyrites. To start with, we selected  $\text{CuAlS}_2$  as the host compound, since it has the widest band gap among members of the chalcopyrite series, a band gap which is wide enough to accommodate any emission lines in the visible-to-infrared wavelength region.

Single crystals of  $\text{CuAlS}_2$  doped with 0.5 or 1 wt% Mo were grown by the chemical vapor transport technique using iodine as a transporting agent. The starting materials were the constituent elements at the appropriate molar ratios. In this paper, Mo concentration is expressed as a weight percentage of the total amount of starting materials. The transport was carried out for ten days with the temperature at the source zone being controlled at 900°C and that at the growth zone at 700°C. The resultant crystals were green and transparent similar to undoped crystals. By secondary ion mass spectroscopic (SIMS) measurements, incorporation of Mo was confirmed, although it could not be estimated quantitatively. The measurement of photoluminescence (PL) was performed for the wavelength region of 350–1800 nm (0.69–3.54 eV) using an Ar-ion laser (514.5 nm, 100 mW), a JASCO CT-25C monochromator and a Northcoast EO-817L liquid nitrogen-cooled Ge detector. All the data were corrected for the spectral response of the system.

Figure 1 shows the PL spectra between 400 and 900 nm measured at 20 K in single crystals of Mo-doped, Mo- and Mn-doped and Mo- and Ni-doped  $\text{CuAlS}_2$ . The nominal concentration of Mo, Mn and Ni in the starting material was 0.5 wt%. An emission band around 400 nm (3.1 eV) was commonly observed in all the Mo-doped crystals studied. For the longer wavelength region, a different structure was ob-

served: for Mo- and Mn-doped samples, a d-d transition due to  $\text{Mn}^{2+}$  (ref. 5) was observed, while for other samples the so-called SA emission bands which are often observed in undoped  $\text{CuAlS}_2$  were observed.<sup>6)</sup> The 400-nm PL band has been observed in undoped  $\text{CuAlS}_2$  and assigned to the D-A pair emission.<sup>5,7)</sup> although appearance of the emission peak is sporadic. The D-A pair emission is also observed when a rare earth element is added to the crystals. Therefore, it is thought that the emission is due to some defects (e.g., anti-site defect or vacancy) caused by the addition of ions of a larger size. Thus no Mo-related emissions could be observed in this wavelength region.

Figure 2(a) shows an infrared (IR) PL spectrum of  $\text{CuAlS}_2$  doped with 0.5 wt% Mo at 6 K. A fine-structure emission line was observed around 1600 nm (0.78 eV) in addition to a sharp strong emission line at 1724 nm (0.72 eV), the latter having been assigned to the ligand-field transition of  $\text{Fe}^{3+}$  as assigned by one of the authors (K.S.), previously.<sup>8)</sup> The fine-structure emission line is thought to be peculiar to the molybdenum ion, since no corresponding emission has been observed in  $\text{CuAlS}_2$  crystals undoped or doped with other 3d transition atoms. The small line-width of the emission indicates that the transition is of the intra-center type. Temperature-dependent PL measurements revealed the existence of thermal quenching above 60 K, whose activation energy was estimated to be about 4 meV.

A similar fine-structure emission line in the photoluminescence spectrum with a peak at 1557 nm (0.796 eV) was reported for  $\text{Nb}^{2+}$  doped in GaAs and was assigned to  $^2T_1 \rightarrow ^4T_1$  transition of  $4d^3$ .<sup>3)</sup> Since molybdenum is adjacent to niobium on the periodic table,  $\text{Nb}^{2+}$  and  $\text{Mo}^{3+}$  share the same electron configuration of  $4d^3$ . The sharpness of the fine structure indicates that the transition is subjected to a weak electron-phonon interaction and should be assigned to spin-forbidden transitions. We therefore assigned the emission to  $^2T_1 \rightarrow ^4T_1$  in  $4d^3$  manifold of  $\text{Mo}^{3+}$ . In addition, our recent ESR investigation at 2 K in the same crystal as used in the PL experiment shows evidence of the existence of a  $d^3$  center, since three nearly isotropic resonance lines were observed around  $g \approx 2$ , which exhibited temperature dependence with the same activation energy of 4 meV as the PL emission. Details of the ESR results will be published elsewhere.

The fine structure of the emission can be assigned to zero-phonon lines and phonon replicas as shown in Table I, if two zero-phonon lines at 0.796 eV and 0.775 eV are assumed and reported phonon energies<sup>9)</sup> are taken into account. These de-

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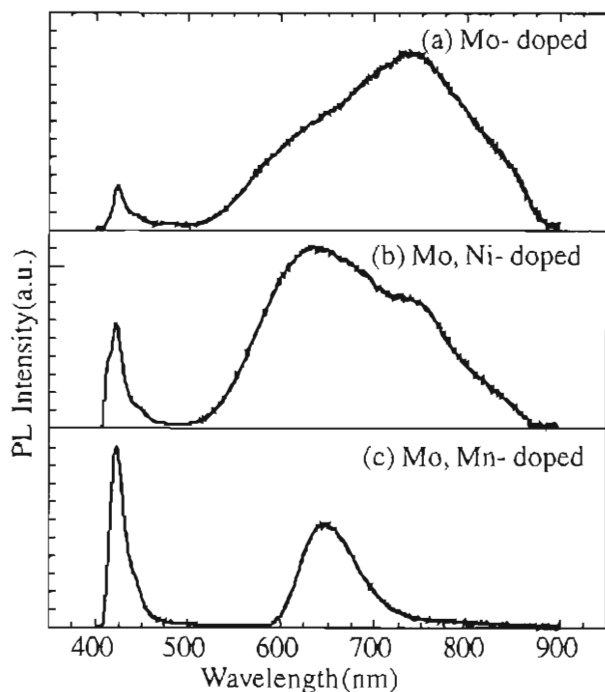


Fig. 1. Photoluminescence spectra in (a) Mo-doped, (b) Ni, Mo-doped and (c) Mn, Mo-doped  $\text{CuAlS}_2$  at 20 K in the visible region.

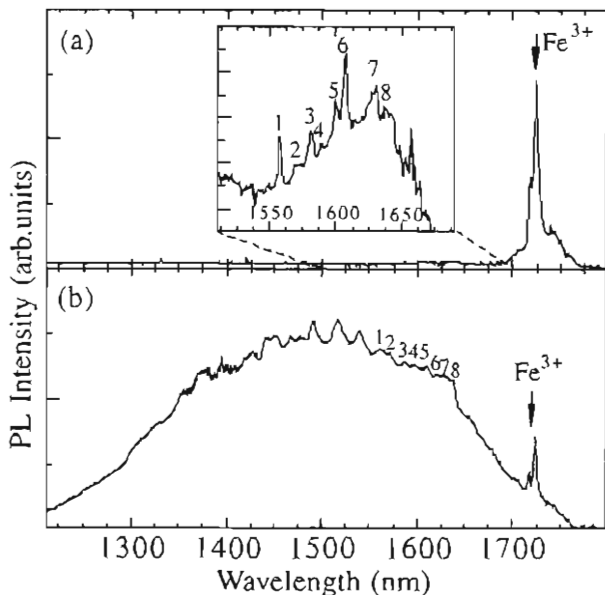


Fig. 2. IR-PL spectra of (a) 0.5 wt% and (b) 1 wt% Mo-doped  $\text{CuAlS}_2$  at 6 K.

tails will be reported in a later publication.

On the other hand, the 1 wt%-Mo-doped crystal showed an IR emission band with a peak at 1500 nm (0.83 eV) and a full-width at half maximum (FWHM) of 172 meV as shown in Fig. 2(b). Superposed on this broad emission band were also found  $\text{Mo}^{3+}$  and  $\text{Fe}^{3+}$  emission lines. A similar broad emission band was observed in  $\text{Mo}^{2+}$  doped GaAs,<sup>3)</sup> which was assigned to the ligand-field transition in  $\text{Mo}^{2+}$  ions taking into account the similarity of shape and FWHM to the emission band in  $\text{Cr}^{2+}$ -doped III-V<sup>10)</sup> and II-VI<sup>11)</sup> compounds. The latter assignment, however, was revised later to intra-center transition in the  $\text{Cr}^{2+}$ -X complex<sup>12)</sup>

It should be noted that in this 1 wt%-Mo-doped crystal, the

Table I. The phonon replica of IR-PL of  $\text{CuAlS}_2$  Mo shown in Fig. 2.

Emitted line	Energy difference (meV)	Phonon energy of $\text{CuAlS}_2$ <sup>8)</sup> (meV)
1	796	0
2	784	12.0
3	775	0
4	770	26.0
5	760	15.0
6	757	27.0
7	748	36.0
8	743	41.0

$\text{Fe}^{3+}$ -related emission at 0.72 eV significantly lost its absolute intensity. It has been clarified through our studies that the  $\text{Fe}^{3+}$ -related IR emission is due to the substitution of the copper site of  $\text{CuAlS}_2$  by iron.<sup>13)</sup> The decrease in the intensity of the  $\text{Fe}^{3+}$ -related IR emission in the 1 wt%-Mo-doped crystal suggests that Mo atoms substitute not only for the Al sites but also for the Cu sites, which in turn causes a decrease in the number of the  $\text{Fe}^{3+}$  ions substituting for the Cu sites. Consequently, Mo at the Al site in  $\text{CuAlS}_2$  becomes trivalent and shows emission lines at around 1600 nm, whereas Mo at the Cu site becomes divalent accompanied by  $\text{Fe}^{2+}$  formation, which may introduce a  $\text{Mo}^{2+}$ - $\text{Fe}^{2+}$  complex, and shows a PL band with a peak at 1500 nm. However, we cannot completely exclude the possibility that the broad emission is caused by some defect center introduced by the doping of Mo ion in the chalcopyrite lattice.

In conclusion, we have measured PL spectra in Mo-doped single crystals of  $\text{CuAlS}_2$ . A fine-structure PL emission line was observed around 1600 nm and was tentatively assigned to the ligand field transition in the  $4d^3$  manifold of  $\text{Mo}^{3+}$  ions. For higher doping levels, a broad emission appeared at 1500 nm and was tentatively attributed to intra-center transition in the  $\text{Mo}^{2+}$ -X complex.

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