

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243727923>

# Time-Resolved Photoluminescence Spectra in Single Crystals of CuAlS<sub>2</sub>:Mn

Article in *Japanese Journal of Applied Physics* · February 1991

DOI: 10.1143/JJAP.30.307

---

CITATIONS

15

READS

36

4 authors, including:



**Katsuaki Sato**

Tokyo University of Agriculture and Technology

293 PUBLICATIONS 3,507 CITATIONS

SEE PROFILE

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



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](#)



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

## Time-Resolved Photoluminescence Spectra in Single Crystals of $\text{CuAlS}_2\text{:Mn}$

Katsuaki SATO, Koki ISHII\*, Kunio WATANABE\*\*  
and Kensei OHE\*\*\*

Faculty of Technology, Tokyo University of Agriculture and Technology,  
2-24-16, Nakacho, Koganei, Tokyo 184

(Received August 31, 1990; accepted for publication December 22, 1990)

Time-resolved spectra were measured in single crystals of  $\text{CuAlS}_2$  doped with different concentrations of Mn, as well as in an undoped crystal, to elucidate the recombination mechanisms associated with the red photoluminescence band at 1.96 eV. The 0.01 wt% Mn-doped sample shows a broad emission band around 2.5 eV, 25 ns after the excitation, which loses intensity rapidly, transferring energy to an infrared peak. At 10  $\mu\text{s}$  both bands are quenched, leaving the red band at 1.96 eV. On the other hand, the PL spectrum in 1 wt% Mn-doped samples at 25 ns consisted of a purple peak at 3 eV and a red peak at 1.96 eV. The purple PL peak relaxed rapidly with a decay time of 50 ns, while the red peak showed a slow decay with a time constant of 100  $\mu\text{s}$ . The possibility of energy transfer between the host impurity/defect states and the Mn ion is discussed.

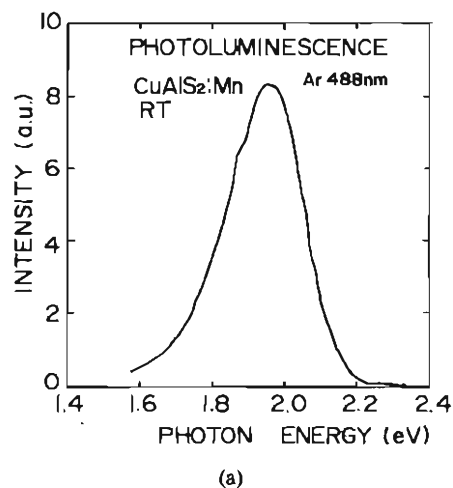
**KEYWORDS:**  $\text{CuAlS}_2\text{:Mn}$ , chalcopyrite-type semiconductor, photoluminescence, time-resolved spectroscopy, energy transfer, donor-acceptor pair emission, ligand-field transition

### §1. Introduction

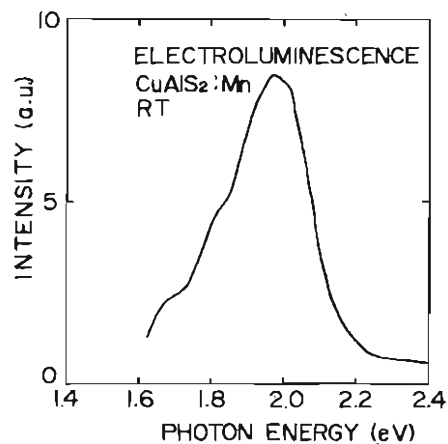
We have been working with diverse optical properties of various transition atom impurities in I-III-VI<sub>2</sub> semiconductors,<sup>1-6)</sup> of which Mn-doped  $\text{CuAlS}_2$  is the only one case that leads to a visible light emission related to a transition atom. A red photoluminescence (PL), as well as a red electroluminescence (EL), has been observed in single crystals of  $\text{CuAlS}_2$  doped with manganese.<sup>5,6)</sup>

The PL spectrum and the EL spectrum of 1.76 wt% Mn-doped  $\text{CuAlS}_2$  are shown in Figs. 1(a) and 1(b), respectively. They show quite similar spectral shapes indicating that the same luminescent center is involved. The excitation spectra allowed us to assign the PL band to the ligand-field transition from the lowest excited state  $^4T_1$  to the ground state  $^6A_1$  in the  $3d^5$  manifold of the  $\text{Mn}^{2+}$  ion, for which the ligand-field parameters were determined.<sup>5)</sup> This assignment is rather analogous to the transition responsible for the orange luminescence in  $\text{ZnS:Mn}$ .<sup>7)</sup> The latter has been extensively studied as a material for efficient thin-film EL displays, and a number of models have been proposed to explain the recombination mechanisms. For  $\text{CuAlS}_2\text{:Mn}$ , however, no models have been proposed to date on the recombination mechanism of the  $\text{Mn}^{2+}$  luminescence following the excitation beyond the gap.

Time-resolved spectrum (TRS) measurements have been known to provide a powerful tool for assignment of the PL center and determination of the PL mechanism: in Mn-doped ZnS, Busse *et al.* discriminated PL lines associated with isolated Mn centers from Mn-pairs by measuring TRS.<sup>8)</sup> Tanaka and Kobayashi compared the time-resolved EL and PL spectra in a  $\text{ZnS:Mn}$  EL cell



(a)



(b)

Fig. 1. Photoluminescence (PL) and electroluminescence (EL) spectra in  $\text{CuAlS}_2$  doped with 1.76 wt% Mn. (a) PL spectrum measured with the 488-nm line of  $\text{Ar}^+$  ion laser at room temperature.<sup>6)</sup> (b) EL spectrum of a MJM diode measured with an AC voltage of 200 Vpp at room temperature.<sup>6)</sup>

\*Matsushita Electronics Ltd., Takatsuki, Osaka 569.

\*\*Seiko-Epson Ltd., Fujimi, Nagano 399-02.

\*\*\*Victor Company of Japan, Yokosuka, Kanagawa 239.

and concluded that different mechanisms are involved in EL and PL.<sup>9</sup> We, therefore, carried out TRS studies in CuAlS<sub>2</sub>:Mn to elucidate the recombination mechanism in this material.

In the preliminary TRS studies on CuAlS<sub>2</sub> doped with 1.76 wt% Mn described in ref. 6, we found no prominent variation of spectral shapes of the Mn-origin PL band in the time interval between 20 ns and 30  $\mu$ s. However, the measurement provided little information on the energy transfer mechanism between the host and the Mn center because of the lack of the short wavelength spectrum. This is due to the low-pass filter inserted to remove the spurious fluorescence from the N<sub>2</sub> laser, which completely cut off wavelengths shorter than 500 nm (=2.48 eV).

We, therefore, carefully reexamined the TRS, employing a monochromator in the excitation beam path to avoid the spurious fluorescence from the laser, and selecting suitable filters to insert in the detection path to cut off the scattered N<sub>2</sub> laser light. In addition, in the present study, we prepared CuAlS<sub>2</sub>:Mn crystals with a wide range of Mn concentration to determine the Mn-concentration dependence of the luminescence. We also measured TRS in an undoped crystal to elucidate the PL bands inherent to the host material.

## §2. Experimental

### 2.1 Crystal growth

Single crystals of undoped CuAlS<sub>2</sub> and those doped with 0.01, 0.1 and 1 wt% Mn were grown by the chemical transport technique using iodine as a transporting agent. The starting materials were the polycrystalline powders of CuAlS<sub>2</sub> and MnS synthesized from the constituent elements by the solid-state reaction. Doping of manganese was performed by mixing an appropriate amount of MnS powder to CuAlS<sub>2</sub> powder. The doping ratio of Mn in the present paper is expressed as a percentage of Mn weight to the total amount of CuAlS<sub>2</sub>:Mn. The powder (about 4 g) was sealed in vacuo (10<sup>-6</sup> Torr) into a fused silica ampoule (13 mm in diameter and 20 cm in length) with an appropriate amount of iodine (15 mg per cm<sup>3</sup> of inner volume of the ampoule). The inner wall of the silica tube was coated by pyrolytic carbon before vacuum sealing of the starting materials. The silica tube was placed in a two-zone furnace with the hot-zone temperature of 850°C and the cold-zone temperature of 700°C for about one week.

The obtained crystals were needlelike with typical dimensions of 7 mm  $\times$  2 mm  $\times$  1 mm. Bulky crystals of undoped CuAlS<sub>2</sub> were bluish green in color. Crystals with a low Mn concentration were slightly blue in color, but further Mn doping bleached the color, increasing the transparency in the material. Some crystals were slightly reddish.

The obtained crystals were analyzed by X-rays. The major surface of the crystals was determined to be one of the {112} planes of the chalcopyrite structure.

### 2.2 Measurement of time-resolved spectra

The time-resolved spectra (TRS) were measured by means of the apparatus illustrated in Fig. 2. We employed a nitrogen laser (pulse width of 3 ns with peak

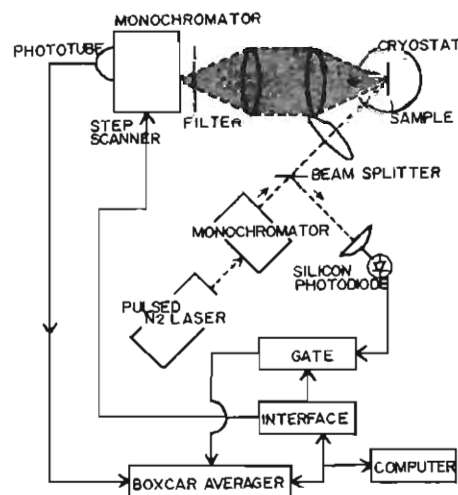


Fig. 2. A schematic illustration of the experimental setup of time-resolved spectroscopy.

power of 5 kW) as an excitation light source. To remove a number of undesirable spurious fluorescence lines other than the 337 nm line of the N<sub>2</sub> laser, we inserted a Ritsu MC-10N monochromator as a band-pass filter in the excitation light path.

We also employed a pulsed Xe lamp (pulse width of 5  $\mu$ s) to measure the PL decay characteristics for time intervals longer than 10  $\mu$ s. In this case a glass filter with band-path characteristics of selecting 400 nm light was adopted. Measurements were carried out either at room temperature or at liquid nitrogen temperature. The emitted light was dispersed with a JASCO CT-25C monochromator with a 1200-grooves/mm grating blazed at 750 nm, and detected by a photomultiplier with S-20-type photosensitivity. Appropriate combinations of colored glass filters were used to prevent the excitation light from entering into the slit of the monochromator as well as to remove the higher-order light due to the grating used in the monochromator.

An EG & G-PAR Type 4420 Boxcar Integrator controlled by a NEC PC9801F2 personal computer through the GPIB was employed to average the photosignal. The triggering pulse for the averager was provided by a silicon PIN-photodiode which detects a part of the excitation light pulse lead by the beam splitter. Data processing was performed with the help of the personal computer. Spectra were calibrated for the spectral sensitivity of the system and were plotted against energy as the intensity per unit energy range.

Absorption spectra in these crystals were measured at room temperature using a Hitachi U-3410-type spectrophotometer which covers the wavelength region from 200 nm to 2000 nm. The absorption coefficient was deduced from the measured data. Since we paid no attention on the reflection at the sample surfaces, the absolute values of the absorption coefficient may be slightly overestimated.

## §3. Results

### 3.1 Time-resolved spectra in undoped CuAlS<sub>2</sub>

Figures 3(a) and 3(b) illustrate the TRS in a single crystal of undoped  $\text{CuAlS}_2$  measured at room temperature and 77 K, respectively. The undoped sample shows an orange emission when excited by the  $\text{N}_2$  laser.

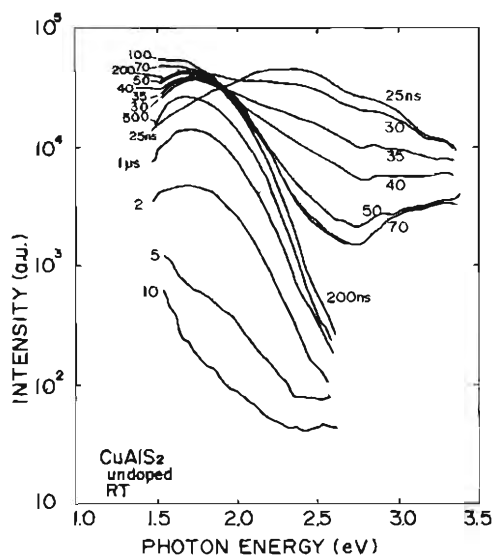
At the shortest measurable delay time (25 ns) after excitation, the PL spectrum at room temperature (RT) shows a broad PL band extending below the band edge with a peak at 2.3 eV. The orange band loses intensity rapidly with a time constant of about 40 ns. A red emission band with a peak at 1.7 eV grows with a rise time of 100 ns. This red emission peak decays with a much longer time constant (nearly equal to 2  $\mu\text{s}$ ).

The time-resolved spectra measured at 77 K shown in Fig. 4(b) are somewhat different from those at room temperature. In addition to the low-energy PL peak as observed at room temperature, a small peak at 3 eV and a shoulderlike PL structure around 2.2 eV which shows a

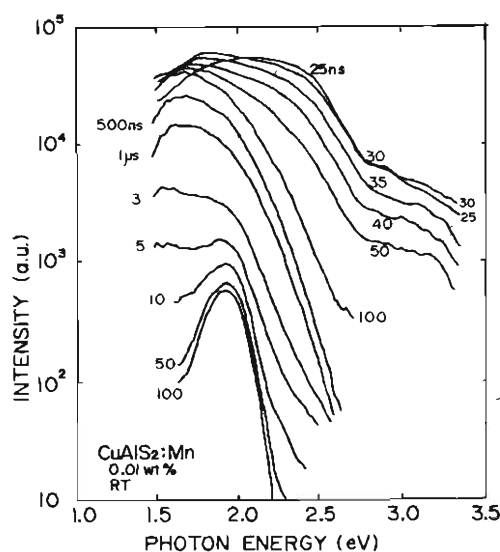
red shift to 1.9 eV surviving until the longest time delay of our measurement, were observed. A tentative interpretation on the origin of this 1.9 eV peak will be discussed in §4.3 in terms of a donor-acceptor pair emission. Here we only point out that the PL peak is related to some impurity/defect states in the host crystal.

### 3.2 Time-resolved spectra in a 0.01 wt% Mn-doped crystal

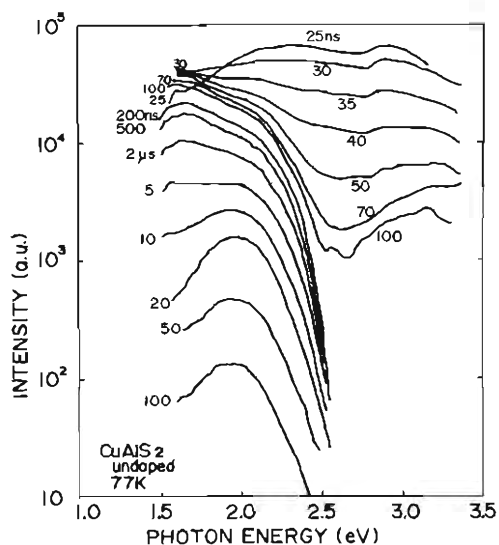
The spectrum in a sample with 0.01 wt% Mn concentration at room temperature shows a striking resemblance to that of the undoped sample, as seen in Fig. 4(a). The different spectral behavior starts around 10  $\mu\text{s}$  when a 1.96-eV peak becomes clearly discriminated. The 1.96-eV peak in Mn-doped samples has been assigned to the ligand field transition in  $\text{Mn}^{2+}$  from our previous measurements of the excitation spectrum.<sup>5)</sup>



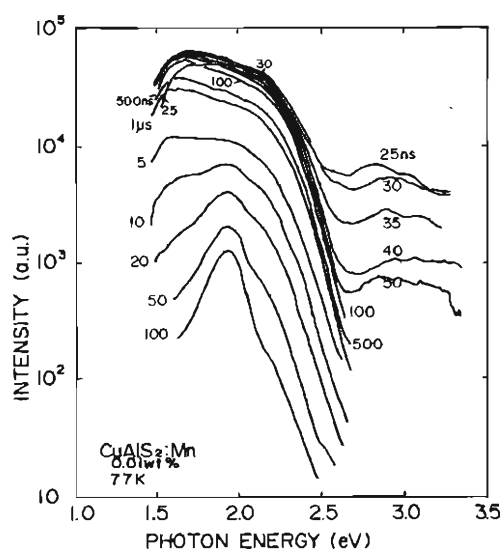
(a)



(a)



(b)



(b)

Fig. 3. Time-resolved spectra in an undoped  $\text{CuAlS}_2$  crystal measured at (a) room temperature and (b) 77 K.

Fig. 4. Time-resolved spectra in a 0.01 wt% Mn-doped  $\text{CuAlS}_2$  crystal measured at (a) room temperature and (b) 77 K.

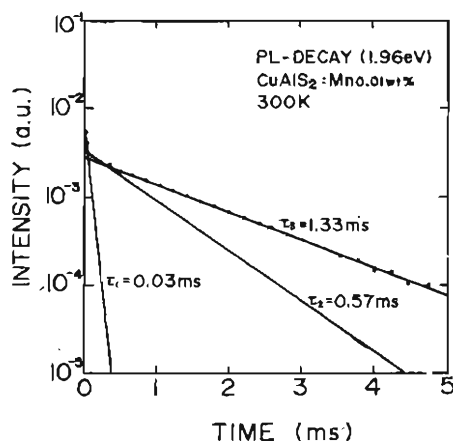


Fig. 5. Decay curve of 1.96 eV luminescence in 0.01 wt% Mn-doped  $\text{CuAlS}_2$ , measured at room temperature.

It should be noted that the energy position of the 1.96 eV peak is very close to that of the peak observed around 1.9 eV in the undoped sample at 77 K. The Mn-origin 1.96-eV band has a somewhat narrower bandwidth than the peak in the undoped sample.

Using a pulsed Xe lamp excitation, the decay characteristics of luminescence for the  $\text{Mn}^{2+}$  emission were measured. The result is shown in Fig. 5. As shown in Fig. 5, the decay curve consists of three decay constants. Only the longest decay component with  $\tau = 1.33$  ms can be associated with the Mn-origin emission, since the ligand-field transition  ${}^4T_1 \rightarrow {}^6A_1$  in  $\text{Mn}^{2+}$  is a spinforbidden transition. The faster decay components with decay constants of 30  $\mu\text{s}$  and 570  $\mu\text{s}$  may be interpreted as due to the superposition of the low-energy luminescence bands just after the excitation.

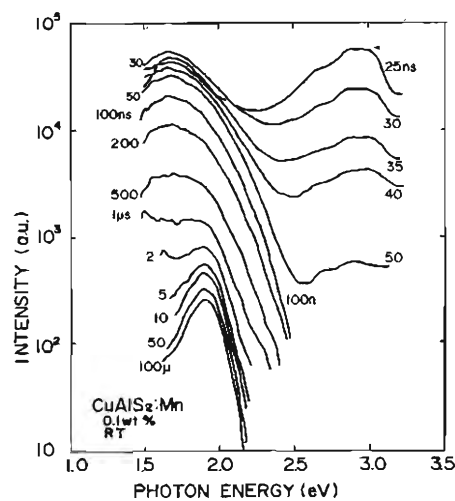
### 3.3 Time-resolved spectra in a 0.1 wt% Mn-doped crystal

As shown in Figs. 6(a) and 6(b), the 25-ns spectrum for the 0.1 wt% Mn-doped sample consists of a broad band with a peak at 3 eV and a band at 1.7 eV. The 3-eV band decreases in less than 50 ns and the 1.7-eV peak decays with a time constant of about 500 ns. The  $\text{Mn}^{2+}$ -origin peak around 2 eV becomes distinct from 2  $\mu\text{s}$ , with the decay time of 1.4 ms. The low-temperature TRS shown in Fig. 6(b) demonstrates that the decay of the 1.7-eV band becomes so slow that the  $\text{Mn}^{2+}$  emission becomes resolved from as late as 10  $\mu\text{s}$ .

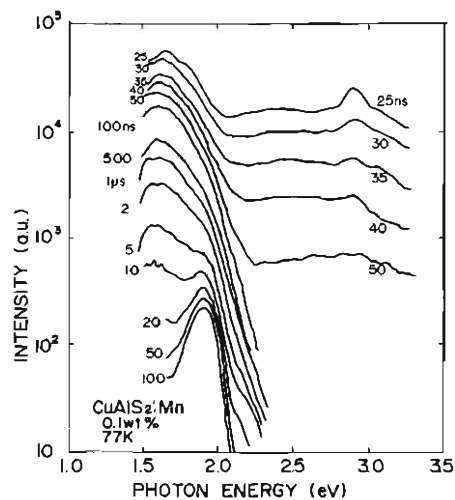
### 3.4 Time-resolved spectra in 1 wt% Mn-doped crystal

Figures 7(a) and 7(b) illustrate the TRS in a 1 wt% Mn-doped crystal. In this sample, the purple luminescence at 3 eV becomes more distinct than in the 0.1 wt% Mn-doped crystal. This emission peak can be observed at both RT and 77 K. The decay time constant of this emission is less than 50 ns.

At the delay time of 25 ns the low-energy peak is seen at 1.7 eV, just as it is in less concentrated crystals. A well-defined Mn-related red peak at 1.96 eV becomes clear at the delay time of as early as 30 ns. The peak intensity does not change between 30 and 50 ns. The red peak



(a)



(b)

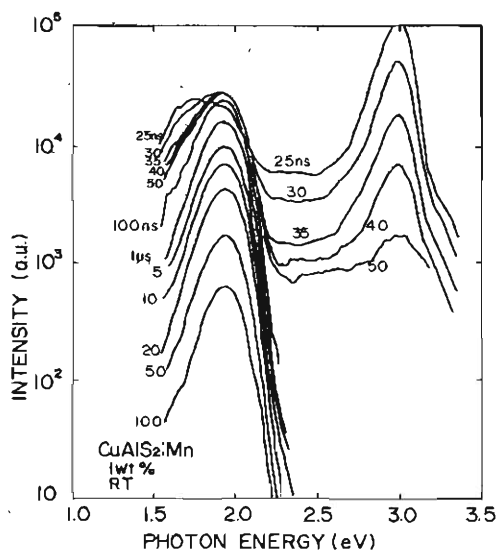
Fig. 6. Time-resolved spectra in a 0.1 wt% Mn-doped  $\text{CuAlS}_2$  crystal measured at (a) room temperature and (b) 77 K.

decays more rapidly than that observed in crystals with lower Mn concentrations. At 77 K, the Mn-origin PL band rises considerably later than that at RT. The higher-energy-side slope of the red band becomes quite steep at 77 K in the 1 wt% sample.

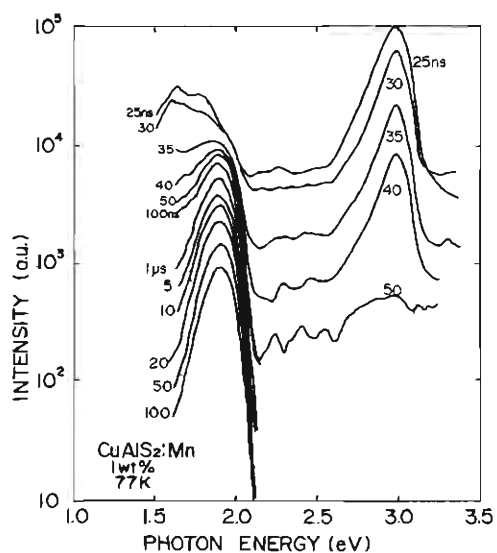
As shown in Fig. 8, the decay of the Mn emission in the 1 wt% Mn-doped crystal becomes much more rapid than the decay in the lower concentration samples. The decay time constant  $\tau$  is determined as 133  $\mu\text{s}$ . The faster decay components with  $\tau = 53$   $\mu\text{s}$  and 22  $\mu\text{s}$  may be caused by the superposition of luminescence bands with peaks at different energies which appear only in the early stages of recombination.

### 3.5 Absorption spectrum of undoped and Mn-doped $\text{CuAlS}_2$

To elucidate the origin of the 3-eV peak, we measured the absorption spectrum in samples with different concentrations of Mn ion, as well as in the undoped sample. The results are plotted in Fig. 9. The absorption edge of the



(a)



(b)

Fig. 7. Time-resolved spectra in a 1 wt% Mn-doped  $\text{CuAlS}_2$  crystal measured at (a) room temperature and (b) 77 K.

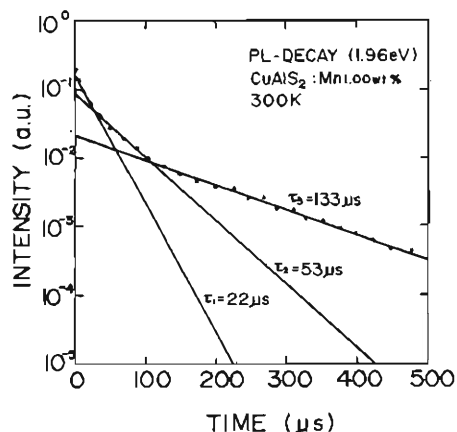


Fig. 8. Decay curve of 1.96 eV luminescence in 1 wt% Mn-doped  $\text{CuAlS}_2$  measured at room temperature.

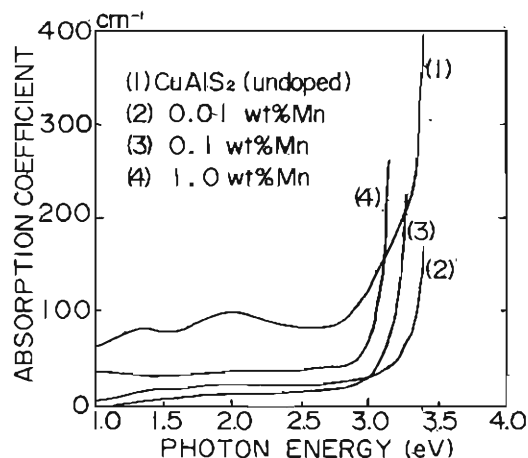


Fig. 9. Absorption spectra in (1) undoped, (2) 0.01 wt% Mn-doped, (3) 0.1 wt% Mn-doped and (4) 1 wt% Mn-doped  $\text{CuAlS}_2$  crystals measured at room temperature.

undoped sample is located around 3.4 eV. The edge shifts towards lower energies as the concentration of Mn increases. The energy difference of the absorption edge between the 1 wt% Mn-doped and the undoped crystals amounts to as large as 0.3 eV.

In addition to the edge shift, we should also note that the below-gap absorption which is observed in the undoped crystal (curve 1) becomes dramatically reduced by the slightest doping of manganese, as shown by curve 2. This corresponds to the change in the color of the crystal after Mn doping.

#### §4. Discussion

##### 4.1 Summary of experimental results

We summarize our experimental results as follows:

(1) The broad structure (shoulder) around 2.5 eV with a decay time of less than 50 ns is observed in both the undoped and the 0.01 wt% Mn-doped crystals at room temperature. Some kinds of impurity/defect-origin deep levels in the host lattice seem to be involved in this structure.

(2) The 1.7–1.8 eV peak showing a slight red shift with the decay time of 1–10  $\mu\text{s}$  is observed in 0.01 and 0.1 wt% Mn-doped samples at both room temperature and 77 K. In the 1 wt% Mn-doped sample, this peak is observable only at 77 K with a decay time constant of 100 ns.

(3) The purple luminescence peak with a maximum at 3 eV is prominent in samples with higher Mn concentrations. The decay time constant of the purple emission is approximately 50 ns. We suspect that there exists some relationship between this emission peak and the apparent shift of the absorption edge in heavily doped samples.

(4) The red PL band ascribed to the ligand-field transition  ${}^4T_1 \rightarrow {}^6A_1$  in  $\text{Mn}^{2+}$  ions survives in the spectra at long delay times. The spectral shape is identical to that of the CW PL spectrum. The decay time constant is about 1.3–1.4 ms in less concentrated samples, while it is about 100  $\mu\text{s}$  in the 1 wt%-doped sample. The emission band shows no change in line shape or peak energy throughout the time interval of the measurement. The linewidth of

the emission band remains constant regardless of the Mn concentration. The linewidth decreases at low temperature.

(5) In the undoped crystal at 77 K, a shoulderlike structure is seen at 2.2 eV, which shifts towards lower energies as time proceeds. The decay time of the latter is approximately 50  $\mu$ s. The peak position of this band at the delay time of longer than 20 ns is 1.9 eV, which is very close to the peak position, 1.96 eV, of the  $Mn^{2+}$  emission band. This seems to mean that energy transfer occurs between the band state of the host and the localized state of the Mn center through resonance with the 1.9 eV impurity/defect state.

#### 4.2 Purple luminescence and the apparent band edge shift

It is very important to elucidate the origin of the purple luminescence seen in the sample with higher Mn concentrations. The purple emission seems to be related to an apparent low-energy shift of the absorption edge, as observed in the absorption spectrum shown in Fig. 9. We consider that this shift is not due to the variation of the band gap of the host crystal. This consideration is supported by the result of a preliminary experiment of phase shift difference spectroscopy on undoped and Mn-doped samples, in which we found a peak shift of as small as 0.04 eV corresponding to the difference in the band gap for the undoped and the 1 wt% Mn-doped samples.<sup>10)</sup> This value is much smaller than the observed shift of 0.3 eV between the two crystals. We therefore attribute the apparent shift to the presence of an intense absorption band below the band gap. We note a presence of a shoulderlike structure around 3.2 eV in the 0.01 wt% Mn-doped sample. When Mn concentration is increased, the intensity of the shoulderlike structure becomes so strong that the absorption edge is subject to an apparent shift towards the low-energy side. The existence of the additional peak is only an assumption at the present stage and should be verified experimentally using thin-film samples. Such studies are planned for our future projects.

In the following, we give a possible interpretation of the additional absorption: Mn ions doped in  $CuAlS_2$  occupy both Cu and Al sites satisfying the charge neutrality requirement. The  $[Mn]_{Cu}$  (Mn occupying the Cu site) forms a donor level, while the  $[Mn]_{Al}$  (Mn occupying the Al site) forms an acceptor level. Provided that the Fermi level is in the middle of the band gap, both the donor and the acceptor are ionized. A strong optical absorption is expected for the transition from the valence band to the donor state because it is a charge transfer transition from the ligand 3p orbitals of sulfur to the 3d orbitals in manganese, changing  $Mn^{2+}$  into  $Mn^+$ . On the other hand, a strong absorption cannot be expected for the transition from the acceptor state to the conduction band, since the transition from 3d orbitals to the conduction band consisting of 3s-orbitals of Cu and Al is parity-forbidden. We therefore assign the additional absorption to the transition from the valence band to the  $[Mn]_{Cu}$  donor level located at about 0.3 eV below the bottom of the conduction band.

The existence of the  $[Mn]_{Al}$  acceptor accounts for the dramatic bleaching of the bluish color of undoped  $CuAlS_2$  by Mn doping, as follows. The bluish color has been associated with an unintentional incorporation of  $Fe^{3+}$  impurities.<sup>2)</sup> Existence of  $Fe^{3+}$  in "undoped"  $CuAlS_2$  crystals can easily be confirmed by measuring the infrared PL spectrum, since one of the present authors (K.S.) elucidated that the  $Fe^{3+}$  ion shows a sharp PL line at 0.72 eV in  $CuAlS_2$ .<sup>3)</sup> Our recent infrared PL studies in the  $CuAl_xGa_{1-x}S_2$  system revealed that the unintentionally incorporated Fe in  $CuAlS_2$  occupies the Cu site and becomes trivalent.<sup>3)</sup> In the present studies we have confirmed the existence of the  $Fe^{3+}$ -related PL also in slightly Mn-doped  $CuAlS_2$ .  $[Mn^{2+}]_{Al}$  supplies an electron to the  $[Fe]_{Cu}$  center reducing  $Fe^{3+}$  to  $Fe^{2+}$ , which causes no absorption bands in the visible region and reduces the color.

As for the mechanism of the purple luminescence, we propose the following model. The  $N_2$  laser irradiation produces electron-hole pairs in the material since the photon energy, 3.7 eV, of the laser is large enough for a transition across the gap to occur. The electron may be captured by the  $[Mn]_{Cu}$  donor making a neutral donor state, i.e.,  $[Mn^+]_{Cu}$ , while the hole is captured by the  $[Mn]_{Al}$  acceptor making a neutral acceptor, i.e.,  $[Mn^{3+}]_{Al}$ . We tentatively assign the purple luminescence at 3 eV to an electron transition from the donor to the acceptor. This transition ionizes both the  $[Mn^+]_{Cu}$  donor and the  $[Mn^{3+}]_{Al}$  acceptor accompanying the formation of two  $Mn^{2+}$  centers. Since our previous excitation spectrum measurement verified that there is a weak absorption band due to the ligand-field transition in  $Mn^{2+}$  around 2.9–3 eV,<sup>4)</sup> we can postulate that the purple luminescence energy may be rapidly (less than 50 ns) transferred to the ligand-field multiplets in the  $Mn^{2+}$  center, which in turn relaxes to the ground state, emitting the characteristic red emission.

It is widely accepted that the donor-acceptor pair emission suffers a red shift of the peak as time proceeds. However, our observation showed no shift at all between 25 and 50 ns. Concerning the peak shift, one should remember that there is a type of D-A pair emission showing no peak shift, for which no Coulomb term is involved.<sup>11)</sup> We believe this is the case in our purple luminescence spectrum.

The fact that such a high-energy PL peak has never been observed in undoped samples but is found only in Mn-doped samples suggests a possibility of obtaining a blue-light-emitting material by doping some other kind of divalent element which does not transfer the energy to the localized multiplets as in the case of Mn. We would like to point out that divalent alkalineearth ions which play the same role as Mn and have no d-electrons to be excited are candidates.

#### 4.3 Mechanism of the $Mn^{2+}$ luminescence

As for the red luminescence with a peak at 1.96 eV, the experimental results that no prominent difference in the spectral shape or the peak position is observed between slightly doped and heavily doped samples suggests that the luminescence is associated with the ligand-field

transition in the  $3d^5$  manifold of a single  $\text{Mn}^{2+}$  center.

The decay time shows a marked decrease in the heavily doped material, which may be interpreted in terms of the increased probability of the dipole-dipole or the multipole-multipole interaction between Mn centers. There is a possibility the shortening of the decay time is caused by the formation of the Mn pair, as we pointed out in the previous paper,<sup>6</sup> although no prominent change of the PL lineshape corresponding to the change in the concentration of manganese has been observed. The broad structureless feature of the PL spectrum makes it difficult to carry out a detailed analysis of the pair luminescence. Studies at liquid helium temperature may help us to resolve the fine structures in the broad emission band.

Several mechanisms can be postulated for the red (1.96 eV) luminescence associated with the  $\text{Mn}^{2+}$  center. One is the direct excitation mechanism. The higher-lying excited state in the  $3d^5$  manifolds of the  $\text{Mn}^{2+}$  center may be mixed with the continuum of the empty band states. The across-the-gap excitation partly excites the electrons to the higher-lying excited states directly. They relax with phonon emission to the lowest excited multiplets,  $^4T_1$ , from which a radiative recombination occurs to the ground multiplets  $^6A_1$ . The PL intensity through this mechanism should be weak since no strong hybridization between the Mn 3d orbitals and the conduction band state is expected.

On the other hand, we can postulate another recombination model. As pointed out in §3.2, the impurity/defect-origin photoluminescence peak was observed at 77 K showing a considerable energy shift from 2.2 eV to 1.9 eV in the undoped crystal. Such a shift is characteristic of a D-A pair emission. Since no corresponding emission is observed at room temperature some kind of shallow state is suspected to be involved in addition to a deep level. Both the shallow and the deep states observed in the host crystal will also be found in crystals doped with an extrinsic impurity, provided that the concentration of the impurity is very low. By comparing Figs. 3(b) and 4(a), we come to the conclusion that the D-A pair inherent in the host crystal transfers energy to the  $\text{Mn}^{2+}$  center through a kind of resonance between the centers, because of the closeness of their energies.

A third model involves the Mn-related D-A pair recombination, as introduced in the preceding subsection. Excited carriers are trapped by the  $[\text{Mn}]_{\text{Cu}}$  donor and the  $[\text{Mn}]_{\text{Al}}$  acceptor. A D-A pair recombination produces two  $\text{Mn}^{2+}$  centers which are excited by absorbing the D-A pair energy and then relax to the lowest excited state emitting the red PL. This mechanism requires pairs of Mn-related centers and is important in the heavily doped case.

Further studies such as high resolution excitation spectrum measurements may be necessary to determine which of the above mechanisms is responsible for the Mn-origin PL peak.

## §5. Conclusions

Time-resolved spectra were measured in single crystals of  $\text{CuAlS}_2$  doped with different Mn concentrations, as

well as in undoped crystals. The time-resolved spectrum in a 0.01 wt% Mn-doped sample at the delay time of 25 ns showed a broad-band emission peak around 2.5 eV, just as did the 25 ns spectrum of an undoped crystal. The intensity of the broad band rapidly decreased and an infrared peak developed. At the delay time of 10  $\mu\text{s}$  after excitation, only the red emission band at 1.96 eV was observed. The decay time of the red band was approximately equal to 1 ms. No clear evidence for the energy transfer between the impurity/defect center associated with the host and the Mn center was obtained for slightly Mn-doped samples. However, the 77 K time-resolved PL spectrum in the undoped crystal suggests an evolution of the 1.9-eV impurity/defect level, which is suspected to act as a resonant energy transfer center between the host and the  $\text{Mn}^{2+}$  center.

On the other hand, the PL spectrum in the heavily doped samples showed a purple peak at 3 eV just after the excitation and a red Mn-origin peak at 1.96 eV developed after a slight delay. The purple PL peak relaxes rapidly with a decay time of 50 ns, while the red peak shows a slow decay with a time constant of 100  $\mu\text{s}$ . The origin of the purple band was attributed to the recombination in the donor-acceptor pair introduced by Mn doping. The possibility of an energy transfer between the host impurity/defect states and the Mn center was also suggested.

## Acknowledgments

The authors are much indebted to Prof. E. Nakazawa of Kogakuin University and Mr. S. Okamoto of NHK Science and Technical Laboratories for their helpful technical advice and fruitful discussion. Thanks are also due to Prof. H. Kobayashi and S. Tanaka of Tottori University for their kind advice and suggestions in the interpretation of the time-resolved spectra. This work has been partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (New Functionality Materials) from the Ministry of Education, Science and Culture.

## References

- 1) K. Sato, H. Tsunoda and T. Teranishi: *Ternary and Multinary Compounds*, eds. S. Deb and A. Zunger (Mater. Res. Soc., Pittsburgh, 1987) p. 113, and references therein.
- 2) K. Tanaka, K. Ishii, S. Matsuda, Y. Hasegawa and K. Sato: *Jpn. J. Appl. Phys.* **28** (1989) 12.
- 3) K. Sato and T. Teranishi: *J. Phys. Soc. Jpn.* **37** (1974) 415.
- 4) K. Sato, K. Tanaka, K. Ishii and S. Matsuda: *J. Cryst. Growth* **99** (1990) 772.
- 5) K. Sato, S. Okamoto, M. Morita, A. Morita, T. Kambara and H. Takenoshita: *Prog. Cryst. Growth & Char.* **10** (1984) 311.
- 6) K. Sato, K. Ishii, S. Matsuda and S. Mizukawa: *Electroluminescence*, eds. S. Shionoya and H. Kobayashi (Springer, Berlin, 1989) p. 390.
- 7) D. S. McClure: *J. Chem. Phys.* **39** (1963) 2850.
- 8) W. Busse, H.-E. Gümlisch, B. Meissner and D. Theis: *J. Lumin.* **12/13** (1976) 693.
- 9) S. Tanaka and H. Kobayashi: *J. Appl. Phys.* **47** (1976) 5393.
- 10) K. Sato, K. Ishii, K. Ohe, K. Watanabe and Y. Kudo: to be published in *Proc. 8th Int. Conf. Ternary and Multinary Compounds, Kishinev, 1990* (Moldavia Academy of Sciences, Kishinev, 1991).
- 11) C. H. Henry, P. J. Dean and J. D. Cuthbert: *Phys. Rev.* **166** (1968) 754.