

Photoluminescence at Low Temperature in $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ Doped with Al and P Atoms

MASUO ISHIKANE*, MASASI INOUE**, HISAO YAGI**

(Received Apr. 1, 1975)

In the as-grown and annealed $\text{Cd}_{1-x}\text{Mg}_x\text{Te:P}$, the sharp emission band (centered at 540~550 nm) due to recombination of bound excitons has been found at low temperature below 50 K. In addition, it is shown that the luminescent efficiencies of the L, L' and S bands caused by P and Al atoms approach to their own constant values with lowering of temperature. However, the vibronic structure for these emission bands which is characteristic of the donor-acceptor pair emission, has not been observed in this mixed crystal. The absence of the pair emission may be stemmed from the complicated phonon spectrum compared with a typical II-VI or III-V semiconductor.

1. Introduction

Along with the early work done by Shitaya *et al.*¹⁾, we have measured the emission spectra of the as-grown and annealed crystals $\text{Cd}_{1-x}\text{Mg}_x\text{Te:P}$ or Al atoms over the temperature range 110~300 K, and have found that there are three kinds of emission bands, the L band (centered at 715 nm), the L' band (690 nm), and the S band (640 nm)²⁾: The L and L' bands are observed in the as-grown (P- and Al-doped) crystals, but they become very faint or almost disappear when the crystals are annealed in Cd-vapor at 800°C for 2~5 hours, while the S band is observed only in the annealed P-doped crystal. From the temperature dependence of the emission intensities for each band, we have tentatively assigned relevant recombination centers with respect to the band edge; these are two acceptor-levels of about 0.3 eV due to Cd-vacancy and of 0.25 eV due to substitutional P-atoms, and shallow donor-levels of Te-vacancy or interstitial P-atoms.

In order to confirm the proposed model and to gain insight into the photoluminescent process involved, in particular a possibility of edge emission or donor-acceptor recombination as observed in other II-VI and III-V semiconductors³⁻⁶⁾, we have extended the similar measurements down to liquid helium temperature; these emission bands are not examined in the mixed crystal of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ yet. In what follows, we shall present the results; in addition to the L, L' and S bands, another

*Physics Department, Faculty of Education. **Department of Applied Physics.

emission band arising from the bound-exciton is found to exist in the P-doped crystals.

2. Experimental

A schematic diagram of the optical apparatus is shown in Fig. 1. The crystal mount-

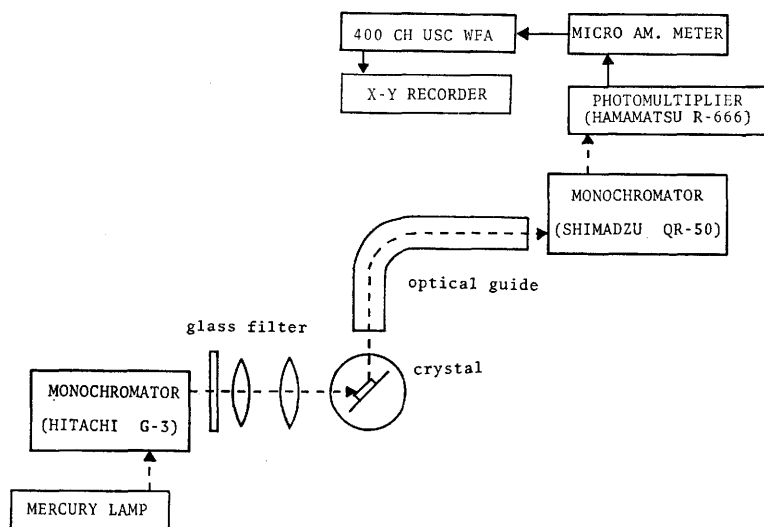


Fig. 1. Schematic diagram of the optical apparatus.

ed on a cold finger inside a metal dewar designed for low temperature experiment, is excited by 365 nm light selected from a high pressure mercury lamp through a grating monochromator (Hitachi G-3) and a glass filter (Toshiba UV-D25). The light emitted from the crystal is led through an optical guide to a prism monochromator (Shimadzu QR-50) which is driven by a synchronous motor, and is detected by a photomultiplier (Hamamatsu R 666). The photocurrent of the photomultiplier is amplified by a micro am. meter, and is led to a multichannel analyzer (Toshiba 400 channel USC) and averaged out several times to reduce thermal noise. The emission spectrum thus obtained is displayed on an X-Y recorder and also can be printed digitally. A gold-cobalt-copper thermocouple is used for temperature measurement. The samples used are the same as the previous work.

3. Experimental Results and Discussion

3.1 As-grown $\text{Cd}_{1-x}\text{Mg}_x\text{Te:P}$

In Fig. 2 are shown the emission spectra of the as-grown $\text{Cd}_{1-x}\text{Mg}_x\text{Te:P}$ crystal at different temperatures. In addition to the L' band reported in ref. 2, it is found that there exist two emission bands at 540 and 560 nm (designated as E_1 and E_2 bands, respectively) near the fundamental absorption region. As the temperature is

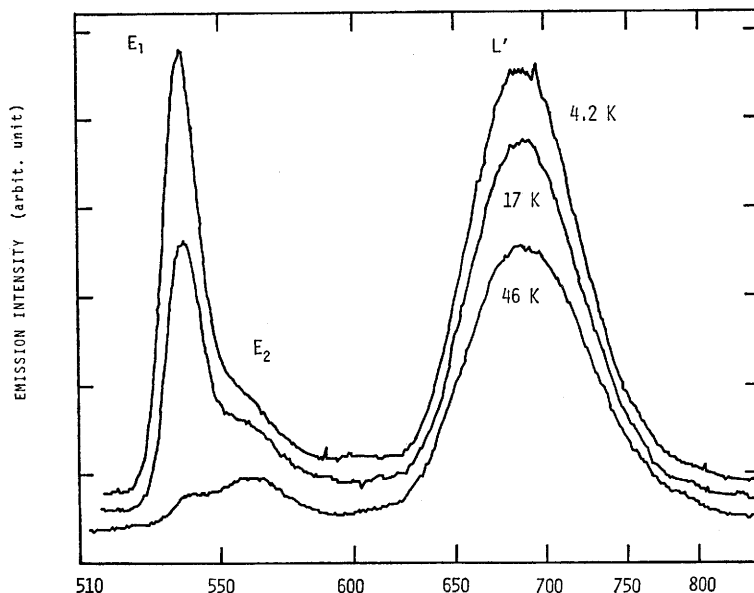


Fig. 2 Emission spectra of the as-grown $\text{Cd}_{1-x}\text{Mg}_x\text{Te:P}$ at various temperatures. The peak positions are approximately 540 nm (for the E_1 band), 560 nm (for the E_2 band), and 690 nm (for the L' band).

decreased, the E_1 band becomes sharper and more intense compared with the E_2 band.

The temperature dependence of the intensities of the L' and E_1 bands are shown in Fig. 3, but that of the E_2 band is not shown because of low intensity. The L' band is less temperature dependent at low temperature compared with the previous data obtained at high temperature. The intensity of the L' band may be explained by using eq. (1) in ref. 2, which expresses the temperature dependence of intensity of donor-acceptor (D-A) pair luminescence. However, a vibronic structure for the L' band which is one of the characteristic properties of pair luminescence, cannot be observed even at 4.2 K. On the other hand, the variation of intensity of the E_1 band with temperature is explainable by introducing a thermal quenching process with an activation energy of about 0.01 eV.

The excitation intensity dependence of E_1 and E_2 at 4.2 K is shown in Fig. 4, where it is assumed that the intensity of the L' band is proportional to excitation

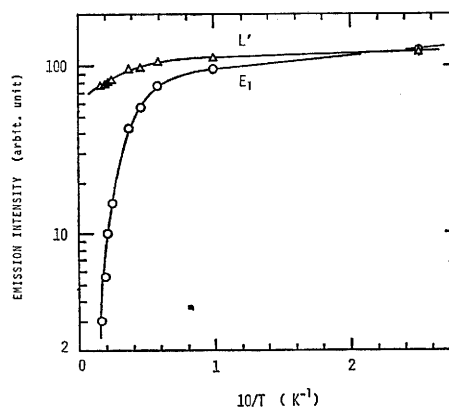


Fig. 3 Temperature dependence of emission intensity in arbitrary scale for the L' and E_1 bands.

intensity. The intensity of the E_1 band $I_e^{(1)}$ at 4.2 K can be expressed by

$$I_e^{(1)} = k_1 I^{1.5}, \quad \dots\dots(1)$$

where k_1 is a constant, and I is the excitation intensity. This super-linearity suggests us that the E_1 band is attributed to recombination of the bound excitons⁵. The intensity of the E_2 band $I_e^{(2)}$, on the other hand, is given by

$$I_e^{(2)} = k_2 I^{1.0}, \quad \dots\dots(2)$$

where k_2 is another constant. This fact indicates that the E_2 band is not the phonon structure of the E_1 band, and that the E_2 band is emitted from unknown centers. Although we can get the relation given by eq. (2), we can not refer to anything about the E_2 band. Therefore, detailed experiments are required for assignment of it.

3.2 Annealed $Cd_{1-x}Mg_xTe:P$

Figure 5 shows the emission spectra of the annealed $Cd_{1-x}Mg_xTe:P$. A sharp emis-

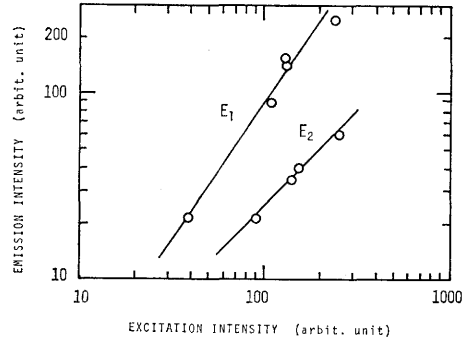


Fig. 4 Relative emission intensity of the E_1 and E_2 bands with respect to that of the L' band at 4.2 K. It is assumed that the intensity of the L' band is proportional to the excitation intensity.

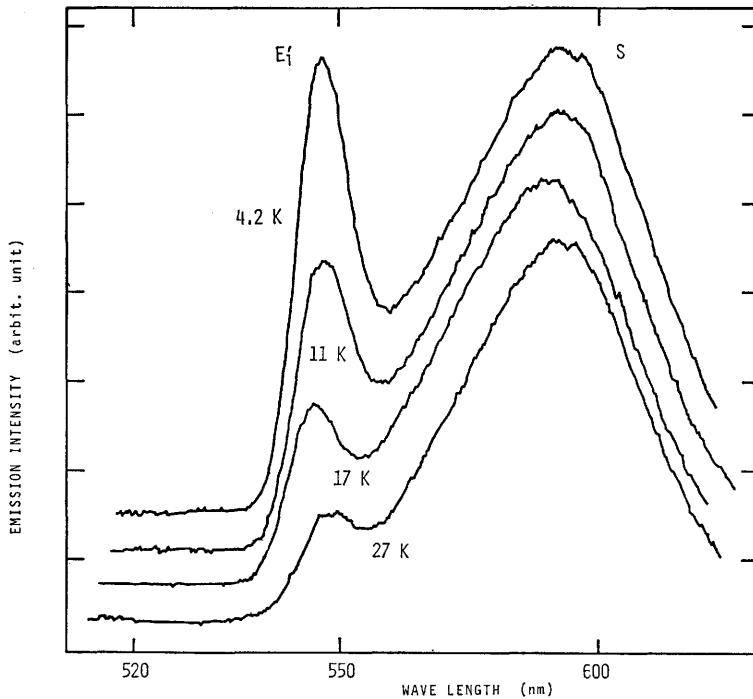


Fig. 5 Emission spectra of the annealed $Cd_{1-x}Mg_xTe:P$ at different temperatures, the E_1 band being at 546 nm.

sion band at 546 nm (designated as E'_1 band) is seen at low temperature; this band is considered to correspond to the E_1 band in the as-grown crystal. However, no band corresponding to the E_2 band is detectable clearly. The temperature dependence of intensity for both S and E'_1 bands shows the similar behavior to that of the L' band, as shown in Fig. 6. As to the E'_1 band, the activation energy for thermal quenching process is obtained to be 0.027 eV from Fig. 6, which is different from that for the E_1 band (0.01 eV).

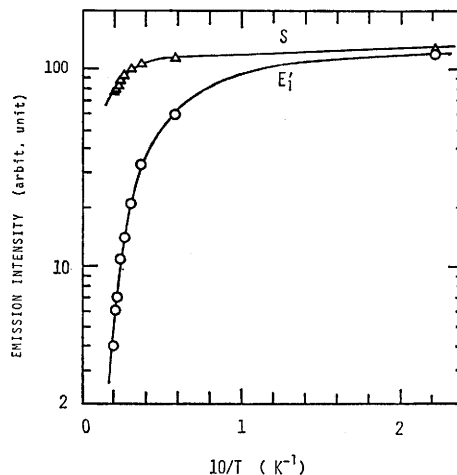


Fig. 6 The temperature dependence of emission intensity for the S and E'_1 bands.

3.3 As-grown $Cd_{1-x}Mg_xTe:Al$

In Fig. 7 is shown the emission spectrum of the as-grown $Cd_{1-x}Mg_xTe:Al$. There is no sharp band even at 4.2 K. The vibronic structure characteristic of D-A recombination can not be observed in this material, probably because of a complicated phonon spectrum in the mixed crystals. The temperature dependence of the intensity of the L band is similar to that of the L' or S band (Fig.8). Accordingly, the intensity is also expressed by eq. (1) in ref. 2.

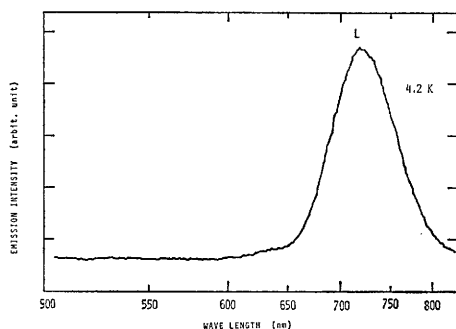


Fig. 7 Emission spectra of $Cd_{1-x}Mg_xTe:Al$ at 4.2 K.

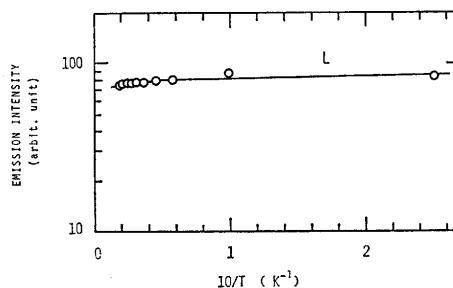


Fig. 8 Temperature dependence of emission intensity of the L band.

3.4 Annealed $Cd_{1-x}Mg_xTe:Al$

Finally, we show the emission spectra of the annealed $Cd_{1-x}Mg_xTe:Al$ in Fig. 9. The spectra are found to be rather complicated, depending on temperature. In addition to the L' band (690 nm), there appears a broad line at 576 nm and there is no sharp band just as the E_1 band. The excitation intensity dependence of the

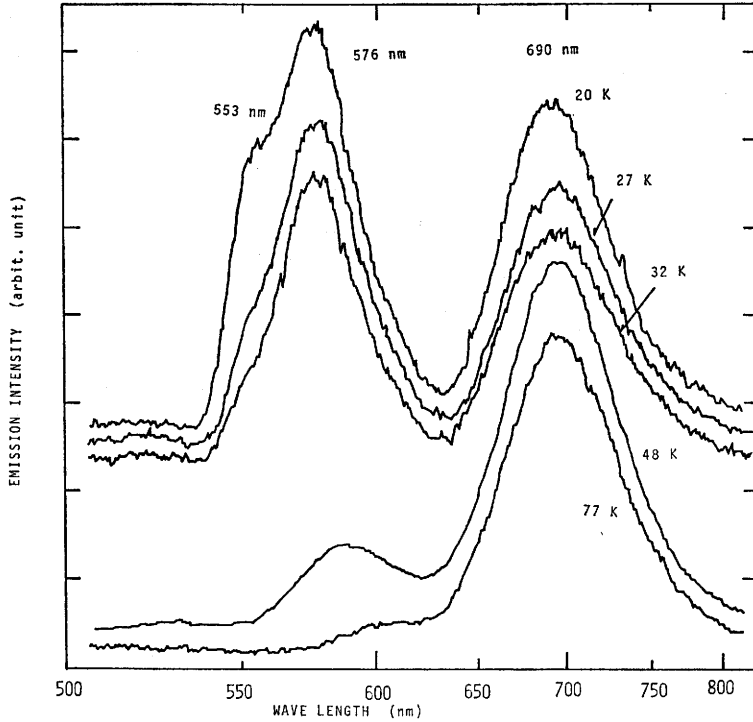


Fig. 9 Emission spectra of the annealed $\text{Cd}_{1-x}\text{Mg}_x\text{Te}:\text{Al}$.

emission band centered at 576 nm is linear, as shown in Fig. 10. Therefore, this band is not considered to be due to bound excitons.

Acknowledgments

The authors would like to thank to Dr. H. Sato, T. Shitaya, and T. Ishida of Wireless Research Laboratory, Matsushita Elec. Ind. Co, Osaka for supplying of the crystals. Thanks are due to K. Tanaka and T. Morita for help in taking the measurement.

References

- 1) T. Shitaya, T. Ishida and H. Sato: *J. appl. Phys. Letters* **21** (1972) 523.
- 2) M. Ishikane, M. Inoue and H. Yagi: *Memoirs Fac. Eng. Fukui Univ.* **23** (1975) 91.
- 3) M. Tajima and M. Aoki: *Japan. J. appl. Phys.* **13** (1974) 812.
- 4) M. Tajima and M. Aoki: *Japan. J. appl. Phys.* **13** (1974) 819.
- 5) T. Taguchi, J. Shirafuji and Y. Inuishi: *Japan. J. appl. Phys.* **12** (1974) 1558.
- 6) Y. Kokubun, H. Watanabe and M. Wada: *Japan. J. appl. Phys.* **13** (1974) 1393.

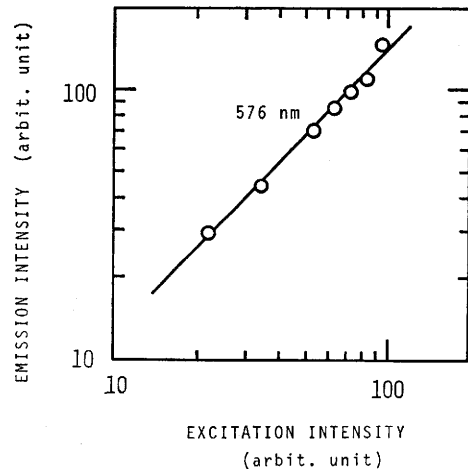


Fig. 10 Emission intensity of the 675 nm band against the excitation intensity at 20 K.