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## RADIATIVE RECOMBINATION OF LOCALIZED EXCITONS IN AMORPHOUS AND CRYSTALLINE $\text{As}_2\text{S}_3$

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**Abstract** - Two photo-luminescence bands characterized by their excitation in  $\text{c-As}_2\text{S}_3$  shows a surprising similarity to those in  $\text{a-As}_2\text{S}_3$ . In addition, a band in  $\text{c-As}_2\text{S}_3$  can be interpreted as due to the recombination of localized excitons as well as a luminescence band in  $\text{a-As}_2\text{S}_3$ . The luminescence bands in  $\text{a-As}_2\text{S}_3$  are discussed on the basis of the luminescence processes in  $\text{c-As}_2\text{S}_3$ .

In  $\text{a-As}_2\text{S}_3$ , it is suggested from the time resolved spectrum<sup>1)2)</sup> and the polarization memory of luminescence<sup>3)4)</sup> that two kinds of luminescence processes exist. One process produces a broad luminescence  $A_1$ <sup>5)</sup> with the peak energy of about 1.15eV. The other process produces another broad luminescence  $A_2$  with the peak energy, 1.4-1.7eV, depending on the excitation energy<sup>1)3)6)</sup>. Some discussions about these luminescence processes are made on the basis of the model specific to amorphous materials but it is also important to compare these luminescence phenomena with the luminescence in the corresponding crystalline materials,  $\text{c-As}_2\text{S}_3$ .

In  $\text{c-As}_2\text{S}_3$ , Kolmiets et al<sup>5)</sup> and Mollot et al<sup>7)</sup> observe a spectrum of luminescence ( $C_1$ ) with the peak energy of about 1.2eV while Street et al<sup>8)</sup> and Bosch et al<sup>9)</sup> observe another spectrum of luminescence ( $C_2$ ) with the peak energy of about 1.6eV. The luminescence  $C_1$  is compared with luminescence  $A_1$  by Kolomiets et al<sup>5)</sup> and they suggest that the luminescence  $A_1$  is responsible for a deep center similar to the center of  $C_1$ .

The authors find in detailed measurements that the luminescence,  $C_1$  and  $C_2$ , in  $\text{c-As}_2\text{S}_3$  are due to the different recombination processes depending on the excitation energy<sup>10)</sup>. In this paper, we will report the two luminescence processes in  $\text{c-As}_2\text{S}_3$  and compare these processes with those in  $\text{a-As}_2\text{S}_3$ .

High quality natural crystals of orpiment were cleaved into sheets prior to measurements of the luminescence and optical absorption. An Ar ion laser provided the excitation light for the luminescence, which was analyzed by a monochromator and detected with a photo-multiplier or a Ge photo diode.

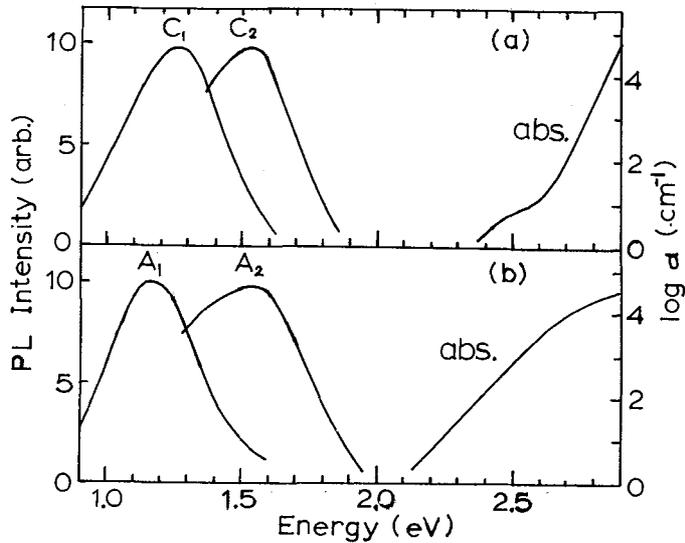
The absorption spectrum in  $\text{c-As}_2\text{S}_3$  observed at 2 K is shown in Fig. 1(a). We observed a shoulder at 2.5eV superimposed on the steep rise of the absorption at higher energies which is due to the band to band transitions. Zakis and Fritzsche<sup>11)</sup> also report a large shoulder at the same position. They propose that the process is due to the high energy transition between a band and a shallow level produced by an impurity.

The luminescence spectra obtained from the same sample with two different

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Fig. 1 - Optical absorption edges and photoluminescence bands in (a)  $c\text{-As}_2\text{S}_3$  and (b)  $a\text{-As}_2\text{S}_3$  at liquid helium temperature. Data of the luminescence  $A_1$  from Street<sup>12)</sup> and the luminescence  $A_2$  from Murayama<sup>1)</sup>.



excitation photon energies are revealed in Fig. 1(a). The high energy luminescence is excited by 2.54eV irradiation. The excitation energy of 2.54eV is close to the peak energy of the above discussed shoulder in absorptance. The peak energy for the high energy luminescence is 1.53eV. The luminescence corresponds to  $C_2$  in its peak energy and the band width. The second luminescence band in Fig. 1(a) is excited by 2.71eV irradiation. Similar line shape but much larger Stokes shift are exhibited. The luminescence corresponds to  $C_1$ . The spectrum of the luminescence bands  $A_1$  and  $A_2$  in  $a\text{-As}_2\text{S}_3$  are shown in Fig. 1(b) to compare with  $C_1$  and  $C_2$  in  $c\text{-As}_2\text{S}_3$ , respectively. We notice a surprising similarity between the luminescence spectra in the crystal and amorphous solid.

Fig. 2 reveals the photo luminescence excitation spectra of  $C_1$  and  $C_2$ . The position of the excitation spectrum of  $C_2$  corresponds closely to the shoulder. Therefore, we conclude that the luminescence  $C_2$  is originating from excitation between the band edge and a shallow level. On the other hand, the excitation curve for the luminescence  $C_1$  increases monotonically with increasing excitation energy. It is apparent that the luminescence  $C_1$  is originating from the onset of band to band transitions.

The temperature dependence of the luminescence intensity is shown in Fig. 3. The thermal activation energies of  $C_1$  and  $C_2$  are 107 meV and 27 meV, respectively.

We discuss first the luminescence  $C_2$  which can be assigned to a defect related process. The excitation from a band edge to a shallow level can be considered to produce a localized electron-hole pair bound at the impurity (bound exciton). The large Stokes shift of the luminescence  $C_2$  is considered to be due to a strong electron-phonon coupling. The process producing the luminescence  $C_2$  is displayed as G in the configurational coordinate diagram shown in Fig. 4(a). A bound exciton excited in the process G relaxes into a deep state. This is accomplished by displacement of atoms through an electron-phonon interaction. Radiative recombination of the bound exciton is then responsible for the observed emission with the large Stokes shift.

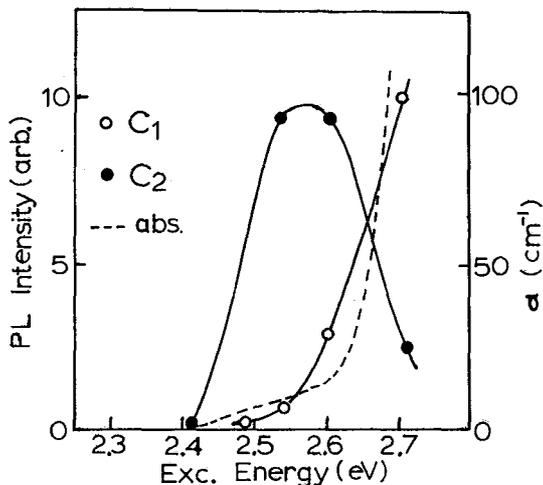


Fig. 2 - Photoluminescence excitation spectra of the luminescence  $C_1$  and  $C_2$  and optical absorption edge in  $c\text{-As}_2\text{S}_3$  at 2K.

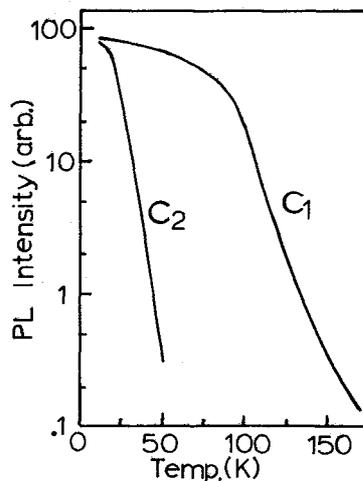


Fig. 3 - Temperature dependence of the intensities of the luminescence  $C_1$  and  $C_2$  in  $c\text{-As}_2\text{S}_3$ .

The luminescence  $C_1$  is obtained by the band to band excitation. In this case, the electron-hole pair produced by the band to band excitation is trapped by a strongly electron-phonon coupled localized state. The subsequent recombination gives rise to the luminescence  $C_1$ . This process is displayed as N in the configurational coordinate diagram shown in Fig. 4(a). The nature of the trapping center is not clear because electron-hole pairs in bands can find many kinds of trapping states, for example, self-trapping states or donor-acceptor states, etc.

Potential fluctuations due to disorder produce shallow localized states at band edges in amorphous semiconductors. If the shallow state in  $a\text{-As}_2\text{S}_3$  is similar to the shallow state produced by impurities in  $c\text{-As}_2\text{S}_3$ , we expect the luminescence process G to occur in  $a\text{-As}_2\text{S}_3$ . In this case, since the shallow states are distributed in energy due to the potential fluctuations, the spectrum of the luminescence due to the recombination of excitons localized at shallow states depends on the excitation energy. The luminescence produced in the process G in  $a\text{-As}_2\text{S}_3$  is estimated to be  $A_2$ . The process G in  $a\text{-As}_2\text{S}_3$  is shown in Fig. 4(b). On the other hand, the luminescence in the process N has no memory for the exciting light because an electron-hole pair excited into band in the process N transfers to a localized state. It means that the spectrum of the luminescence does not depend on the excitation energy though the localized state is distributed in energy by the potential fluctuations as shown in Fig. 4(b). The luminescence in the process N is considered to correspond to the luminescence  $A_1$  in  $a\text{-As}_2\text{S}_3$ . It is suggested that two luminescence bands in  $a\text{-As}_2\text{S}_3$  are produced in the processes similar to those in  $c\text{-As}_2\text{S}_3$ . It is considered to be due to that microstructure in  $a\text{-As}_2\text{S}_3$  is similar to that in  $c\text{-As}_2\text{S}_3$  because the nature of a localized center strongly depends on the microstructure.

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Higashi and Kastner<sup>6)</sup> report a spectrum with a flat peak from 1.1 to 1.6eV obtained by time resolved spectroscopy in  $a\text{-As}_2\text{S}_3$ . The luminescence spectrum can be interpreted due to overlapping of the luminescence  $A_1$  and  $A_2$ .

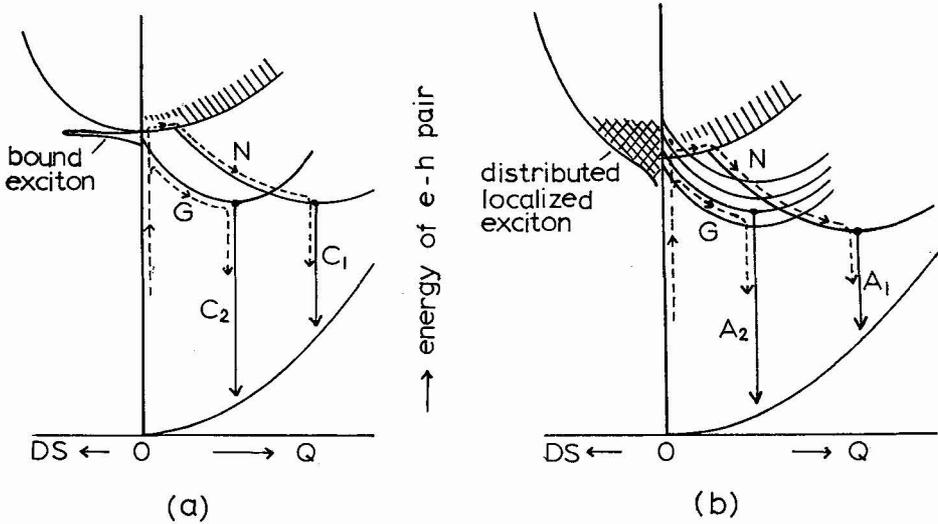


Fig. 4 - Luminescence processes and configurational coordinate diagrams in (a) crystalline and (b) amorphous solids. Density of states of an electron-hole pair is also illustrated.

#### References

- 1) K. Murayama, T. Ninomiya, H. Suzuki and K. Morigaki, *Solid State Commun.* **24**, 197 (1977).
- 2) M. A. Bösch and J. Shah, *Phys. Rev. Lett.* **42**, 118 (1979).
- 3) K. Murayama, H. Suzuki and T. Ninomiya, *J. Non-Crystalline Solids* **35/36**, 915 (1980).
- 4) K. Murayama, K. Kimura and T. Ninomiya, *Solid State Commun.* **36**, 349 (1980).
- 5) B. T. Kolomiets, T. N. Mamontova and A. A. Babaev, *J. Non-Crystalline Solids* **4**, 289 (1970).
- 6) G. S. Higashi and M. Kastner, to be published.
- 7) F. Mollot, J. Cernogora and C. Benoit a la Guillaume, *Phys. Status Solidi A*, **21**, 281 (1974).
- 8) R. A. Street, I. G. Austin, T. M. Searle and B. A. Smith, *J. Phys. C* **7**, 4185 (1974).
- 9) M. A. Bösch, R. W. Epworth and D. Emin, *J. Non-Cryst. Solids* **40**, 587 (1980).
- 10) K. Murayama and M. A. Bösch, *Phys. Rev. B* **23** (1981), to be published.
- 11) J. R. Zakis and H. Fritzsche, *Phys. Status Solidi b*, **64**, 123 (1974).
- 12) R. A. Street, *Adv. Physics* **25**, 397 (1976).