

Transient Characteristics of Luminescence from CdS-Doped Glass

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Time-resolved luminescence spectra were measured at 300 K and 77 K in CdS-doped glass under N₂ laser excitation. Transient characteristics of luminescence were affected by trapping and detrapping of electrons with trapping states. The experimental results were in agreement with calculated results based on a four-level system.

KEYWORDS: semiconductor-doped glass, CdS, photoluminescence,
time-resolved spectrum

Semiconductor-doped glasses have attracted much attention because of potential applications to nonlinear optical signal processing with fast response time. The dynamics of excess carriers in these materials have been reported by many authors. However, these results are diversified. For example, Yao et al.¹⁾ reported fast response time (less than 16 ps), and Tomita et al.²⁾ reported a fast (440 ps) and slow (more than 2 μ s) response time in CdSSe-doped glasses. We report on measurements of luminescence decay time of CdS-doped glass to investigate the origin of these differences.

The sample investigated was a glass filter (Toshiba Y-47). The Y-47 filter contains CdS microcrystals but does not contain CdSSe microcrystals. Luminescence spectra were measured, using the following apparatus, at 300 K and 77 K. The excitation source was a pulsed N₂ laser (Laser Photonics LN120; $\lambda = 337.1$ nm, pulse duration = 300 ps, repetition rate = 7 Hz). The laser beam was set at an angle of about 40° off the normal incidence to the surface of the sample and was focused on a spot about 1 mm² in area by a quartz lens (focal length $f = 150$ mm). The peak intensity of the laser light on the sample was about 50 kW/cm² (photodarkening was not observed at this excitation intensity). The luminescence was collected normal to the sample surface and was focused on the end of an optical fiber by a glass lens ($f = 70$ mm). The luminescence was then led to the entrance slit of a 27-cm monochromator (Jarrell-Ash Monospec 27). Luminescence spectra were measured with an optical multichannel analyzer (Princeton Instruments D/SIDA- 700).

Figure 1 shows the time-resolved luminescence spectra of CdS-doped glass at 300 K. Spectra were measured with the gate time $t_g = 50$ ns. Two bands are observed at 450 nm and 600 nm. The 450-nm band may be attributed to the band-to-band-type transition and the 600-nm band to the trapping state-to-band-type transition. While the 600-nm band is not so dominant at a short delay time, the relative intensity of the 600-nm band increases with increasing delay time.

Figure 2 shows luminescence intensities at 450 nm and 600 nm as a function of the delay time at 300 K. The decay rate of the 450-nm band becomes slower with increasing delay time and reaches a decay rate similar to that of the 600-nm band for $t_d \geq 1.3$ μ s. The similar decay rates of these bands for $t_d \geq 1.3$ μ s suggest that the electrons in the trapping states are thermally excited to the conduction sublevel. The detrapping of

trapped electrons has been proposed by Eychmüller et al. in quantum-sized CdS colloids.³⁾ The trapping states function as a reservoir for electrons and lead to a long decay time.

Detrapping is expected to become inefficient with decreasing temperature. Figure 3 shows luminescence intensities at 450 nm and 600 nm as a function of the delay time at 77 K. The decay rate of the 450-nm band at 77 K is faster than that at 300 K, and the decay rate of the 600-nm band at 77 K is slower than that at 300 K. However, the decay rate of the 450-nm band becomes slower with time, even at 77 K. This result is explained by considering the four-level system shown in Fig. 4. The deep trapping state is related to the 600-nm band. Although the electrons in the deep trapping state are not thermally excited to the conduction sublevel at 77 K, the electrons in the shallow trapping state are thermally excited to the conduction sublevel.

The trapping states probably originate from surface states of CdS microcrystals. The trapping states are thought to be distributed according to the size distribution of microcrystals. The broad luminescence band peaking at about 600 nm probably arises from the distributed trapping states. We consider the shallow and deep trapping states instead of the distributed states for simplicity.

The densities of electrons at the conduction sublevel and the trapping states are calculated as a function of time using the rate equations based on the four-level system in Fig. 4. The calculated results are solid curves in Figs. 2 and 3. The density of electrons at the conduction sublevel corresponds to the intensity of the 450-nm band, and that at the deep trapping state to that of the 600-nm band. The calculated results are in agreement with the experimental results, except for the discrepancy in the 600-nm band at $t_d \leq 0.3 \mu\text{s}$. This discrepancy is improved by using faster trapping rates. In a real system, the values of k_{st} and k_{dt} are possibly larger than those used in the present calculation. This difference in the trapping rates may be due to the simplification of the trapping states.

Trap depth is estimated using the Arrhenius equation. The detrapping rate is³⁾

$$k = 10^{13} \exp(-E/k_B T), \quad (1)$$

where E is the trap depth. If we set $E = 404 \text{ meV}$ for the deep trapping state, we obtain $k = 1.6 \times 10^6 \text{ s}^{-1}$ at 300 K and $3.8 \times 10^{-14} \text{ s}^{-1}$ at 77 K. These results are in agreement with

the values of k_{dd} at 300 K and 77 K. On the other hand, the difference in photon energy between the 450-nm band and the 600-nm band is 690 meV, which is higher than the trap depth, $E = 404$ meV. This result indicates that the 600-nm band may be due to a donor-acceptor-type recombination. Trap depth of the shallow trapping state is estimated using eq. (1). If we set $E = 100.7$ meV, we obtain $k = 2.6 \times 10^6 \text{ s}^{-1}$ at 77 K. Thus the trap depth is about 100 meV.

Yao et al.¹⁾ and Tomita et al.²⁾ observed fast response; however, we did not. This may be due to the detrapping effect and the low time resolution of the experimental apparatus. The extremely fast response reported by Yao et al.¹⁾ is probably due to a photodarkening effect.⁴⁾

In summary, time-resolved luminescence spectra of CdS-doped glass are reported. The decay rate of luminescence caused by the band-to-band-type transition becomes slower due to the detrapping of electrons from the trapping states. Reduction of the density of trapping states may lead to fast response.

References

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Figure captions

Fig. 1. Time-resolved luminescence spectra of CdS-doped glass. Peak intensities are normalized.

Fig. 2. Luminescence intensities at 450 nm and 600 nm as a function of the delay time at 300 K. Solid curves are calculated results.

Fig. 3. Same as Fig. 2 but for 77 K.

Fig. 4. Scheme of luminescence. C: conduction sublevel, V: valence sublevel, ST: shallow trapping state, DT: deep trapping state. Rate constants are as follows: $k_f = 5.4 \times 10^6 \text{ s}^{-1}$ (300 K) and $7.6 \times 10^6 \text{ s}^{-1}$ (77 K), $k_{st} = 4 \times 10^6 \text{ s}^{-1}$, $k_{sd} = 4 \times 10^6 \text{ s}^{-1}$ (300 K) and $2.6 \times 10^6 \text{ s}^{-1}$ (77 K), $k_s = 6 \times 10^5 \text{ s}^{-1}$, $k_{dt} = 1.8 \times 10^6 \text{ s}^{-1}$, $k_{dd} = 1.6 \times 10^6 \text{ s}^{-1}$ (300 K) and 0 s^{-1} (77 K), $k_d = 5 \times 10^5 \text{ s}^{-1}$.

Fig. 1

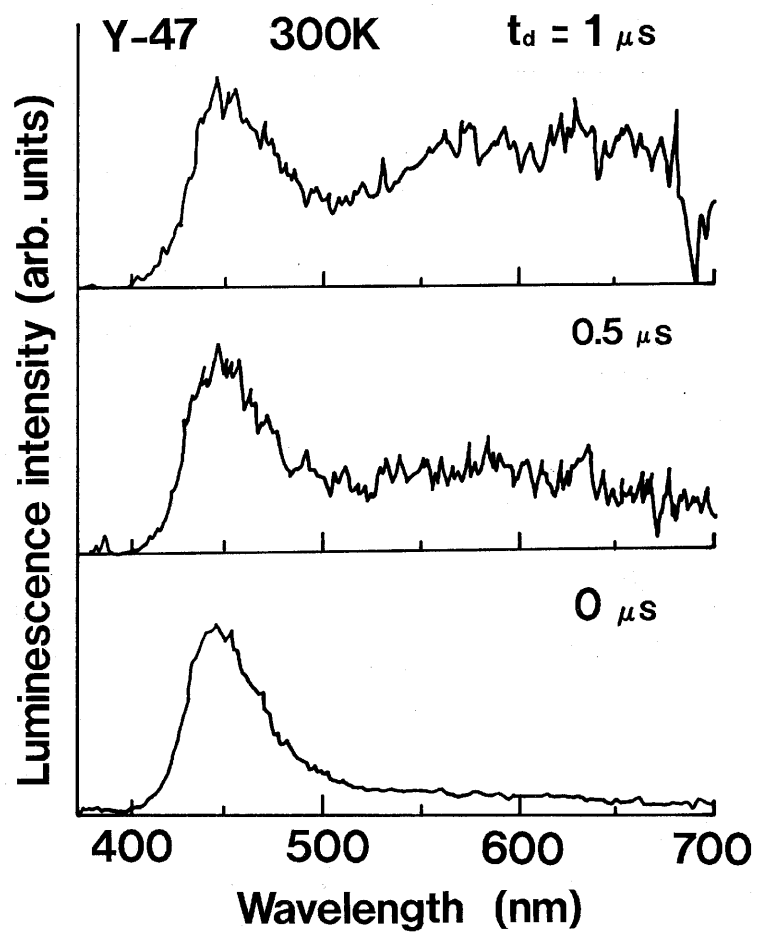


Fig. 2

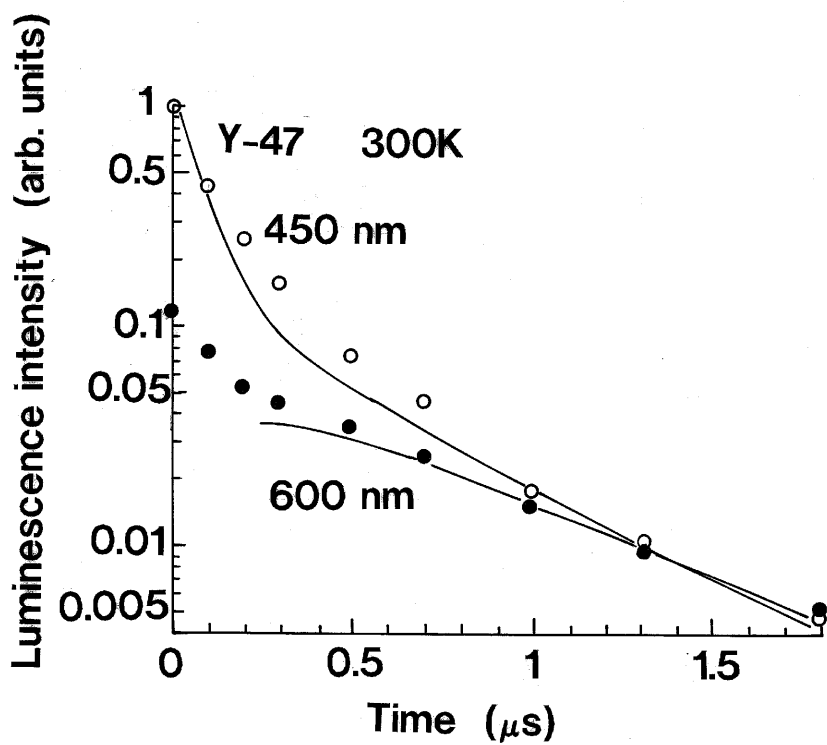


Fig. 3

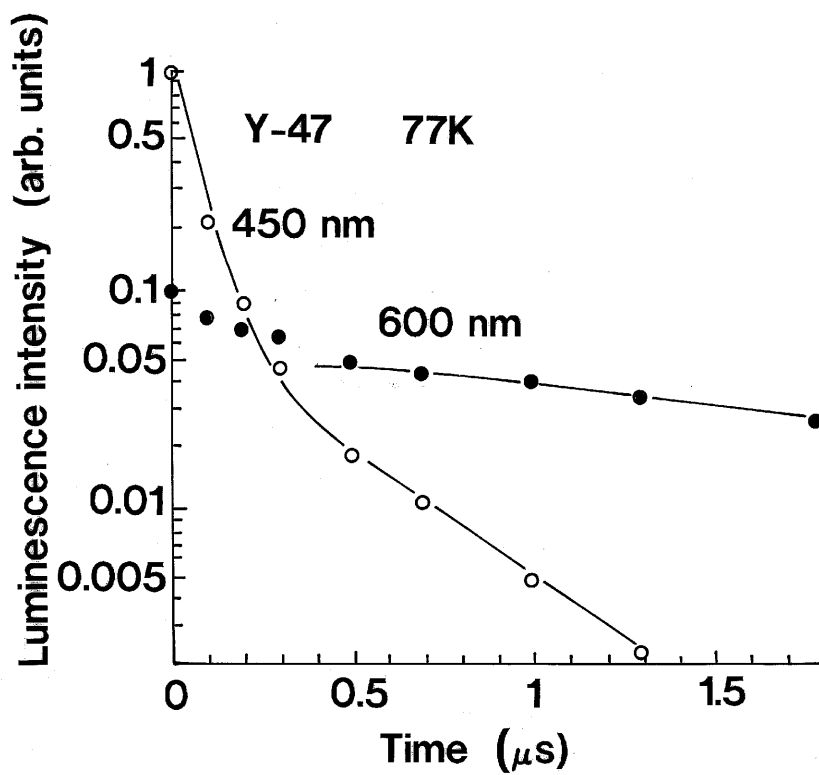


Fig. 4

