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Thermoluminescence of X-Ray-Irradiated CdS-Doped Glass

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Thermoluminescence has been observed in X-ray-irradiated CdS-doped glass. The intensity of thermoluminescence is proportional to the X-ray dose up to 10 Gy. The intensity of thermoluminescence for Asahi Y-44 is approximately 0.5% of that of phosphor for a commercial radiation dosimeter: MSO-S (Mg_2SiO_4:Tb). Photofading of Y-44 is markedly lower than that for MSO-S.

KEYWORDS: semiconductor, nanocrystal, X-ray irradiation, thermoluminescence, radiation dosimeter

Thermoluminescence is observed in rare-earth-doped phosphors and used for radiation dosimetry.[1] Thermoluminescence was also observed in CdS-doped glasses, which were exposed to intense light.[2–4] CdS-doped glass contains nanocrystals of CdS in glass. Thermoluminescence is explained by the following process. Photogenerated electrons in CdS nanocrystals migrate into the glass, and are trapped in the glass matrix. Photogenerated holes remain in CdS nanocrystals. When the sample is heated, trapped electrons in the glass are considered to be excited by thermal energy and recombine radiatively with holes in CdS nanocrystals. In previous papers,[4,5] we reported that thermoluminescence was also observed in X-ray irradiated CdS-doped glasses. Here, we report the intensity of thermoluminescence as a function of X-ray dose and photofading characteristics.

The sample investigated was commercial CdS-doped filter glass, Asahi Y-44. The absorption edge of this glass was approximately 430 nm. The concentration of CdS was approximately 0.4 wt%.[6] The size of CdS nanocrystals was approximately 3 nm.[7] The glass was exposed to X-ray from an X-ray source (Hitachi Medico MBR-1520R; W target, 150 kV, 20 mA) at 300 K. Low-energy X-ray was eliminated using a filter, which is composed of an Al plate with a thickness of 0.5 mm and a Cu plate with a thickness of 0.1 mm. Effective X-ray energy was approximately 48 keV. Some samples were exposed to white light from a fluorescent lamp to investigate the photofading characteristics. Thermoluminescence was measured using a thermoluminescence dosimeter (TLD) reader (Kyokko 2500). The glow curve was recorded using a pen recorder. Thermoluminescence of phosphor for commercial TLD, Kyokko MSO-S (Mg_2SiO_4:Tb), was also measured for comparison. MSO-S is highly sensitive to X-ray and γ-rays.

Thermoluminescence measurements were performed by heating the irradiated sample to 770 K. The heating rate was 4 K/s. One glow peak is observed at 480 K.[3,5] From the glow curve, we evaluated the location of traps using the initial rise method.[1] The energy difference between the traps and the conduction band edge of glass, E, is 1 eV.[3] Since glass is an amorphous material, the traps are thought to be distributed in energy. The value of $E = 1$ eV indicates the position of the traps nearest to the conduction band of glass. The intensity of thermoluminescence for Y-44 is approximately 0.5% of that for MSO-S. In the previous paper,[5] we reported that the intensity of thermoluminescence for Y-44 was

approximately 5% of that for MSO-S. The possible origin of the difference in the intensity of thermoluminescence is the difference in X-ray energy. In the previous study,[5] we used an X-ray diffractometer as an X-ray source. Energy of X-ray from the diffractometer was 8 keV (Cu Kα line). If X-ray energy is lower than 20 keV, X-ray is absorbed by the glass capsule for MSO-S. Consequently, the intensity of thermoluminescence decreases. Since Y-44 does not have a glass capsule, the intensity of thermoluminescence may be relatively high for low-energy X-ray.

The intensity of thermoluminescence was measured as a function of X-ray dose. Figure 1 shows the result. The intensity of thermoluminescence is proportional to X-ray dose up to 10 Gy, and supralinearity is observed above 10 Gy. Therefore, the upper limit of the measurement range is 10 Gy. The upper limit is 10 times larger than that for MSO-S.

If the X-ray irradiated sample is exposed to light, the trapped electrons in glass are excited by photon energy and recombine with holes in CdS nanocrystals. Thus, the intensity of thermoluminescence may decrease (photofading). If photofading is high, samples must be treated in a darkroom. In order to investigate the degree of photofading, Y-44 was exposed to white light from the fluorescent lamp. X-ray doses are 0, 0.1, 1 and 10 Gy. Light intensity is 9000 lx, and irradiation durations are 3, 6, 12 and 24 h. The intensity of thermoluminescence decreases after exposure to light for samples with X-ray doses of 1 and 10 Gy as shown in Fig. 2. On the other hand, the intensity of thermoluminescence decreases initially, and then increases for the sample with X-ray dose of 0.1 Gy. The intensity of thermoluminescence increases for the sample without X-ray irradiation. These results are explained by the following process. Light excites some of the trapped electrons to higher energy levels in glass, some of which migrate into CdS nanocrystals and recombine with holes in the nanocrystals. On the other hand, electrons in the valence band of CdS nanocrystals are excited to the conduction band upon light irradiation; they migrate into the glass, and are trapped in the glass matrix. Therefore, the rate equation for trapped electrons in glass is

$$dN/dt = A_1 J - A_2 N J, \tag{0.1}$$

where N is the number of trapped electrons in glass, A_1 and A_2 are rate constants, and

J is the light intensity. The solution of this equation is

$$N = [A_1 - (A_1 - A_2 N_0) \exp(-A_2 J t)]/A_2, \tag{0.2}$$

where N_0 is the value of N at $t = 0$ (before light irradiation). The value of N becomes A_1/A_2 for long-time exposure. This value is independent of N_0. This disagrees with the experimental result. We consider deeper traps. Since the energy levels of the traps are deep, the trapped electrons are not excited to the conduction band of glass upon light irradiation. The number of trapped electrons increases with irradiation time, since electrons are supplied from semiconductor nanocrystals. Therefore, the revised solution is

$$N = [A_1 - (A_1 - A_2 N_{01}) \exp(-A_2 J t)]/A_2 + N_{02} + A_3 J t, \tag{0.3}$$

where A_3 is the rate constant, N_{01} is the number of trapped electrons in the shallow traps and N_{02} is that in the deep traps at $t = 0$. Curves in Fig. 2 show the calculated results. The results are in agreement with the experimental results. We observed that the glow peak shifted to a higher temperature after light irradiation. This is consistent with the assumption, that two types of traps exist.

The intensity of thermoluminescence after light irradiation for 10 min is approximately 50% of that before irradiation for MSO-S with X-ray dose of 1 Gy. Therefore, photofading of Y-44 is markedly less than that of MSO-S, and Y-44 can be treated in a lighted room. On the contrary, thermal fading of Y-44 is more than that of MSO-S. We measured the intensity of thermoluminescence of Y-44, which was exposed to X-ray with a dose of 1 Gy and stored in the dark for four weeks at 300 K. The intensity of thermoluminescence after storage is approximately 80% of that before storage. On the other hand, thermal fading was not observed for MSO-S. This is considered to be due to the difference in the location of traps. Since the temperature of the glow peak for MSO-S (500 K) is higher than that for Y-44 (480 K), the energy difference between the traps and the conduction band edge for MSO-S is considered to be larger than that for Y-44.

A thermoluminescence dosimeter can be used repeatedly after thermal annealing. Y-44 is also reusable. However, an increase in the intensity of thermoluminescence was observed in the samples which were exposed to X-ray with a dose of higher than about 10 Gy. This

is considered to be due to the creation of defect centers, which act as traps, by X-ray irradiation.

We attempted to use Y-44 as a dosimeter. Y-44 and MSO-S were placed in baggage and exposed to X-ray from the baggage inspecting apparatus at the Yamaguchi-Ube Airport and Tokyo-Haneda Airport. The intensities of thermoluminescence are 0.5 for Y-44 and 17.5 for MSO-S after inspection at the Yamaguchi-Ube Airport. The X-ray dose measured by MSO-S is 29 μGy. The intensities of thermoluminescence are 0.8 for Y-44 and 22.5 for MSO-S after inspection at the Yamaguchi-Ube Airport and Tokyo-Haneda Airport. The X-ray dose is 37 μGy. However, these values include contribution from natural radiation, 21 μGy. Consequently, the net X-ray dose from one baggage inspecting apparatus is 8 μGy. If X-ray energy is lower than 20 keV, the intensity of thermoluminescence decreases, and the value of the X-ray dose is underestimated. The intensity of thermoluminescence for Y-44 is approximately 4% of that for MSO-S. The relatively high intensity of thermoluminescence for Y-44 suggests that the energy of X-ray from the baggage inspecting apparatus may be lower than that from the X-ray source (MBR-1520R).

In summary, thermoluminescence has been observed in X-ray irradiated CdS-doped glasses. The intensity of thermoluminescence is proportional to X-ray dose up to 10 Gy. The intensity of thermoluminescence for Asahi Y-44 is approximately 0.5% of that for phosphor for a commercial dosimeter, MSO-S. Since the lower limit of X-ray detection is 1 μGy for MSO-S, that for Y-44 is approximately 0.1 mGy. Photofading characteristics of Y-44 are explained by the model, which considers detrapping of trapped electrons and trapping of electrons from semiconductor nanocrystals.

References

1) S. W. S. McKeever: *Thermoluminescence of Solids*, eds. R. W. Cahn, E. A. Davis and I. M. Ward (Cambridge University Press, Cambridge, 1985).

2) V. Ya. Grabovskis, Ya. Ya. Dzenis, A. I. Ekimov, I. A. Kudryavtsev, M. N. Tolstoi and U. T. Rogulis: Sov. Phys. Solid State **31** (1989) 149.

3) T. Miyoshi, H. Sera, N. Matsuo and T. Kaneda: Jpn. J. Appl. Phys. **40** (2001) 2327.

4) T. Miyoshi, Y. Makidera, T. Kawamura, S. Kashima, N. Matsuo and T. Kaneda: Jpn. J. Appl. Phys. **41** (2002) 5262.

5) T. Miyoshi, Y. Makidera, T. Kawamura, N. Matsuo and T. Kaneda: J. Lumin. **102–103** (2003) 614.

6) T. Yanagawa, H. Nakano, Y. Ishida and K. Kubodera: Opt. Commun. **100** (1993) 118.

7) T. Miyoshi, H. Matsuki and N. Matsuo: Jpn. J. Appl. Phys. **34** (1995) 1837.

Figure captions

Fig. 1. Intensity of thermoluminescence of Y-44 as a function of X-ray dose.

Fig. 2. Photofading characteristics of Y-44. Light intensity is 9000 lx. Circles, squares and triangles indicate experimental results, and curves indicate calculated results. The parameters used for this calculation are as follows: $A_1 = 66$, $A_2 = 1.1$, $A_3 = 24$, $J = 0.3$, $N_{01} = 28000$ for 10 Gy, 2800 for 1 Gy, 280 for 0.1 Gy and 0.4 for 0 Gy, $N_{02} = 8000$ for 10 Gy, 800 for 1 Gy, 80 for 0.1 Gy and 0.1 for 0 Gy.

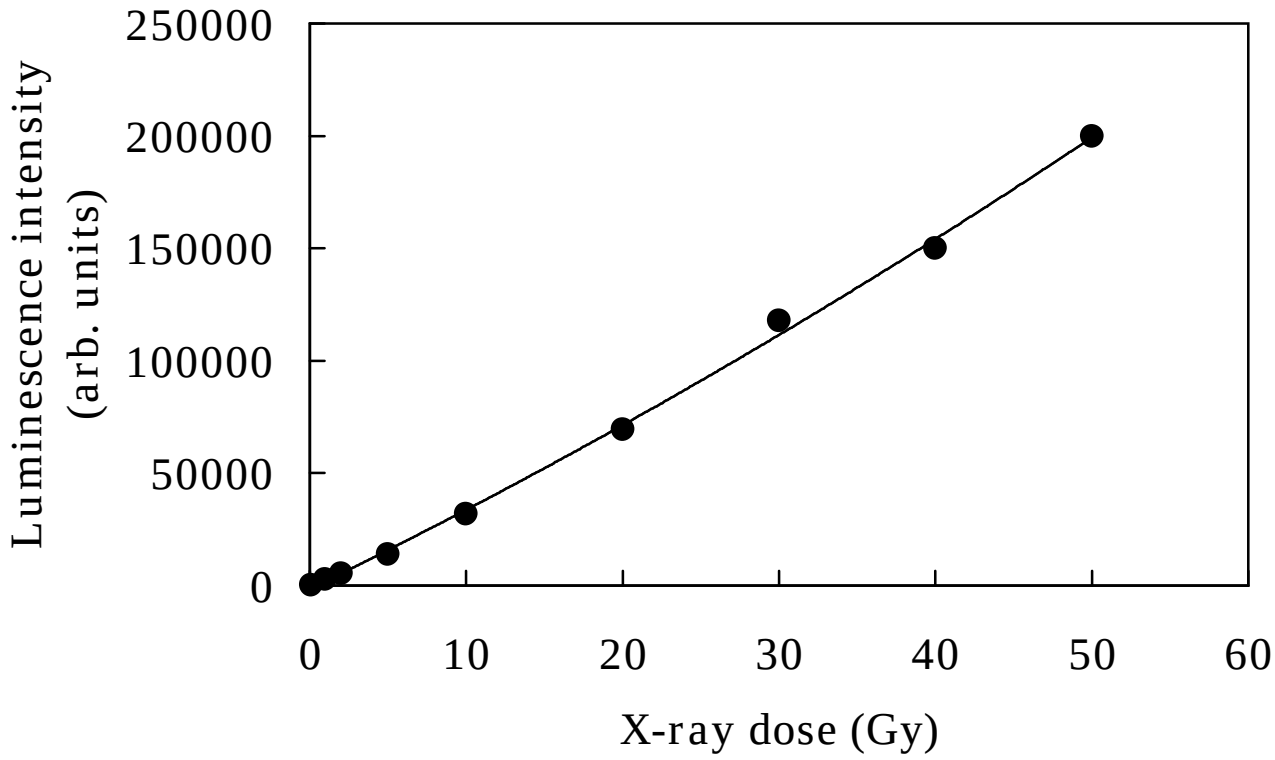
Luminescence intensity
(arb. units)
250000
200000
150000
100000
50000
0
0
10
20
30
40
50
60
X-ray dose (Gy)

Fig. 1

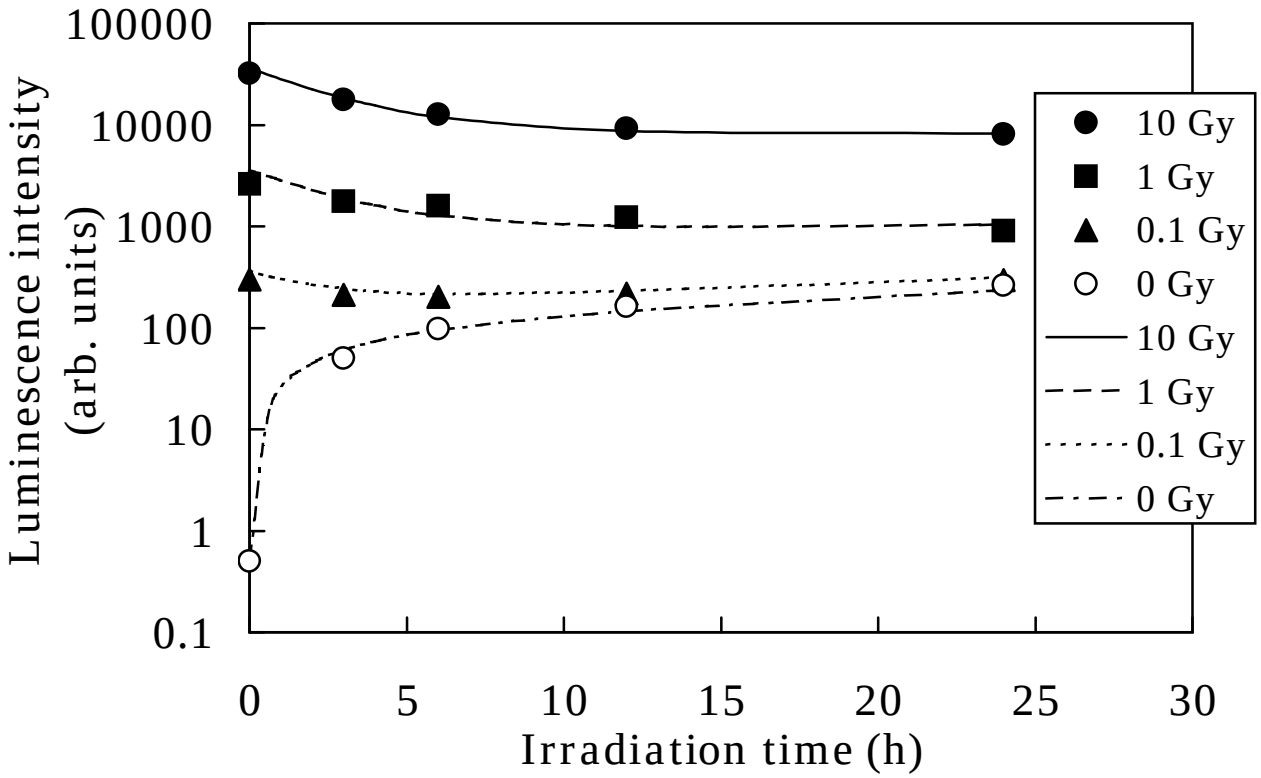
100000
10000
1000
100
10
1
0.1
Luminescence intensity
(arb. units)
0
5
10
15
20
25
30
Irradiation time (h)
10 Gy
1 Gy
0.1 Gy
0 Gy
10 Gy
1 Gy
0.1 Gy
0 Gy

Fig. 2