J Mater Sci (2008) 43:203–206
DOI 10.1007/s10853-007-2141-5

Thermoluminescence and induced absorption in X-ray-irradiated CdS-doped glasses

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Received: 7 June 2007 / Accepted: 4 September 2007 / Published online: 29 September 2007

Abstract Thermoluminescence of X-ray-irradiated CdS-doped glasses has been measured, and relation between thermoluminescence and induced absorption in the X-ray-irradiated CdS-doped glasses has been investigated. The effect of thermal annealing and the X-ray energy dependence of thermoluminescence is different from that on the induced absorption. Therefore, defects, which are responsible for thermoluminescence, are considered to be different from those responsible for the induced absorption.

Introduction

Photo-induced changes in the optical properties have been observed in semiconductor-doped glasses [1]. Induced absorption has been observed in laser-irradiated semiconductor-doped glasses [2]. This phenomenon is called photodarkening. Grabovskis et al. [3] reported that the induced absorption and thermoluminescence were observed in the X-ray-irradiated glasses [3]. However, they showed neither glow curve of thermoluminescence above room temperature nor relation between the induced absorption and thermoluminescence.

In previous articles, we reported thermoluminescence of laser- and X-ray-irradiated CdS-doped glasses above room temperature [4, 5] and the induced absorption in X-ray-irradiated CdS-doped glass [6]. However, relation between the induced absorption and thermoluminescence remained unclear. Here, we report relation between the induced absorption and thermoluminescence in the CdS-doped glasses.

Experimental procedure

The sample mainly investigated was commercial CdS-doped filter glass, Asahi Y-44. The optical absorption edge of the glass was approximately 430 nm. The size of the CdS nanocrystals was approximately 3 nm. The size of the sample was 10 mm in width and length and 2.5 mm in thickness for transmission measurement, and 2 mm in width, 2.5 mm in thickness and 10 mm in length for thermoluminescence and electron spin resonance (ESR) measurement. The concentration of CdS was approximately 0.4 wt.% [7]. Other CdS-doped glasses, Asahi L-42, Y-46 and Y-48, and undoped glasses, UV-29, UV-31, UV-33, UV-35, UV-37, and L-39, were also investigated for comparison. These undoped glasses do not contain semiconductor nanocrystals. The composition of these glasses was 70% SiO_2, 10% Na_2O, 10% ZnO, 6% K_2O, and 3% B_2O_3 [7].

The glass was exposed to X-rays from an X-ray source (Hitachi Medico MBR-1520R, W target, 150 kV, 20 mA)

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at 300 K. The effective X-ray energy was 10 keV. When low energy X-rays were eliminated using a filter, which was composed of an Al plate and a Cu plate, effective X-ray energy increased. The effective X-ray energies were 33 keV using an Al plate with a thickness of 1.0 mm, 48 keV using both an Al plate with a thickness of 0.5 mm and a Cu plate with a thickness of 0.1 mm, and 65 keV using both an Al plate with a thickness of 0.5 mm and a Cu plate with a thickness of 0.3 mm. The filter mainly used was composed of an Al plate with a thickness of 0.5 mm and a Cu plate with a thickness of 0.1 mm, and consequently the effective X-ray energy was 48 keV. Isochronal annealing was performed by heating the irradiated samples at temperatures varying from 50 to 350 °C. The annealing time was 15 min.

Thermoluminescence was measured using a thermoluminescence dosimeter (TLD) reader (Kasei Optonix 2500). Thermoluminescence was detected by a photomultiplier through optical filter, Hoya C500S, to reduce the effect of thermal radiation. The filter transmits light with wavelengths in the range of 340–620 nm. Therefore, the intensity of thermoluminescence is integrated in the range of wavelengths. Thermoluminescence measurements were performed by heating the irradiated sample up to 500 °C. The heating rate was 4 °C/s. The glow curve was recorded using a pen recorder. Transmission spectra were measured using a spectrophotometer (JASCO V-550) at 300 K. ESR spectra were measured using an X-band ESR spectrometer (Bruker ELEXSYS E-500) at 300 K using a cylindrical cavity operating at 9.8 GHz with a 100 kHz modulation frequency. The microwave power was 10 mW, and modulation amplitude was 0.1 mT. The response time constant was 0.16 s with the field-sweeping rate of 20 mT/84 s.

Results and discussion

Figure 1 shows the transmission spectra of the X-ray-irradiated and unirradiated CdS-doped glass, Y-44, and the undoped glass, UV-31, at 300 K. Decrease in the transmittance (the induced absorption) is observed in the irradiated glasses around their absorption edges.

Figure 2 shows glow curves of thermoluminescence of the X-ray-irradiated CdS-doped glass, Y-44, and the undoped glass, UV-31. One glow peak is observed at 210 °C in Y-44 and at about 300 °C in UV-31. Similar glow curves with peak at 210 °C were observed in other CdS-doped glasses, Asahi L-42, Y-46, and Y-48. On the other hand, the glow curves observed in other undoped glasses, UV-29 and UV-33, showed a peak around 300 °C. Grabovskis et al. [3] reported that glow curve of thermoluminescence at lower temperatures (lower than 250 K) in CdS-doped glass was the same as that in undoped glass.

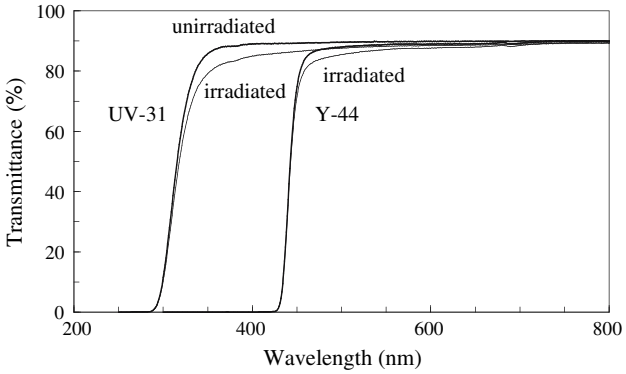

Fig. 1 Transmission spectra of X-ray-irradiated and unirradiated CdS-doped glass, Y-44, and undoped glass, UV-31, at 300 K. Thick curves indicate spectra for unirradiated samples and thin curves for irradiated samples. The X-ray dose is 20 Gy, and the effective X-ray energy is 48 keV

This indicates that shallower traps are responsible for thermoluminescence in both glasses. On the contrary, the glow curve of the CdS-doped glass above room temperature is different from that of the undoped glass.

In order to examine the origin of the difference in glow curves, we measured ESR spectra of Y-44 and UV-31. Figure 3 shows the ESR spectra of these two glasses at 300 K. Two signals are observed in Y-44 at $g = 2.01$ (350 mT) and $g = 1.99$ (353 mT). On the other hand, a signal is observed in UV-31 at $g = 2.01$. Therefore, the glow peak at 210 °C is considered to be related to the ESR signal at $g = 1.99$, and that at about 300 °C to the ESR signal at $g = 2.01$. The ESR signal at $g = 1.99$ vanishes by the thermal annealing at 200 °C [8]. The ESR signal at $g = 1.99$ is attributable to a trapped electron on a Cd^{2+} ion in the glass matrix, and the signal at $g = 2.01$ to oxygen hole center [8].

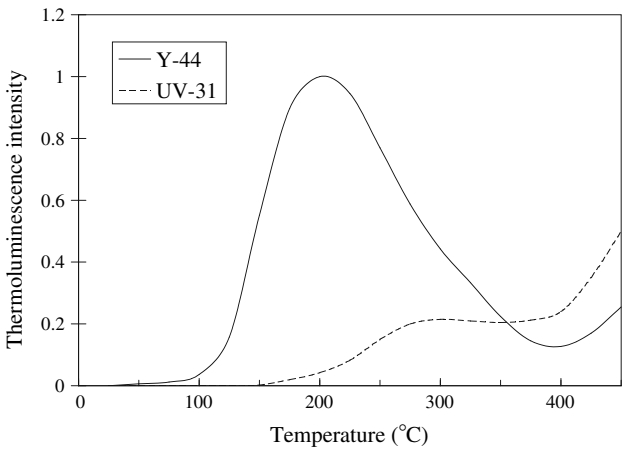

Fig. 2 Glow curves of thermoluminescence of X-ray-irradiated CdS-doped glass, Y-44, and undoped glass, UV-31. The X-ray dose is 1 Gy, and the effective X-ray energy is 48 keV

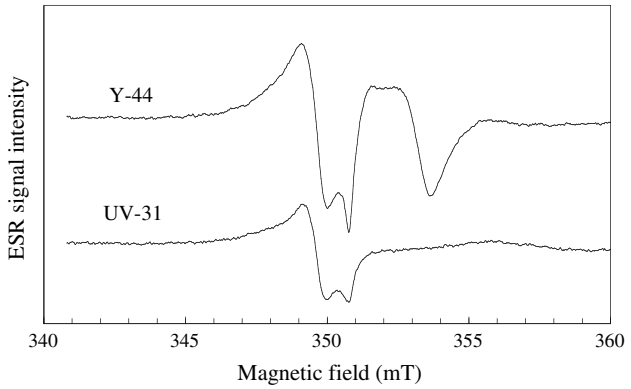

Fig. 3 ESR spectra of X-ray-irradiated CdS-doped glass, Y-44, and undoped glass, UV-31, at 300 K. The X-ray dose is 40 Gy, and the effective X-ray energy is 48 keV

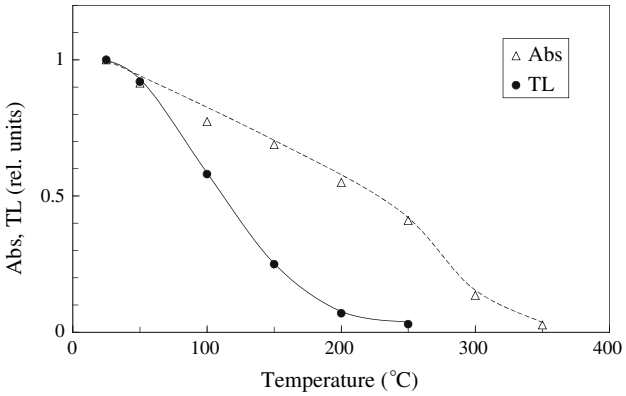

Fig. 4 Isochronal annealings of Y-44. The X-ray dose is 1 Gy for thermoluminescence and 20 Gy for the induced absorption. The effective X-ray energy is 48 keV. The annealing time is 15 min. The data points for the induced absorption are from Ref. [6]. Curves were drawn through the data points as visual guides

The ESR signals at $g = 1.99$ and 2.01 are observed in other CdS-doped glasses, L-42, Y-46 and Y-48. The ESR signal at $g = 2.01$ is observed in other undoped glasses, UV-29 and UV-33. On the contrary, the ESR signal is not observed in the undoped glasses, UV-35, UV-37 and L-39. Thermoluminescence is very weak in these glasses. On the other hand, the induced absorption is observed in UV-35 and UV-37. The induced absorption in UV-37 is larger than that in UV-31, and induced absorption in UV-35 is approximately 50% of that in UV-31. These results indicate that thermoluminescence is correlated with the ESR signals, and it is not correlated with the induced absorption in the undoped glasses.

Partial correlation between thermoluminescence and the induced absorption is observed in the CdS-doped glasses. Relative thermoluminescence intensity in Y-46 to Y-44 is 0.69, and the relative induced absorption in Y-46 to Y-44 is 0.7. However, relative thermoluminescence intensity in L-42 is 0.42, and the relative induced absorption in L-42 is 1.46. In order to examine correlation between thermoluminescence and the induced absorption in CdS-doped glasses, we have investigated the effect of thermal annealing and X-ray energy dependence of thermoluminescence and the induced absorption.

The isochronal annealings of Y-44 for temperatures ranging from 50 to 350 °C are shown in Fig. 4. Solid circles show data for the thermoluminescence, and open triangles for the induced absorption. The data points for the induced absorption are from Ref. [6]. Signal intensity decreases with increasing temperature. The intensity of thermoluminescence decreases to 60% of its original value at 100 °C, and it almost vanishes at 250 °C. The effect of thermal annealing on the ESR signals [8] is almost the same as that of thermoluminescence. On the other hand, the induced absorption decreases to about 80% of its original value at 100 °C, and it almost vanishes at 350 °C. Therefore, the effect of thermal annealing on thermoluminescence is different from that on the induced absorption.

The X-ray energy dependence of thermoluminescence of Y-44 was examined and compared with that of the induced absorption. Figure 5 shows the result. The X-ray dose is 1 Gy for thermoluminescence (solid circles) and 20 Gy for the induced absorption (open triangles). The data points for the induced absorption are from Ref. [6]. The intensities are normalized. Thermoluminescence decreases with decreasing effective X-ray energy. The X-ray energy dependence of thermoluminescence is different from that of the induced absorption. On the other hand, X-ray energy dependence of the ESR signal intensity [8] is the same as that of thermoluminescence.

The effect of thermal annealing and the X-ray energy dependence of thermoluminescence is different from that

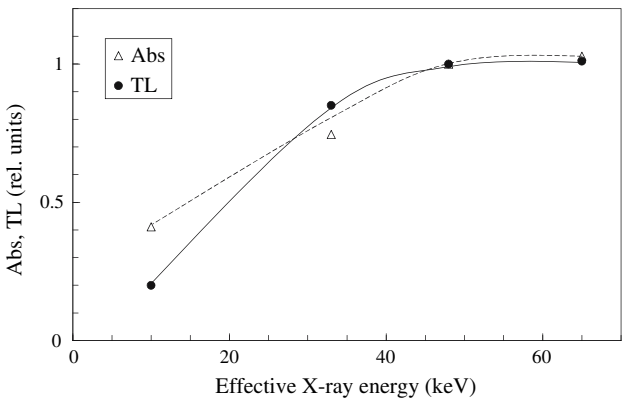

Fig. 5 Intensities of thermoluminescence and the induced absorption of Y-44 as a function of effective X-ray energy. The intensities are normalized. The X-ray dose is 1 Gy for thermoluminescence and 20 Gy for the induced absorption. The data points for the induced absorption are from Ref. [6]. Curves were drawn through the data points as visual guides

of the induced absorption. Therefore, defects, which are responsible for thermoluminescence, are considered to be different from those responsible for the induced absorption. The induced absorption is attributable to intrinsic hole radiation color centers H_4^+ in the glass matrix [6, 9].

The CdS-doped glasses are possibly used for radiation dosimetry with thermoluminescence, ESR, and the induced absorption. The lower limit of X-ray detection is approximately 1 mGy for thermoluminescence, 500 mGy for ESR and the induced absorption. Therefore, sensitivity of X-ray detection is highest for thermoluminescence. However, repeated measurement is impossible for thermoluminescence, while it is possible for both ESR and the induced absorption.

Conclusion

Relation between thermoluminescence and induced absorption in X-ray-irradiated CdS-doped glasses has been investigated. Defects, which are responsible for thermoluminescence, are considered to be different from those responsible for the induced absorption. Thermoluminescence is attributable to a trapped electron on a Cd^{2+} ion in a glass matrix and to oxygen hole center, and the induced absorption to the intrinsic hole radiation color centers H_4^+ in the glass matrix.

Acknowledgements This work was performed using the spectrophotometer in the laboratory of Professor K. Kasatani. The authors are grateful to Professor K. Kasatani. This work is partly supported by a Grant-in-Aid (No. 17560048) for Scientific Research (C) from Japan Society for the Promotion of Science.

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