Photostimulated Long-lasting Phosphorescence in Rare-earth-doped Glasses

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Tb^{3+}-doped glass sample emits bright and long-lasting phosphorescence after irradiation by an 800-nm femtosecond pulsed laser. Long-lasting phosphorescence is observed once again after further excitation by 365-nm UV light when the femtosecond laser-induced long-lasting phosphorescence cannot be detected.

Photostimulated luminescence and long-lasting phosphorescence phenomena have been observed in various rare-earth-doped glasses.[1–4] These glasses are expected to become a new family of materials for X-ray sensors, optical memory and optical displays.

In this letter, we report on a new phenomenon in a rare-earth-doped transparent glass sample. The glass sample showed bright and long-lasting phosphorescence after irradiation by an 800-nm femtosecond laser. Long-lasting phosphorescence was observed once again after further excitation by 365-nm UV light when the femtosecond laser-induced long-lasting phosphorescence could not be detected. We demonstrated three-dimensional data storage and read-out using the observed phenomenon.

The composition of the glass sample prepared was $60ZnO{\cdot}20B_2O_3{\cdot}20SiO_2{\cdot}0.1Tb_2O_3$ (mol%). Reagent-grade ZnO, B_2O_3, SiO_2, and Tb_3O_4 were used as the starting materials. Approximately 30-g batches were mixed and then melted in Pt crucibles at 1450 °C for 60 min in an ambient atmosphere; the melt was then quenched to room temperature. The glass sample was then cut and polished. In our study, we employed a regeneratively amplified 800 nm Ti:sapphire laser to emit 120 fs, 1 kHz, mode-locked pulses. The laser beam, with an average power of 50 mW, was focused by a 10X objective lens with a numerical aperture of 0.30 on the interior of the glass sample with the help of an XYZ stage. The light intensity was 2.3×10^{15} W/cm^2. For the measurement of phosphorescence spectra and decay curves, the glass sample was first irradiated by the femtosecond laser. All of the measurements were carried out at room temperature except for the thermoluminescence curve.

We measured the photoluminescence, excitation and phosphorescence spectra of the glass sample. Emission peaks observed at 490, 547, and 584 nm can be ascribed to the $^5D_J \rightarrow {}^7F_{J'}$ ($J = 4$, $J' = 4$–6) transitions of the Tb^{3+} ions.[5] We also observed a broad peak at around 400 nm in the photoluminescence spectrum of the glass sample. The peak can be assigned to the active site associated with Zn^{2+} since the similar emission band was observed in a crystalline ZnO-embedded and Tb^{3+}-free glass sample.[6] After irradiation by the focused femtosecond laser, bright and long-lasting phosphorescence was observed for the glass sample in the dark after the removal of the activating light. The appearance of the femtosecond laser-induced phosphorescence was similar to that of the photoluminescence spectrum. All peaks could be assigned to the $^5D_J \rightarrow {}^7F_{J'}$ ($J = 3$, 4, $J' = 3$–6) transitions of Tb^{3+}. Though no long-lasting phosphorescence could be detected in the non-irradiated glass sample after excitation by 365-nm UV light, apparent long-lasting phosphorescence was observed once again in the femtosecond laser irradiated glass sample after the excitation by the 365-nm UV light when the femtosecond laser-induced long-lasting phosphorescence could not be detected. The appearance of the photostimulated long-lasting phosphorescence spectra was the same as that of the long-lasting phosphorescence spectrum.

Figure 1 shows the decay curve of the photostimulated long-lasting phosphorescence at 547 nm in the femtosecond laser-irradiated glass sample after the removal of the activating 365-nm UV light. The time dependence of the inverse of the photostimulated long-lasting phosphorescence intensity is also shown in Figure 1. The intensity of the phosphorescence decreases in inverse proportion to time, indicating the phosphorescence may be a decay process due to a heat-assisted tunneling effect.[7]

Figure 2 shows the thermoluminescence curves of the glass sample at a heating rate of 10°C/min. We observed a peak at 342 K in the thermoluminescence curve of the glass sample after irradiation by the femtosecond laser. The peak at 342 K disappeared and a peak at 405 K appeared in the glass sample 24 h after the removal of the femtosecond laser, when the femtosecond laser-induced long-lasting phosphorescence could not be detected. The peaks at both 342 K and 405 K can be assigned to the traps, in which the trapped electrons can and cannot be released by heat energy at room temperature, respectively. No

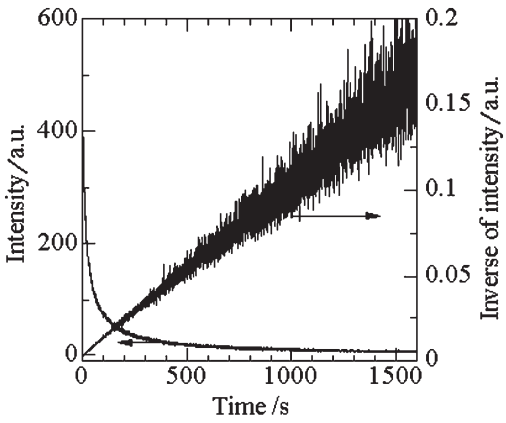

Figure 1. Decay curve of the photostimulated long-lasting phosphorescence at 547 nm in a femtosecond laser-irradiated Tb^{3+}-doped glass sample after the excitation by 365 nm UV light for 1 min.

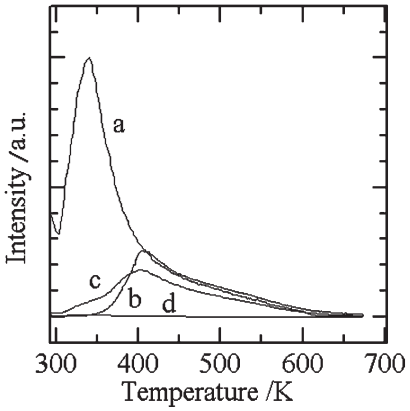

Figure 2. Thermoluminescence curves of a Tb^{3+}-doped glass sample. (a) upon the removal of the femtosecond laser. The laser irradiation duration was 2 min. (b) 24 h after the removal of the femtosecond laser. The laser irradiation duration was 2 min. (c) 24 h after the removal of the femtosecond laser, and further irradiated by 365 nm UV light for 2 min. (d) upon the removal of 365 nm UV light. The 365 nm UV light irradiation duration was 2 min.

peak was observed in the femtosecond laser-unirradiated glass sample, while a shoulder peak at 342 K was observed in the femtosecond laser-irradiated glass sample after the excitation by the 365 nm for 2 min. Therefore, after the excitation by the 365-nm UV light, some electrons trapped in deep traps were excited to high energy levels, and then retrapped by the shallow traps. The recombination of electrons released from shallow traps with trapped holes by heat energy resulted in the long-lasting phosphorescence at room temperature.

We observed a broad absorption band peaking at 400 nm in the wavelength region from 280 to 750 nm in the absorption spectra of the glass sample after irradiation by the femtosecond laser. The increased absorbance can be ascribed to, for instance, the absorption of electron-trapping centers in which electrons were trapped by oxygen ion vacancies associated with Zn^{2+}.[8] The induced absorption fading at room temperature agrees with the decay in the phosphorescence. We consider that the disappearance of defects is related to the decay of the phosphorescence at room temperature. After the excitation by the 365-nm UV light when the femtosecond laser-induced long-lasting phosphorescence could not be detected, no apparent spectral hole was observed near 365 nm in the absorption spectrum. Therefore, the excitation by 365-nm UV light resulted in the rearrangement of electrons and holes in traps induced by the femtosecond laser.

We suggest that free electrons and holes were formed in the glass sample through multiphoton process after irradiation by the femtosecond pulsed laser since the light intensity was sufficient to induce various nonlinear optical reactions. The electrons or holes were trapped by defect centers. Some of the electrons or holes were released by heat energy at room temperature, and recombined with holes or electrons trapped by other defect centers. Recombination of electrons and holes and energy transfer from the recombination centers to the rare-earth ions resulted in the characteristic rare-earth ion emissions. The hole or electron trap depth is broadly distributed and shallow, resulting in the long-lasting phosphorescence at room temperature. After the electrons or holes at shallow traps were all released by thermal energy at room temperature, then no long-lasting phosphorescence could be detected. However, electrons and holes in deep traps were excited to shallow traps, and rearrangement of the electrons and holes into shallow traps occurred during the excitation by the 365-nm UV light; therefore, photostimulated long-lasting phosphorescence was observed after the excitation by the 365-nm UV light at room temperature.

We drew a butterfly image into the glass sample with the femtosecond laser. The image contained many spots, and each spot was irradiated by the femtosecond laser for 1/63 s. (i.e. 8 pulses). After the femtosecond laser, the spot became gray and slightly decayed after 1 h, and then remained almost unchanged at room temperature. After keeping the sample in the dark for longer than two months, we could still clearly observe the butterfly image emitting long-lasting phosphorescence in the dark 30 min after the removal of the activating 365-nm UV light.

In conclusion, we observed photostimulated long-lasting phosphorescence in an infrared femtosecond laser-irradiated rare-earth-doped glass sample. We believe that the phenomenon has promising applications in the fabrication of three-dimensional optical displays, rewriteable three-dimensional optical memory devices with both an ultrahigh recording speed and ultrahigh storage density.

References

1 J. Qiu, Y. Shimizugawa, Y. Iwabuchi, and K. Hirao, *Appl. Phys. Lett.*, **71**, 759 (1997).
2 J. Qiu and K. Hirao, *Solid State Commun.*, **12**, 759 (1998).
3 J. Qiu, K. Miura, H. Inouye, Y. Kondo, T. Mitsuyu, and K. Hirao, *Appl. Phys. Lett.*, **73**, 1763 (1998).
4 M. Yamazaki, Y. Yamamoto, S. Nagahama, N. Sawanobori, M. Mizoguchi, and H. Hosono, *J. Non-Cryst. Solids*, **71**, 241 (1998).
5 A. Yamamoto, in "Handbook of Phosphors," ed. Keikoutai Dougakukai Ohm Press, Tokyo (1987), p. 138.
6 D. Ruter and A. W. Bauhofer, *Appl. Phys. Lett.*, **69**, 892 (1996).
7 I. F. Chang and P. Thioulouse, *J. Appl. Phys.*, **53**, 5873 (1982).
8 H. Kawazoe, R. Suzuki, S. Inoue, and M. Yamane, *J. Non-Cryst. Solids*, **111**, 16 (1989).

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