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Optically Stimulated Luminescence in Tm-Doped Calcium Fluoride Phosphor Crystal for Application to a Novel Passive Type Dosimeter

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An intense optically stimulated luminescence (OSL) with four emission bands in the wavelength range from 290 to 420 nm is observed for the first time in X-ray-irradiated Tm-doped CaF_2 (CaF_2:Tm) phosphor crystal. The OSL intensity increases almost linearly with increasing X-ray absorbed dose. Thermally stimulated luminescence (TSL) glow curves with four peaks are also observed in X-ray-irradiated CaF_2:Tm phosphor crystal. It is confirmed that the shape of the TSL glow curve in X-ray-irradiated CaF_2:Tm phosphor crystal is the same as that of a commercially available dosimeter (TLD-300). An OSL emission and stimulation mechanism of X-ray-irradiated CaF_2:Tm phosphor crystal is proposed.

1. Introduction

Similarly to the thermally stimulated luminescence (TSL) phenomenon, which is used for personal and environmental radiation dosimetry, the optically stimulated luminescence (OSL) phenomenon is based on the electron and/or hole traps and luminescence centers in storage phosphor materials. The ionizing radiation creates free electrons and holes that are trapped at the crystal lattice site or impurities in the phosphor

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materials. Detrapping of these electrons and holes requires energy, which, in the TSL process, is provided by heating the phosphor materials. In the OSL process, photons are absorbed from the stimulating light during detrapping transition and the free carriers created as a result recombine with luminescence centers, whereby photons from visible to infrared wavelengths are emitted. Since the density of trapped electrons and/or holes, that is, OSL intensity, is in most cases proportional to the dose of ionizing radiation, the storage phosphor materials with OSL can be used as a novel passive sensor for ionizing radiation for personal and environmental radiation monitoring.

Up to now, OSL materials, such as C-doped Al_2O_3[1,2] for personal, environmental, medical, and space dosimetry applications, BeO[3–5] for personal dosimetry, Tb-doped MgO[6] for personal dosimetry, Cu-doped SiO_2 (quartz crystal)[7,8] for optical fiber dosimetry, Sm:Ce-codoped *X*S (*X* = Mg, Ca, Sr)[9–11] for optical fiber dosimetry, Ce-doped CaF_2[12] for personal dosimetry, Eu-doped Ba*FX* (*X* = Br, Cl, I),[13–15] RbBr,[16] CsBr,[17] and K*X* (*X* = Br, Cl)[18–20] for personal dosimetry and two-dimensional X-ray imaging, and Sn-doped borate and phosphate glass for personal dosimetry,[21] have been investigated for a long time. Consequently, personal dosimeters using C-doped Al_2O_3 and BeO storage phosphors as well as two-dimensional X-ray imaging sensors using Eu-doped BaF*X*, Eu-doped CsBr for computed radiography are now commercially available. However, many problems must be solved, such as low OSL intensity in C-doped Al_2O_3 and BeO storage phosphors and degradation of OSL properties due to deliquescency in alkali halide phosphors.

By surveying possible phosphor materials, especially fluoride and glass phosphor materials, we found that Tm-doped CaF_2 (CaF_2:Tm) exhibits an efficient OSL and fairly good dosimetric properties. In this paper, the OSL characteristics in X-ray-irradiated CaF_2:Tm phosphor crystals are reported for the first time.

2. Experimental Procedure

Tm^{3+}-doped CaF_2 phosphor samples were fabricated using the conventional solidification method developed by Tokuyama Corporation.[22] Starting materials were prepared from the stoichiometric mixture of 99.9% pure CaF_2 and TmF_3 powders produced by Stella Chemifa Corporation. The Tm^{3+} concentration was varied from 0.1 to 10 mol%. The powder mixtures placed in a carbon crucible in a stainless steel chamber with a carbon resister were heated at 400 °C for 8 h in vacuum at around 10^{-2} Pa in order to remove trace oxygen. After baking at 400 °C in vacuum, the chamber was filled with high-purity Ar gas (5N) and CF_4 gas (5N) to restore ambient pressure. The crucible was then annealed up to the melting point of CaF_2, about 1430 °C, for 30 min. Prepared CaF_2 crystals were polished and then cut into 1 × 2 × 5 mm^3 pieces to measure luminescence properties such as PL, OSL, and TSL.

Optical properties such as PL and OSL were measured using a Hitachi F-4500 fluorescence spectrometer and optical absorption spectra using a Hitachi spectrophotometer (U-2000). X-ray irradiation was carried out using an X-ray tube with a Mo target operated at 60 kV and 35 mA.

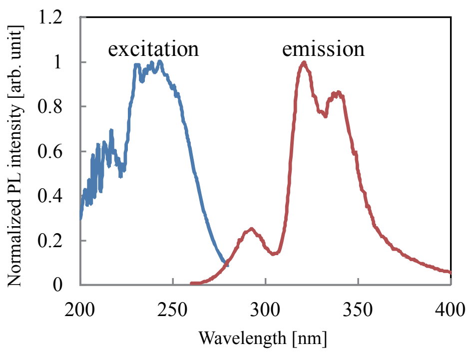
3. Results and Discussion

The CaF_2:Tm (0.1 mol%) phosphor sample without X-ray irradiation exhibits an efficient PL peak in the wavelength range from 290 to 420 nm. Figure 1 shows typical PL emission and excitation spectra. It can be seen from the figure that there are four emission bands at about 298, 340, and 350 nm, which correspond to internal Tm transitions.[23] These PL emission bands were observed when the CaF_2:Tm phosphor sample was excited with 220 and 240 nm light.

An intense OSL with several peaks in the wavelength range from 280 to 430 nm was observed when an X-ray-irradiated CaF_2:Tm phosphor sample was stimulated with about 500 and 600 nm light. Typical OSL emission and stimulation spectra are shown in Fig. 2. The OSL emission bands that coincide with the PL emission bands are assigned to inner ionic transitions of isolated Tm^{3+} ions occupying at cation (calcium ion) sites.

Figure 3 shows the dependence of the OSL spectra on X-ray irradiation dose in the absorbed dose range from 0.001 to 0.1 Gy. The OSL spectra as a function of X-ray absorbed dose in a high absorbed dose range from 1 to 10 Gy are shown in Fig. 4. It was found that the OSL intensity increases with increasing X-ray absorbed dose, as shown in Fig. 5. This result strongly suggests that the CaF_2:Tm phosphors can be used as the storage phosphor materials of the passive OSL dosimeter that can be applied to personal and environmental monitoring as well as computed radiography.

An intense TSL was also observed in the X-ray-irradiated CaF_2:Tm phosphor sample. Typical TSL glow curves of an X-ray-irradiated sample in a fairy low absorbed dose range from 0.0005 to 0.001 Gy are shown in Fig. 6. The TSL glow curves of an X-ray-irradiated phosphor sample in the absorbed dose range from 0.01 to 0.1 Gy are also shown in Fig. 7. It was found that the TSL intensity increases with X-ray absorbed dose, as shown in Fig. 8. The personal dosimeter using the TSL in CaF_2:Tm was first introduced in 1977[24] and sold by Bicron-NE (Harshow) as TLD-300. The TSL glow curve



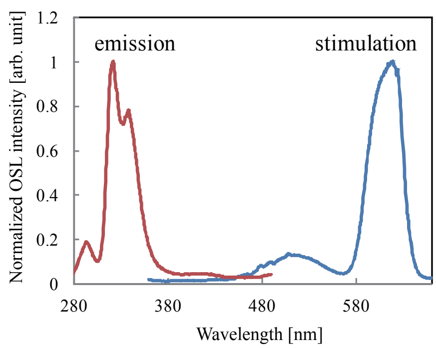
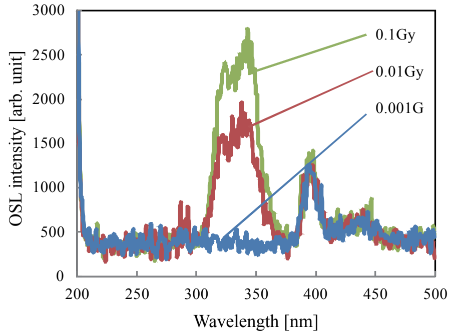


Fig. 1 (left). (Color online) Typical PL emission and excitation spectra of CaF_2:Tm phosphor sample without X-ray irradiation.

Fig. 2 (right). (Color online) Typical OSL emission and stimulation spectra of X-ray-irradiated CaF_2:Tm phosphor sample.



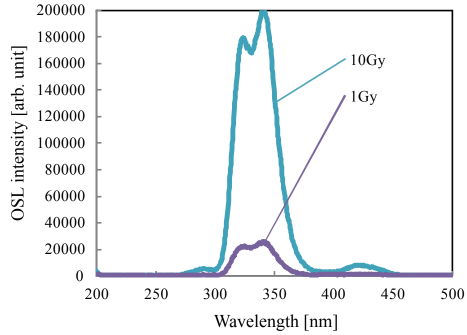
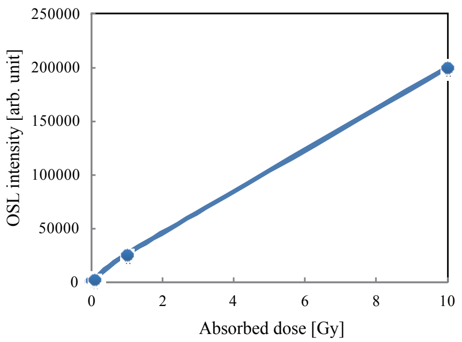


Fig. 3 (left). (Color online) Dependence of the OSL spectra on X-ray absorbed dose in the absorbed dose range from 0.001 to 0.1 Gy.
Fig. 4 (right). (Color online) Dependence of the OSL spectra on X-ray absorbed dose in the absorbed dose range from from 1 to 10 Gy.



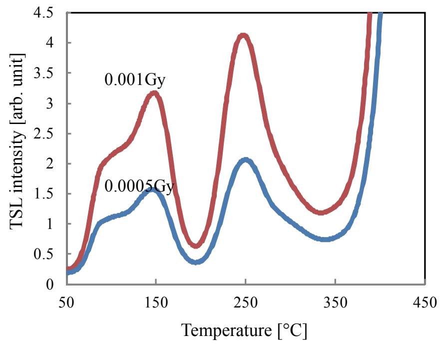
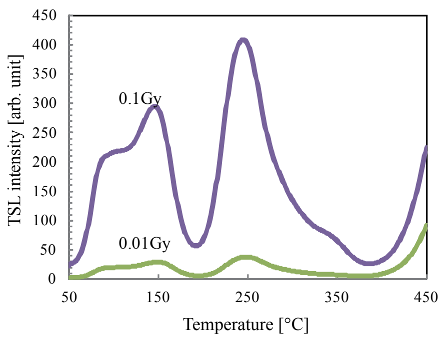


Fig. 5 (left). (Color online) OSL intensity of an X-ray-irradiated CaF_2:Tm phosphor sample as a function of absorbed dose.
Fig. 6 (right). (Color online) Typical TSL glow curves of an X-ray-irradiated sample in low absorbed dose range from 0.0005 to 0.001 Gy.



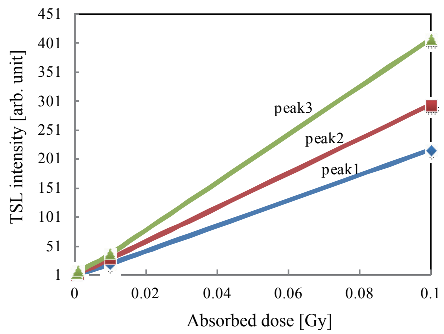


Fig. 7 (left). (Color online) TSL glow curves of an X-ray-irradiated phosphor sample in the absorbed dose range from 0.01 to 0.1 Gy.
Fig. 8 (right). (Color online) Intensities of TSL peaks, such as 70 (peak 1), 150 (peak 2), and 250 °C (peak 3) as a function of absorbed dose, in X-ray-irradiated CaF_2:Tm phosphor sample.

of the TLD-300 consists of several well known separated peaks in the temperature range from 100 to 300 °C. It was confirmed that the TSL glow peaks at about 70, 150, 250, and 300 °C in our phosphor sample almost coincide with those of commercially available TLD-300.[22] Kafadar *et al*.[23] have reported that these TSL peaks obey first-order kinetics, that is, the electrons stimulated from traps recombine with the hole traps without retrapping. Therefore, the following OSL emission and stimulation mechanism can be proposed. Free electrons and holes created by X-ray irradiation are trapped at anion (florin) vacancies to produce color centers such as F and F_2 centers, and at Tm^{3+} ions to produce Tm^{4+} ions, respectively. By subsequent stimulation with about 500 and 600 nm light, electrons, which are optically released from electron traps such as anion vacancies, recombine with the holes trapped at the Tm^{4+} ions leading to excited Tm^{3+} ions from which the OSL is emitted, in accordance with the following reactions:

$$Tm^{4+} + e^- \rightarrow (Tm^{3+})^* \rightarrow Tm^{3+} + \text{OSL emission}$$

where $(Tm^{3+})^*$ is the trivalent thulium excited state and e^- is the free electron created by optical stimulation from electron traps. In this process, all electrons stimulated from electron traps to the conduction band recombine with holes at Tm^{4+} ions without retrapping, because the TSL peaks obey first-order kinetics.

It was confirmed that 1 and 10 mol% Tm-doped CaF_2 phosphor samples exhibited low OSL intensities. Thus, the Tm doping concentration should be optimized in a future study.

4. Conclusions

An intense OSL in the wavelength range from 280 to 380 nm is observed, for the first time, by stimulating X-ray-irradiated CaF_2:Tm phosphors with 500 and 600 nm light; such an intense OSL corresponds to the energy that flows from electron traps due to anion vacancies to the conduction band. The OSL intensity increases with the X-ray absorbed dose in the range from 0.001 to 10 Gy, indicating that the OSL phenomenon in CaF_2:Tm storage phosphors can be useful in developing a novel storage phosphor material for solid-state passive dosimeters for personal and environmental radiation monitoring. An OSL stimulation and emission mechanism is also proposed.

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