Thermoluminescence in Sintered CaF₂:Tb

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Thermoluminescence (TL) / Ultraviolet radiation / CaF₂ / TL intensity / Dosimeter

In order to observe and estimate the dose of ultraviolet (UV) radiation, the thermoluminescence (TL) of sintered CaF₂ doped with Tb₂O₃ and Sm₂O₃ was studied. A several kind of lanthanides elements are doped in pure CaF₂ powder crystals and properties of the TL to UV radiation were observed. The TL intensity from CaF₂:Tb was the highest among the samples doped other lanthanide elements. The TL emission may be due to the recombination reaction; Tb²⁺ + hole → Tb³⁺ → Tb³⁺ + hν. The TL peaks are observed at about 353 K, 378 K and 458 K. It was found that the 378 K TL peak intensity of CaF₂:Tb became strong by addition of Sm₂O₃. The 378 K TL peak may also be suitable for use as a dosimeter.

INTRODUCTION

In recent years depletion of ozone layer has been recognized as one of the global environmental problems, because the increased ozone holes cause an increase of harmful sunlight UV radiation reaching the earth. Therefore, the biological effectiveness induced by UV radiation (UV-B, UV-C) has been studied¹⁻⁴. And this situation has been driving the development of an effective sensor of practical use for UV radiation. In previous paper, we reported the possibility of estimation of UV radiation dose using CaF₂:Tb as a thermoluminescence dosimeter (TLD)⁵⁻⁷. And it was found that the TL intensity from CaF₂ doped with Tb₂O₃ showed highest among the samples doped with various lanthanide elements, such as Eu, Dy, Sm, Ho ions, and three TL glow peaks usually observed at about 353 K, 378 K and 458 K, when heated at rate of 20 K.min⁻¹ after UV ray irradiation at room temperature. The purpose of the present work is to obtain a higher TL sensitivity for dosimetry by using CaF₂ and to study the effect of co-doping of Tb₂O₃ and Sm₂O₃. And the influence of sintering temperature is reported.

MATERIALS AND METHODS

Samples were made from mixtures of regent grade CaF₂ (purity 99.99%), Tb₄O₇ (purity 99.99%), and/or Sm₂O₃ (purity 99.99%). The mixture was pressed into plates of about 6 mm diameter and 0.7 mm in thickness, and sintered at 1373 K and 1527 K in a platinum crucible in air for 2 h followed by cooling to room temperature. Samples were exposed to UV radiation (λ = 253.7 nm, L937 low pressure Hg lamp, Hamamatsu Photonics Co. Ltd.). The TL was measured using a homemade apparatus with photomultiplier (HTV-R212, Hamamatsu Photonics Co. Ltd.), and the heating rate was 20K.min⁻¹.

The TL emission spectra over a wide wavelength range and variation in time (i.e. temperature) were measured simultaneously using a SMA (spectrometric multichannel analyzer) system (Princeton Instruments Inc.)⁶⁻⁷.

RESULTS AND DISCUSSION

Fig. 1 shows the TL glow curves for CaF₂ phosphor exposed to UV radiation for 1 min (about 4 × 10⁻³ J.m⁻²), where curve a is for the sample doped with Tb₂O₃ (0.06 wt %) and Sm₂O₃ (0.03 wt %), curve b and curve c; 0.06 wt % Tb₂O₃. Curves a, b and c show the results for the samples sintered at 1527 K, 1473 K and 1373 K, respectively. In CaF₂ doped only with Tb₂O₃, three TL peaks are usually observed at about 353K, 378K and 458K (curve b, c), on the other hand, one TL peak is observed at about 378 K in the sample doped with Tb₂O₃ and Sm₂O₃. The intensity of 458 K glow peak of Tb₂O₃ sample sintered at 1473 K is 1.9 times that of the sample sintered at 1373 K. It can be seen from Fig. 1 that the intensity of 378 K glow peak of the co-doped sample (curve a) is 12.9 times that of 458 K glow peak of Tb₂O₃ doped sample sintered at 1473 K.

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According to our preliminary experimental of the TL intensity of 378 K glow peak of the co-doped sample, the TL intensity of the sample sintered at 1527 K is 1.1 times that of the sample sintered at 1473 K. It is noticed that by existence of Sm2O3, the intensity of the second TL peak (378 K) of CaF2 doped only with Tb4O7 is remarkably intensified. The TL intensity of co-doped sample was compared with that of the sample doped only with Sm2O3. Fig. 2 shows the TL glow curves for CaF2 phosphor exposed to UV radiation, where curve a is for the co-doped sample, and curve b is for the sample doped only with 0.06 wt % Sm2O3. It can be seen that the intensity of 378 K glow peak of the co-doped sample is 60 times that of 347 K glow peak of Sm2O3 doped sample. To examine the TL responses against the UV dose, the 378 K glow peak intensity of CaF2:Tb,Sm was plotted against the exposure time, as shown in Fig. 3. It is seen from Fig. 3 that the response increases linearly up to 120 sec (about $4 \times 10^{-1}\text{J.m}^{-2}$) and comes saturation with further exposure time. It is, therefore, considered that the 378 K glow peak may be used for TLD.

The temperature resolved TL spectra for CaF2:Tb,Sm phosphor is shown in Fig. 4. And the TL spectra were measured after UV ray irradiation ($40 \times 10^{-1}\text{J.m}^{-2}$). Five emission peaks appeared at 380, 435, 485, 540 and 590 nm and were assigned $^3\text{D}_3 \rightarrow ^5\text{F}_6$, $^4\text{D}_3 \rightarrow ^5\text{F}_4$, $^4\text{D}_1 \rightarrow ^5\text{F}_{2,1}$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_4$ of the inner transition of Tb$^{3+}$ ions, respectively, while the emission bands of the Sm$^{3+}$ ion (about 565, 590 and 640 nm) are not observed, since their...
intensities are weak compared with that of the Tb$^{3+}$ ion. As for TL emission from the excited state of Tb$^{3+}$ ions, it is considered that trivalent terbium ions are reduced after UV irradiation in the appropriate wavelength range$^{10,11}$, then the deduced terbium ions are oxidized by thermal excitation, which leads to TL emission due to Tb$^{3+}$ ions.

TL emission is considered to follow the reaction:

$$\text{Tb}^{2+} + \text{hole} \rightarrow \text{Tb}^{3+*} \rightarrow \text{Tb}^{3+} + h\nu (380, 435, 485, 540, 590 \text{ nm}),$$

where, the holes are supplied from traps by thermal excitation.

The fact that the TL intensity is remarkably intensified by the co-doping of Tb$^{3+}$ and Sm$^{3+}$ ions may be explained by considering the energy transfer between them.

**CONCLUSIONS**

From the data above, it is observed that the addition of appropriate amounts of Sm$_2$O$_3$ to the Tb$_4$O$_7$ doped CaF$_2$ remarkably intensifies the second TL peak (378 K), which can be used for dosimetry. The mechanism causing the phenomenon is, however, at present still left unclear.

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