Similarity of trap state and thermoluminescence processes of Y₃Al₅O₁₂ (YAG):Ce for X-ray and UV irradiation

Masanori Koshimizu⁠, Takayuki Yanagida⁠, Kiyomitsu Shinsho⁠, Shin Yanagisawa⁠, Yutaka Fujimoto⁠, Hideki Yagi⁠, Takagimi Yanagitani⁠, Keisuke Asai

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ABSTRACT

We have compared the trap states of electrons and holes responsible for the thermoluminescence of Y₃Al₅O₁₂(YAG):Ce crystals and ceramics after X-ray or UV irradiation. In the case of X-rays, electrons and holes are trapped at different sites, whereas UV irradiation affords the photo-ionization of Ce³⁺ ions, in which electrons are trapped on certain sites and the holes afford Ce⁴⁺ ions. We found a dominant band in the thermoluminescence spectra after irradiation, attributed to the 5d–4f transitions of Ce³⁺ ions. The glow curves in both cases have peaks present at the same temperatures and have similar relative intensities. These results indicate that both the trap states and thermoluminescence processes are similar between the types of irradiation.

1. Introduction

Thermoluminescence is a process in which luminescence is induced by heating. Thermoluminescent materials have been used in radiation detection, such as personal dosimetry and radiation imaging for a long time [1]. The information on the dose and its distribution is obtained from the thermoluminescence intensity, which is directly correlated with the dose. It must be noted, however, that the intensity is not from the thermoluminescence intensity, which is directly correlated with the dose. In addition, thermoluminescence at room temperature is also used in long-lasting phosphors [2,3], in which the thermal energy of room temperature is sufficient to induce thermoluminescence.

Thermoluminescence is caused by recombination of an electron and a hole trapped in different sites. Thermal energy is thus necessary to release the electron and/or the hole from their respective trapping sites. Thermoluminescence glow curves, which describe the thermoluminescence intensity as a function of the heating temperature, carry information on the depth of the trap levels of the electrons and holes and can thus be used for the analysis of trap levels [4]. The thermoluminescence intensity at a given temperature is proportional to the number of recombined electron-hole pairs at said temperature. If we assume that the recombination occurs without re-trapping of the released electrons or holes, it is proportional to the rate released electrons or holes at that temperature. Such trapped electrons and holes can be generated by light or ionizing radiation.

For thermoluminescent materials based on insulators, the trapping processes for electron–hole pairs are described by different mechanisms: in the case of ionizing radiation, electron–hole pairs are produced and trapped at different sites. On the other hand, in the case of light irradiation, the photon energy is lower than the band-gap energy, the process is described as photo-ionization in localized centers. These processes are schematically depicted in Fig. 1. The difference lies in the hole trapping process: holes are initially generated in the host in the case of ionizing radiation, and subsequently trapped at sites including the localized centers. On the other hand, in the case of light irradiation, the holes remain at the photo-ionized localized centers. Comparison of the thermoluminescence properties after light or ionizing irradiation would afford insight into hole-trapping processes.

In this study, we chose Y₃Al₅O₁₂ (YAG):Ce because several papers on its thermoluminescence properties have been reported thus far, and its thermoluminescence properties have been discussed to some extent [5–16]. In addition, the energy levels of Ce³⁺ within the band-gap of the YAG host are well known [5], and its electronic structure is appropriate for the purpose of this study. According to a previous report [5], the highest occupied electronic orbital (HOMO) level of Ce³⁺ is located below the conduction band minimum by ca. 3.5 eV, which indicates that the Ce³⁺ ions are photo-ionized with UV irradiation. On the other hand, the band-gap energy of YAG is ca. 7.5 eV [5]; hence, UV
photons cannot produce electron–hole pairs in the YAG host. In this paper, we report the thermoluminescence properties of YAG:Ce after irradiation with UV light or X-rays. We used both single crystals and transparent ceramics of YAG:Ce.

2. Experimental

Ce-doped YAG single crystals were grown with the floating zone technique using a furnace (FZD0192, Canon Machinery Inc.). Ce was doped at 1 mol%. At first, raw powders were mixed and pressed into a bar with a hydrostatic press. Subsequently, the bar was sintered at 1600 °C for 8 h. Finally, crystals were grown by melting the ceramic bar. During crystal growth, the pull-down and rotation rates were 5 mm/h and 20 rpm, respectively. Transparent ceramics of YAG:Ce were supplied by Konoshima Chemical Co. Ltd, synthesized by the conventional vacuum sintering technique.

The thermoluminescence from the samples was measured after irradiation with UV light or X-rays. Before irradiation, thermoluminescence measurements were performed to verify that the samples exhibited no significant thermoluminescence. The thermoluminescence glow curves were measured without pre-heating from room temperature up to 673 K at a low heating rate of 0.13 K/s to suppress temperature gradients in the sample and obtain glow curves in a more accurate and reproducible manner. The samples were heated on a ceramic heater (Sakaguchi E.H VOC Corp.) in a black box, and the temperature was controlled with a thermoregulator (SCR-SHQ-A, Sakaguchi E.H VOC Corp.). Thermoluminescence photons were detected with a photomultiplier tube (PMT; H11890-210, Hamamatsu). A thermal-radiation-cut filter was used, and no correction was made for the contribution of thermal radiation. Prior to the measurements, the samples were irradiated with X-rays at 1.8 Gy using an X-ray generator (MX-80Labo, mediXtec Japan Corp.) or UV light (254 or 365 nm) using a black light. The samples were irradiated with UV light for about 10 s. The irradiations were performed at room temperature. The thermoluminescence spectra were recorded using a different technique. The samples were irradiated with X-rays at 1.0 Gy with an X-ray generator.
Subsequently, the samples were heated on a ceramic heater and the thermoluminescence photons were guided with an optical fiber and detected with a CCD-based detector (DU-420-OE, Andor) equipped with a monochromator (SR163, Oriel Instruments). The irradiated samples were heated rapidly up to 380 K, and the TSL spectra were obtained by at 380 K.

3. Results and discussion

Fig. 2 shows the thermoluminescence spectra of a single crystal at 380 K after irradiation with UV or X-rays. The dominant band at 550 nm is attributed to the 5d–4f transition of Ce$^{3+}$. This emission band is also observed for the ceramic sample and at different temperatures. This result indicates that the final stage of the thermoluminescence processes involves Ce$^{3+}$ 5d–4f transitions for both UV and X-ray irradiation [5].

Fig. 3 shows the thermoluminescence glow curves of a YAG:Ce single crystal after X-ray or UV irradiation. The sweep rate of the temperature was 0.13 K/s. To compare the relative intensities of the glow peaks, the glow curves are expressed in a semi-logarithmic plot. In both cases, glow peaks are observed at 380, 430, and 530 K, and the relative intensities of the peaks are similar. The temperatures of the glow peaks correspond to trapped states with different binding energies. This result indicates that the trapped states of electron–hole pairs are similar for both UV and X-ray irradiation.

Fig. 4 shows the thermoluminescence glow curves of the YAG:Ce ceramic sample after X-ray or UV irradiation at different wavelengths. As in the previous figure, the glow curves are expressed in a semi-
logarithmic plot. Glow peaks are observed at the same temperatures as those for the single crystal sample. However, in this case, the relative intensities of the glow peaks were different at different TL intensities, i.e., different X-ray doses or UV irradiation duration, as often observed in other thermoluminescent materials. This is clearly illustrated by the glow curves after UV irradiation at 365 nm for 10 irradiation periods, i.e., the relative intensities of the glow peaks at higher temperatures are suppressed at long irradiation times. The glow curve after X-ray irradiation seems to be in line with this trend, and no significant differences were observed for X-ray and UV irradiation at different wavelengths.

The temperatures of the glow peaks correspond to the depths of the trap levels of electrons and holes. The glow peaks at the same temperatures for both X-ray and UV irradiation indicate that the same kind of trap states are generated in both cases. The relative intensities of the glow peaks correspond to the relative populations of electrons and holes at the trap sites. The similar relative intensities after X-ray and UV irradiation indicate that the relative populations are also similar in both cases. Thus, it can be concluded that the trap states before thermal stimulation are quite similar in the case of both X-ray and UV irradiation, which supports the idea that the holes are trapped at Ce\(^{3+}\) ion sites in the case of X-ray irradiation.

Fig. 5 shows the schematic representation of the thermoluminescence process of YAG:Ce. The observation of the emission from Ce\(^{3+}\) ions in the thermoluminescence spectra indicates that Ce\(^{3+}\) ions in their excited 5d state are formed by the thermal stimulation, which is probably caused by the trapping of released electrons by the Ce\(^{4+}\) ions. In this case, the similar glow curves after X-ray and UV irradiations indicate that the electrons are trapped at the similar sites. In the case of X-ray irradiation, no significant emission other than that from Ce\(^{3+}\) suggests that the holes are primarily trapped at Ce\(^{3+}\) ions owing to a lower density of other hole trapping sites and a large trapping cross-section of Ce\(^{3+}\) ions.

Fig. 6 shows the thermoluminescence glow curves of the YAG:Ce ceramic and crystal after X-ray irradiation at 1.8 Gy. The glow peaks are observed at the same temperatures, although the relative intensities of the glow peaks are different. This result indicates that both samples contain the same kind of trap sites, although at different ratios.

4. Conclusion

We have compared the thermoluminescence properties of YAG:Ce crystals and ceramics after X-ray or UV irradiation. In the case of X-ray irradiation, the electrons and holes responsible for the thermoluminescence are trapped at different sites, whereas UV light affords photo-ionized Ce\(^{3+}\) ions in the form of Ce\(^{4+}\) centers. A dominant peak was observed at 550 nm in the thermoluminescence spectra, attributed to the 5d–4f transitions of Ce\(^{3+}\). This result indicates that the final stage of the thermoluminescence processes involves radiative transitions of Ce\(^{3+}\) ions. In the thermoluminescence glow curves after X-ray or UV irradiation, glow peaks were observed at the same temperatures and with similar relative intensities for both the ceramic and crystal samples. These results indicate that the trap states of electrons and holes are quite similar in the case of X-ray and UV irradiation.
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References