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Dosimeter properties of Ce-doped MgO transparent ceramics

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ABSTRACT

We have investigated thermally-stimulated luminescence (TSL) and photo-stimulated luminescence (PSL) properties of MgO transparent ceramic doped with different concentrations of Ce ion (0.001%, 0.01% and 0.1%), together with the photoluminescence (PL) and scintillation properties. The transparent ceramic samples were fabricated by a Spark Plasma Sintering (SPS) method. The measurable PL signal was only detected for the 0.001% Ce doped MgO peaking around 480 nm. From decay constants of the PL emission, it was confirmed that this peak was due to the 5d-4f transitions of Ce^{3+} ion. In the scintillation spectrum of Ce-doped MgO, a broad emission was detected which can be deconvoluted by three Gaussian bands peaking at 330, 406 and 480 nm. TSL glow curve of all the samples showed a main dosimetric peak at 140 °C. The TSL signal was confirmed to respond linearly to irradiation dose over the dose range from 0.1 to 1000 mGy. Furthermore, the 0.001% Ce doped MgO showed not only TSL but also PSL.

1. Introduction

Luminescence materials are used as radiation dosimeters in personal and environmental monitoring and in image plates and neutron detection in computed radiography [1–4]. These materials have a function to store accumulated absorbed energy of ionizing radiation as a form of trapping electrons and holes. The electrons and holes are stored at localized trapping centers, and they recombine to emit light after de-trapping process by external stimulation. Dosimeters based on luminescent materials are mainly divided into three types by different emission mechanisms. The first one is thermally-stimulated luminescence (TSL), which is observed by recombination of electrons and holes de-trapped from trapping centers by heat stimulation. The second one is photo-stimulated luminescence (PSL) in which the stimulation is performed by light (unlike heat in TSL). The last one is radio-photoluminescence (RPL) which is generation of photoluminescence (PL) centers via interactions with ionizing radiation. For example, Ti and Mg doped LiF single crystal [1], C-doped Al_2O_3 crystalline powder [2], and Ag-doped phosphate glass [3] are practically used as TSL, PSL and RPL personal dosimeters, respectively. Preferred properties of dosimeter materials in personal dosimetries are, for example, that the effective atomic number (Z_{eff}) is close to that of soft human body tissue (Z_{eff} = 7.51) and that the dosimeter response monotonically increases with the incident radiation dose. In addition to the dosimetric properties, luminescent materials often show scintillation, which is immediate luminescence upon radiation exposure without any external stimulation. Scintillators are utilized in various fields such as medicine (X-ray computer tomography, PET, flat panel detector), security (luggage inspection system), environmental monitoring and basic science [5–8]. Recently, it was pointed out that a complement behavior was observed between dosimeters and scintillators [9,10]; therefore, it is important to investigate both dosimetric and scintillation properties in order to comprehensively understand luminescence mechanisms induced by ionizing radiation.

Magnesium oxide (MgO) is a wide band-gap insulator (E_g = 7.8 eV) with a rock-salt crystal structure (fcc) under ambient pressure, and the Mg ions occupy the octahedral sites within the anion close-packed structure [11,12]. The luminescence properties of undoped MgO have been studied in various material forms including powders, films, bulk single crystals and ceramics [13–21]. Towards radiation dosimetry applications, TSL properties of MgO have also been reported since the 1970s because of the low effective number (Z_{eff} = 10.8) close to the human soft tissue. When irradiated by X-ray, γ-ray and UV, MgO shows two TSL glow peaks around 100 and 140 °C [22–28]. To date, we have studied MgO transparent ceramic materials in order to develop efficient TSL device, and they were found to show superior properties than those of single crystal [29–32].

In this study, we have fabricated a series of MgO transparent ceramics doped with different concentrations of Ce ion (0.001%, 0.01% and 0.1%) by the spark plasma sintering (SPS) method and investigated the dosimeter properties. In addition, we have characterized the optical and scintillation properties. Ce ion as emission center has attracted much attention in the radiation detection field because it shows bright luminescence in many inorganic phosphors [33–35]. Meanwhile, in the

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SPS process, sintering is performed in a highly reductive atmosphere; therefore, oxygen vacancies are effectively generated, and the dosimeter properties are expected to be enhanced.

2. Experiment

MgO transparent ceramics doped with different concentrations of Ce ions (0.001, 0.01, and 0.1 mol%) samples were synthesized by an SPS method using Sinter Land LabX-100. Here, MgO (99.99%) and CeO_2 (99.99%) raw powders of a reagent grade were homogeneously mixed. The mixture (0.5 g) was then put in a graphite die and held between two graphite punches with a radius of 10 mm. The sintering temperature was elevated from 600 °C to 1500 °C at the rate of 17 °C/min and kept for 60 min while applying the pressure of 80 MPa. After the synthesis, the wide surfaces of the ceramic sample were mechanically polished using a polishing machine (MetaServ 250, BUEHLER). The thickness after polishing was ~0.32 mm. In the course of study, the following measurements were carried out for the obtained samples.

The in-line transmittance was evaluated by using a JASCO V670 spectrometer in the spectral range from 190 to 2700 nm with 1 nm interval. By using Quantaurus-QY (Hamamatsu Photonics), PL emission spectrum was measured with a series of excitation wavelengths to obtain a PL excitation/emission contour plot (PL excitation/emission map). Moreover, an excitation and emission spectra were measured by FP8600 (C002361454, JASCO). In order to determine the origin of emission, the PL decay lifetime was measured with 340 nm excitation while monitoring at 480 nm by using Quantaurus-τ (C11367-04, Hamamatsu) in addition to the PL spectrum.

X-ray induced scintillation spectrum was measured using our lab-constructed setup. The sample was excited using an X-ray generator in which the applied tube voltage and current were 40 kV and 5.2 mA, respectively. While the sample was irradiated by X-rays, the X-ray luminescence from the sample was fed into the spectrometer through a 2 m optical fiber to measure the spectrum. The CCD detector in the spectrometer (Andor DU-420-BU2 CCD with Shamrock SR163 monochromator) was cooled down to 188 K by a Peltier module to reduce the thermal noise. The details of the setup can be found in literature [36]. Further, the scintillation decay constant was measured using an afterglow characterization system equipped with a pulsed X-ray tube [37]. The system is commercially available from Hamamatsu as a custom-ordered instrument. The applied voltage to the pulsed X-ray source was 30 kV, and the system offers the timing resolution of ~1 ns.

In order to investigate TSL dosimetric properties, we have measured a TSL glow curve using a Nanogray TL-2000 [38] after X-ray irradiations with various doses from 0.1 to 1000 mGy. The heating rate used for all the TSL measurements was fixed to 1 °C/s while the sample was heated from 50 to 490 °C during the measurement. Further, an PSL spectrum and decay curve were measured by FP8600 (C002361454, JASCO). The PSL spectrum measurement was carried out after X-ray irradiation of 5 Gy under stimulation light at 600, 700, and 800 nm.

3. Results and discussion

3.1. Sample

Fig. 1 shows Ce-doped MgO transparent ceramics prepared in this study. The top and bottom photographs show the samples under ambient light and UV light (354 nm), respectively. These samples are visually transparent, and the color shifted to yellow with increasing the concentration of Ce ion. When the valence state of Ce ion changes to 4+ from 3+, it is commonly known that the color changes to yellow due to the absorption of Ce^{4+}. Furthermore, only the 0.001% Ce doped MgO showed a pale blue light under UV irradiation.

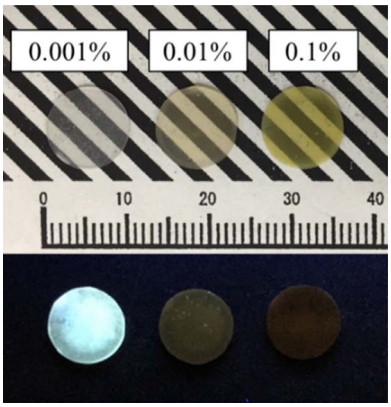

Fig. 1. MgO transparent ceramic samples doped with Ce (0.001%, 0.01% and 0.1%) under room light (top) and UV (365 nm) light (bottom).

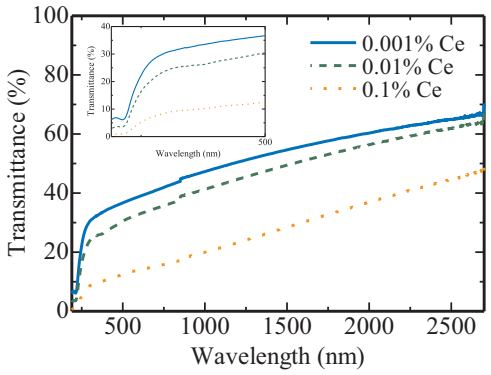

Fig. 2. Transmittance spectra of Ce-doped MgO transparent ceramics. The inset enlarges the 190–500 nm region.

3.2. Optical properties

Fig. 2 compares the transmittance spectra of all the sample in the 190–2700 nm range. In the ultraviolet region (200–250 nm), an absorption band was observed. This is due to deformation-induced defects/vacancy complexes [39]. The fundamental absorption edge was not detected because it lies beyond the measurable range. Although the transmittance in a wide spectral region decreased with the increase of Ce concentration, this is due to large amount of light scattering centers. Fig. 3a and b show the PL excitation/emission maps of all the samples and the excitation and emission spectra of 0.001% Ce-doped MgO, respectively. Only the 0.001% Ce doped MgO sample showed measurable signal, which had a feature of broad emission from 400 to 550 nm and excitation from 300 to 360 nm. The origin should be due to the 5d-4f transitions of Ce^{3+} ions since such an emission was not observed in the undoped MgO [29]. In addition, the emission in MgO:Ce is similar to the positions observed in MgO: Ce,Li [40]. This low emission signal can be due to oxidation of Ce^{3+} transforming into Ce^{4+}. Fig. 4 displays PL decay curve of 0.001% Ce doepd MgO. The monitored emission wavelength was 480 nm during 365 nm excitations. The PL decay curve was approximated by third exponential decay functions. Among three decay constants, the first and second constants are due to Instrumental Response Function (IRF). The third decay constant was 43 ns which is typical for the 5d-4f transitions of Ce^{3+} ion and consistent with the value reported in a previous work [41]. From this result, it can be said that the broad peak detected in the PL excitation/emission map was confirmed to be due to the 5d-4f transitions of Ce^{3+} ion.

3.3. Scintillation properties

X-ray induced scintillation spectra of Ce-doped MgO transparent