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Optical, scintillation and dosimeter properties of MgO translucent ceramic doped with Cr^{3+}

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ABSTRACT

We have investigated the photoluminescence (PL), scintillation and thermally-stimulated luminescence (TSL) dosimeter properties of MgO translucent ceramic doped with Cr^{3+} ion (0.001, 0.01 and 0.1%). The ceramic samples were synthesized by a Spark Plasma Sintering (SPS) technique. The broad and sharp emission peaks appeared around 600–850 nm in all the samples. The PL decay time constants of all the samples were a few ms which were on the typical order of Cr^{3+} doped phosphors. As with the PL, the peak resulted from Cr^{3+} ion was detected in the scintillation spectra. The TSL glow curves showed the main peak around 140 °C. The TSL response was confirmed to be linear to the irradiation dose over the dose range from 0.1 to 1000 mGy.

1. Introduction

Accurate measurements of radiation dose, energy and spatial distribution have been demanded, for example, in medical [1], security [2] and also for personal dose monitoring [3–5] applications. Required dosimeter properties depend on applications, but typically suitable sensitivity, dose linearity, energy response and low fading are considered. In addition, if one is to measure a radiation dose absorbed in human body, it is desirable that the effective atomic number (Z_{eff}) of the dosimeter material, in the view point of bioequivalence, is close to that of the soft tissue (Z_{eff} = 7.13). With such a tissue equivalent detector, no mathematical calibration for energy dependence is required ideally. Therefore, for such dosimeter applications, it is preferred for the detector materials to consist of light elements. Dosimeters using an inorganic phosphor are mainly classified into three types: thermally stimulated luminescence (TSL), optically stimulated luminescence (OSL) and radiophotoluminescence (RPL) dosimeters. Examples of these dosimeter materials used in practice are: Ti and Mg doped LiF ceramics [3], C-doped Al_2O_3 crystalline powder [4] and Ag-doped phosphate glass [5], respectively.

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 [6,7]. In the 1970s, undoped MgO was found to show dosimeter properties. When it was irradiated by X-ray, γ-ray and UV, two TSL glow peaks were found around 90–100 and 140 °C [8–10]. Moreover, it was reported that the emission wavelength appeared at 400 and 710 nm, and the latter is due to contamination of Cr ion. On the other hand, similar studies have been performed for MgO powder doped with isoelectronic impurities and transition metal ions. It was revealed that Cr^{3+}, Mn^{2+} and Ni^{2+} act as emission centers while Fe^{3+}, Co^{2+} and Cu^{2+} act as quenchers in γ-ray induced TSL [11,12].

In addition to the dosimeter properties, the luminescence of undoped MgO has been studied in many material forms including powders, films, bulk single crystals and ceramics [13–22]. In MgO crystals, it has been demonstrated that there are two primary oxygen vacancies, namely F^+ and F color centers, which capture one and two electrons, respectively. Although absorption bands of the F^+ and F color centers have almost the same energy, ~5 eV (~250 nm), they show different photoluminescence (PL) emission bands with the peaks at ~2.3 eV (~500 nm) and ~3.2 eV (~400 nm), respectively [18]. In recent years, with advancement of ceramic fabrication techniques, MgO transparent ceramic was developed [23–27]. It shows phosphorescence (or called long afterglow or persistent luminescence) emission at the wavelength of 390 nm due to the F^+ center acting as a luminescent center [27]. The phosphorescence, in other words, is a form of TSL at room temperature; therefore, the MgO transparent ceramic is potentially applicable for TSL dosimeter if the TSL peak temperature can be

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somehow increased in order to store the dose signal for a long term without fading.

In this study, we have synthesized a MgO translucent ceramic doped with Cr^{3+} ion (0.001, 0.01 and 0.1%) by spark plasma sintering (SPS) and studied the dosimeter properties against X-rays. Since the contamination of Cr in MgO raw powder is unavoidable by purification techniques nowadays, investigations of influences of Cr doping in MgO are important. Further, we have characterized the optical and scintillation properties. Recently, it was pointed out that scintillation and dosimeter are complementarily related in some material systems [28,29] so investigations of both the dosimeter and scintillation properties are important to understand the luminescence phenomena induced by radiations. In general, SPS is performed in a highly reductive atmosphere; therefore, oxygen vacancies are effectively created, and the dosimeter properties are expected to be enhanced.

2. Experiment

MgO transparent ceramic samples were synthesized by an SPS method using Sinter Land LabX-100. Here, a reagent grade of MgO (99.99%) and Cr_2O_3 (99.99%) powder was homogeneously mixed. The total mass of the mixture was 0.5 g. The mixture was then loaded in a graphite die and sandwiched by two graphite punches. The sintering temperature was increased from 600 °C to 1500 °C at the rate of 17 °C/min and held for 60 min while applying the pressure of 80 MPa. After the synthesis, wide surfaces of the ceramic sample were polished. In the course of study, the following measurements were carried out for all the prepared samples.

The in-line transmittance was evaluated by using JASCO V670 spectrometer in the spectral range from 190 to 2700 nm with 1 nm step. The PL emission spectrum and the PL decay lifetime monitoring at 410 nm were measured with 280 nm excitation using Hamamatsu Quantaurus-τ (C11367-04, Hamamatsu) and a short-cut filter (LU0300, Asahi Spectra). The 280 nm excitation is the shortest wavelength of LED equipped with Hamamatsu Quantaurus-τ. In this condition, some leakage from the excitation source would affect the shorter wavelength ranges in the PL spectrum. The X-ray induced scintillation spectrum was measured using our laboratory-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. The scintillation emission was guided to either of the following two spectrometers: Andor CCD-based spectrometer (CCD, DU920-BU2NC, Andor; grating, SR163i-UV, Andor) or Ocean Photonics CCD-based spectrometer (QE65Pro). The details of the setup were described previously [30]. The former spectrometer was used for measuring a spectrum in the UV and visible range while the latter was used for the NIR wavelengths. Further, the X-ray induced afterglow was measured using an afterglow characterization system equipped with a pulsed X-ray tube [31], which was designed and constructed by us, and it became commercially available from Hamamatsu as a custom-ordered instrument. An afterglow level was calculated using the formula of one of the famous companies for scintillation detectors in security applications [32]. After samples were annealed at 1000 °C for 20 min, and then left in the dark for a while, the afterglow was measured. The afterglow is TSL around room temperature and has a significant relation with dosimeter properties.

In order to investigate the properties of MgO ceramic as a TSL dosimetric detector, we have measured a TSL glow curve using Nanogray TL-2000 [33] after X-ray irradiations with various doses from 0.1 mGy to 1000 mGy. The heating rate used for all the TSL measurements was fixed to 1 °C/s, and the sample was heated from 50 to 300 °C to measure the glow curve. Further, TSL spectrum was measured using an Andor CCD-based spectrometer as mentioned above while the sample was heated by an electric heater (SCR-SHQ-A, Sakaguchi E.H Voc) at a constant temperature.

3. Results and discussion

3.1. Sample

The synthesized MgO:Cr^{3+} translucent ceramic samples are illustrated in Fig. 1. The top image shows the samples under room light while the bottom image shows those under UV (302 nm) light. As seen in the figure, these samples are visually transparent. It looks like that the PL emission becomes feeble with higher concentration of Cr added.

3.2. Optical properties

Fig. 2 shows the in-line transmittance spectra of MgO samples. For all the samples, at 220 nm and shorter wavelengths, the transmittance is close to zero. These wavelengths are longer than the wavelength of the bandgap of MgO (~7.8 eV = 159 nm) [6]. The 0.1% Cr-doped sample shows absorption bands in the visible region. The mechanism responsible for these bands is explained in the literature in terms of crystal field splitting [34,35]. The octahedral crystal field around the Cr^{3+} ion splits the ^4F level into a ground state of singlet $^4A_2$ and excited states of triplet $^4T_2$ and $^4T_1$. Also, due to the crystal field, splitting of the free-ion excited state of ^2G gives rise to level ^2E. The broad absorption bands are due to transitions from $^4A_2$ to the $^4T_2$ (absorption around 665 nm) and $^4T_1$ (absorption around 455 nm) levels.

Fig. 3 represents the PL spectra of the MgO ceramic doped with Cr^{3+} (0.001, 0.01 and 0.1%) samples under 280 nm excitation. The emission bands appeared around 350 and 410 nm, and the former peak is due to the excitation leakage. Moreover, the broad and sharp emission peaks appeared around 600–850 nm in all the samples. Since emission wavelength agrees with that of trivalent Cr ion in MgO [36–39], this emission should be due to the electron transitions of Cr^{3+} ion. The sharp peaks around 600–850 nm mainly originate from $^2E \rightarrow {}^4A_2$ transitions in Cr^{3+} ion placed at Mg^{2+} substitutional site with octahedral symmetry. Another broad peak around 600–850 nm is due to $^4T_2 \rightarrow {}^4A_2$ transitions in Cr^{3+} ion if the $^4T_2$ level shifts below the ^2E as expected for Cr^{3+}-Mg vacancy pairs aligned with a MgO[1 1 0] direction [36]. From 0.001 to 0.01%, the peak intensity around 600–850 nm increased. However, from 0.01 to 0.1%, the peak intensity around 600–850 nm

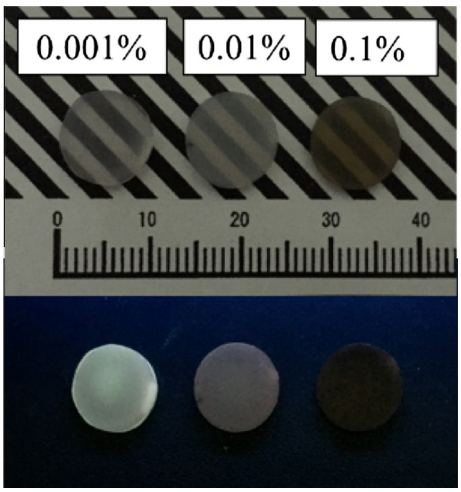

Fig. 1. MgO ceramic doped with Cr^{3+} (0.001, 0.01 and 0.1%) samples under room light (top) and UV (302 nm) light (bottom).