Optical, scintillation and dosimeter properties of MgO transparent ceramic doped with Mn^{2+}

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We have investigated the photoluminescence (PL), scintillation and thermally-stimulated luminescence (TSL) dosimeter properties of MgO transparent ceramics doped with different concentrations of Mn^{2+} ion (0.001, 0.01, 0.1 and 1%). The samples were synthesized by a Spark Plasma Sintering (SPS) technique. All the samples show a PL band emission around 730 nm, and the intensity increases with the dopant concentration. The PL decay time constants were a few milliseconds which is on the typical order for Mn^{2+} ion. In contrast, the scintillation spectrum under X-rays shows additional emissions at 340, 620 and 760 nm. After the samples are irradiated by X-rays, the TSL is observed with a main glow peak appearing around 140°C. The TSL response is linearly related to the irradiation dose at least over the dose range from 0.1 to 1000 mGy.

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1. Introduction

Accurate measurements of radiation dose, energy and distribution have been demanded in a wide range of applications in, for example medicine,¹⁾ border security²⁾ and personal dose monitoring.³⁾⁻⁵⁾ Required dosimeter properties depend on the application, but typically suitable sensitivity, dose linearity, energy response and low fading are mainly 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 soft tissue ($Z_{\text{eff}} = 7.13$). With such a tissue equivalent detector, no mathematical calibration of energy dependence is required. Therefore, to measure radiation dose absorbed in a biological tissue, 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). Selected examples of these dosimeter materials used in practice are: Ti and Mg doped LiF ceramics,³⁾ C-doped Al_2O_3 crystalline powder⁴⁾ 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, tested in a powder form, was found to show dosimeter properties. When it was irradiated by X-rays, γ -rays and UV, two TSL peaks are known to appear around 90–100 and 140°C.⁸⁾⁻¹⁰⁾ 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 TL.^{11),12)} Moreover, the TSL dosimeter properties of crystal MgO doped with Mn^{2+} were intensively studied for fast neutron measurements^{13),14)} since MgO is often used as a moderator in neutron sources such as nuclear reactors.

In addition to the dosimeter properties, the luminescence properties of undoped MgO have been studied in many material forms including powders, films, bulk single crystals and ceramics.¹⁵⁾⁻²¹⁾ In the crystal form, it has been demonstrated that there exist two primary oxygen vacancies, namely F^+ and F centers, which are formed by capturing one and two electrons, respectively. Although absorption bands of the F^+ and F centers are almost the same energy ~ 5 eV (~ 250 nm), they show different photoluminescence (PL) emission bands with at ~ 2.3 eV (~ 500 nm) and ~ 3.2 eV (~ 400 nm), respectively.¹⁹⁾ In recent years, with an advancement of ceramic fabrication techniques, MgO can be fabricated in a form of transparent ceramic.²²⁾⁻²⁴⁾ 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.²⁴⁾ 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 somehow increased in order to store the dose signal for a long term without fading.

In this study, we have synthesized MgO transparent ceramics doped with different concentrations of Mn^{2+} ion (0.001, 0.01, 0.1 and 1%) by spark plasma sintering (SPS) and studied the dosimeter properties against X-rays. The synthesis by SPS under strong vacuum environment is expected to increase dosimeter properties because oxygen vacancies can be effectively generated. Moreover, for laser²⁵⁾ and scintillator²⁶⁾ applications, notable improvement of properties was reported in a form of transparent ceramic compared with those in single crystal, non-transparent ceramic etc. We therefore expect an enhancement of radiation-induced properties as scintillator or dosimeter. Further-

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more, it has been recently pointed out that scintillation and dosimeter are complementarily related^{27),28)} so investigations of both the dosimeter and scintillation properties are important approach to understand the luminescence phenomena induced by radiations.

2. Experiment

MgO transparent ceramic samples were synthesized by an SPS method using Sinter Land LabX-100. Here, a mixture of MgO (99.99%) and MnO (99.9%) powder of reagent grade was loaded in a graphite die and sintered at 1500°C for 60 min while applying a uniaxial pressure of 80 MPa. After the synthesis, the wide surfaces of the ceramic sample were polished. The thickness of all the samples were fixed to ~1.5 mm. In the course of study, the following measurements were carried out for all the samples prepared.

The in-line transmittance was evaluated by using JASCO V670 spectrometer in the spectral range from 190 to 2700 nm with 1 nm interval. The PL excitation and emission spectra were measured using FP-8600 (C002361454, JASCO), a short-cut filter (LV0610, Asahi Spectra) and a long-cut filter (SH0450, Asahi Spectra). The PL decay lifetime monitoring at 410 nm was measured with 280 nm excitation using Hamamatsu Quantaurus- τ (C11367-04, Hamamatsu). The X-ray induced scintillation spectrum was measured using our lab-constructed setup. The radiation source was a conventional X-ray tube operated with an applied tube voltage and current of 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 (QEPro). The details of the setup were described previously.²⁹⁾ The former spectrometer was used for measuring a spectrum in the UV and visible range while the latter was used for the NIR range. Further, the scintillation lifetime by X-ray irradiation was measured using an afterglow characterization system equipped with a pulsed X-ray tube,³⁰⁾ which was designed and constructed by us but it 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 the properties of MgO ceramic as a TSL dosimetric detector, we have measured a TSL glow curve using Nanogray TL-2000³¹⁾ after X-ray irradiations with varying doses from 0.1 to 1000 mGy. The reader was equipped with a thermal radiation cut filter, which allows us to measure the light signal between 320 and 520 nm while extracting near infrared emission from the heater. 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 (CCD, DU920-BU2NC, Andor; grating, SR163i-UV, Andor) 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:Mn²⁺ transparent ceramic samples are illustrated in **Fig. 1**. The left photograph shows the samples under room light while the right photograph shows those under UV (302 nm) light. These samples are visually transparent and predominantly show red PL emission.

Fig. 1. MgO ceramic doped with Mn²⁺ (0.001, 0.01, 0.1 and 1%) samples under room light (left) and UV (302 nm) light (right).

Fig. 2. Transmittance of MgO transparent ceramic samples doped with Mn²⁺ (0.001, 0.01, 0.1 and 1%).

Fig. 3. PL excitation ($\lambda_{\text{em}} = 730$ nm) and emission ($\lambda_{\text{ex}} = 270$ nm) spectra of the MgO transparent ceramic samples doped with Mn²⁺ (0.001, 0.01, 0.1 and 1%).

3.2 Optical properties

Figure 2 shows the in-line transmittance spectra of synthesized samples. For all the samples, the transmittance is close to zero at and shorter wavelengths than 190 nm. These wavelengths are longer than the wavelength that corresponds to the bandgap energy of MgO (~ 7.8 eV = 159 nm).⁶⁾

Figure 3 represents the PL excitation and emission spectra. A single strong emission band appears around 730 nm under 270 nm excitation. The emission intensity at 730 nm effectively increases with increasing the dopant concentration. The origin of latter emission is attributed to the Mn²⁺ ions since emission wavelength and band structure agree with those reported in earlier studies.^{32),33)} The excitation spectrum of the 730 nm emission consists of a band peaked at 270 nm, which can be attributed to the Mn²⁺–O^{2–} charge transfer transition. The excitation spectrum in the range of 300–450 nm would be due to degeneration of the ⁴E and ⁴A₁ levels is released because the octahedral crystal field of Mg²⁺ sites is slightly distorted.³⁴⁾

The PL decay time constants of the MgO:Mn²⁺ transparent ceramics are summarized in **Fig. 4**. The inset shows the mea-

Fig. 4. PL decay times of the MgO transparent ceramic samples doped with Mn^{2+} (0.001, 0.01, 0.1 and 1%). The monitoring PL emission is at 760 nm during the excitation at 280 nm. The inset shows the PL decay profiles.

Fig. 5. X-ray induced scintillation spectra of the MgO transparent ceramics doped with Mn^{2+} (0.001, 0.01, 0.1 and 1%). The inset expands the 250–650 nm range.

sured PL decay curves. Here, the excitation wavelength is 280 nm and the monitoring emission wavelength is 760 nm. The decay curves of all the samples are well approximated by a sum of two exponential functions. The obtained decay time constants of faster components are 226, 216, 340 and 473 μs for the samples doped with 0.001, 0.01, 0.1 and 1% Mn, respectively, and these are due to the instrumental response since we used the micro-second Xe flush lamp. The obtained slower decay time components of 0.001, 0.01, 0.1 and 1% Mn-doped samples resulted 3.35, 3.56, 3.67 and 3.75 ms, respectively. These slower components are due to Mn^{2+} ion because the values are consistent with typical decay times of Mn^{2+} ion.^{35,36} In general, the phosphors doped with manganese activator have a long decay time by the forbidden transitions of Mn^{2+} ions according to the spin selection rule, and the emission properties are strongly dependent on the crystal structure of host materials. For example, according to the literature,^{37–39} Mn^{2+} ion at the tetrahedral coordination, which has a weak crystal field, gives a green emission while it exhibits an orange-to-red emission at the octahedral site due to the strong crystal field artificially created at the liquid nitrogen temperatures. In the present samples, the Mn ions are expected to substitute the octahedral Mg sites in MgO; hence, the same orange-to-red emission are observed.

3.3 Scintillation properties

Figure 5 shows the scintillation spectra of MgO transparent ceramic samples doped with Mn^{2+} (0.001, 0.01, 0.1 and 1%). All the samples showed an emission peak at 760 nm by Mn^{2+} . The emission intensity increased with increasing the Mn^{2+} concentration. Except the 1% Mn-doped sample, the samples showed

Fig. 6. Scintillation decay times of MgO transparent ceramics doped with Mn^{2+} (0.001, 0.01, 0.1 and 1%). The inset shows the scintillation decay profiles.

Fig. 7. TSL glow curves of MgO transparent ceramics doped with Mn^{2+} (0.001, 0.01, 0.1 and 1%) samples.

emission peaks at 340 and 620 nm. The peak at 340 nm is attributed to oxygen vacancies with one electron captured (F^+ center) which was observed in the undoped MgO.^{19,24} The origin of scintillation emission at 620 nm is currently under investigation.

In Fig. 6, the X-ray induced scintillation decay times are summarized. The inset shows the decay time profiles. As for the PL decay time profiles, the scintillation decay curves are well approximated by a sum of two exponential functions. The obtained faster decay time components of 0.001, 0.01, 0.1 and 1% Mn-doped samples are 305, 205, 377 and 74.6 μs , respectively, and these are treated as the instrumental response. On the other hand, the slower decay time components are 4.7, 3.54, 3.52 and 1.14 ms, respectively. Despite the fact that the PL decay time of Mn^{2+} emission is consistent with different concentrations, the scintillation decay times seem to depend on the Mn^{2+} concentration. This difference between the PL and scintillation is blamed to the difference of excitation density. In the scintillation process, high energy X-ray photons are deposited on the sample in a several tens nm scale, hence the excitation density is much higher than PL.

3.4 Dosimeter properties

Figure 7 shows the TSL glow curves measured after the samples were irradiated by X-rays of 1 Gy. All the samples showed a single glow peak around 140°C. This peak is a typical feature of MgO and is consistent with the previous works reported in the literature.^{8–14} In addition, the more amount of dopant added, the lesser TSL intensity at 140°C.

Figure 8 depicts the TSL spectra measured around 140°C. Overall, there are three types of band emissions observed around 340, 620 and 760 nm. The 340 and 760 nm peaks are due to the F^+ center and Mn^{2+} ion, respectively. It is instructive to note that the 620 and 760 nm emissions do not contribute to the TSL glow

Fig. 8. TSL spectra measured at 140°C for the MgO transparent ceramic samples doped with Mn²⁺ (0.001, 0.01, 0.1 and 1%). The inset expands 300–700 nm regions.

Fig. 9. Dose response curves of the MgO transparent ceramic samples doped with Mn²⁺ (0.001, 0.01, 0.1 and 1%). The TSL signal used here is the peak intensity observed at 140°C.

signal due to the presence of a thermal radiation cut filter installed in the instrument. Although the present investigations were done using a common commercial TSL reader, the TSL sensitivity should be improved by using an optimized reader setup in order to include these strong emissions. Moreover, with increasing the concentration of Mn ion, the scintillation intensity increased while the TSL intensity decreased. Thus, the complementary relation between the TSL intensity and scintillation^{27),28)} was observed in the present Mn-doped MgO transparent ceramics.

Figure 9 shows the relation between the TSL intensity and irradiated X-ray dose, or namely called a dose response curve. Knowing the dose response curve, it allows us to calibrate the TSL response to the corresponding dose value. The TSL signal used here is the integrated peak intensity at 140°C in Fig. 7. From our experimental results, the 0.001, 0.01, 0.1 and 1% Mn²⁺-doped MgO transparent ceramics show a linear response against the incident X-ray dose over the dose range of 0.1–1000 mGy. For the 1% Mn-doped sample, the response signal was too small because the emission from F⁺ center was degraded by Mn-doping. However, for those with lower concentrations, the linear response was confirmed over the dose range from 0.1 to 1000 mGy. It is an equivalent sensitivity with commercial personal dosimeters and the highest sensitivity for MgO among the earlier reported works we could find.^{13),40),41)} A dosimeter having a linear response is advantageous because it enables us to easily and accurately calibrate the dose. In addition, the TSL peak temperature slightly increased by doping with Mn ion, which indicates a slight increase in stability of TSL signal.

4. Conclusions

We have synthesized MgO transparent ceramics doped with Mn²⁺ ion by an SPS technique. All the samples were visually

transparent and colorless. Subsequently, we have studied the optical, scintillation and TSL properties. In the PL and scintillation emissions, a strong emission around 760 nm was dominant due to the Mn²⁺ ion acting as luminescent center. The intensity and luminescent decay time were dependent on the dopant concentration, i.e. doping with 1% Mn showed the strongest and fastest emission among the samples studied. The TSL glow curves of all the samples had the main peak around 140°C. Using this glow peak, the MgO:Mn²⁺ samples had a dose detection ability at least over the range 0.1–1000 mGy, except the one with 1% Mn²⁺ as the TSL intensity was insufficient to measure low doses below 1 mGy. Furthermore, the dose response was linear over the dose range tested.

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