Optical, Scintillation and Dosimeter Properties of MgO Transparent Ceramic and Single Crystal

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Abstract

We have synthesized a MgO transparent ceramic by spark plasma sintering (SPS) and studied the dosimeter properties for X-ray detections, in comparison with the single crystal form. Further, we have characterized the optical and scintillation properties. Despite the same material compositions, the photoluminescence (PL) of the ceramic sample showed dominantly around 450 nm whereas the single crystal sample had a dominant emission in the NIR range. The PL lifetime of 450 nm were measured to be ~10 and ~50 ns which were typical for emissions by F^+ center in MgO. The scintillation spectra were similar to those observed in PL, but the lifetime was much longer on the micro-second scale. The TSL glow curves of MgO ceramic showed a main peak around 140 °C. The TSL spectrum at 140 °C had a broad emission band in the 300-400 nm range and around 600 and 750 nm, which approximately coincide with the scintillation spectra. The TSL response was confirmed to be linear to the irradiation dose for both samples over the dose range from 0.1 to 1000 mGy.

Keywords: transparent ceramic, MgO, scintillator, dosimeter, TSL

1. Introduction

The accurate determination of the dose, energy and position of ionizing radiation has attracted much attention in the medical applications [1], security [2] and also for personal dose monitorings [3-5]. Specific properties required for a high precision dosimeter are a suitable sensitivity, dose linearity, energy response and low fading. In addition, it is desirable that the effective atomic number of the dosimeter material in the view point of bioequivalence should be close to that of human body soft tissue ($Z_{eff} = 7.13$). If the effective atomic number of the dosimeter is the same as that of tissue, no mathematical dose reconstruction for energy dependence are required. Therefore, for dosimeter applications, materials consisting of light elements are preferable. Dosimeters are mainly classified to three types with respect to the mechanisms involved: thermally stimulated luminescence (TSL), optically stimulated luminescence (OSL) and radiophotoluminescence (RPL). Examples of these dosimeter materials used in practice are: Ti and Mg doped LiF ceramics [3], C:Al₂O₃ crystalline powder [4] and Ag-doped phosphate glass [5], respectively.

Magnesium oxide (MgO) is a wide band-gap insulator (7.8 eV) with the rock-salt crystal structure (fcc) at ambient pressure, and the Mg ions occupy the octahedral sites within the anion closed packed structure [6, 7]. The luminescence properties of undoped MgO have been studied in many material forms including powders, films, bulk single crystals and ceramics [8-17]. In MgO crystals, it has been demonstrated that there exist 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 are almost the same energy of ~5 eV (~250 nm), they show different photoluminescence (PL) bands with the peaks at ~2.3 eV (~500 nm) and ~3.2 eV (~400 nm), respectively, [13].

In the 1970s, undoped MgO powder was found to show dosimeter properties. When it was irradiated by X-rays, γ -rays, and UV lights, two TSL peaks were found around 90-100 and 140 °C [18-20]. Subsequently, in the later decades, MgO have been intensively studied for dosimeter applications [21-25] due to the bioequivalency. In recent years, with advancement of ceramic fabrication techniques, MgO transparent ceramic was developed [26-30], which shows long afterglow (or persistent luminescence) emission at the wavelength of 390 nm due to the F⁺ center [30]. The long afterglow, in other words, is a form of TSL at room temperature; therefore, the MgO transparent ceramic has an ability to store radiation- (or photo-) induced charges and is potentially applicable for TSL dosimeter.

In this study, we have synthesized a MgO transparent ceramic by spark plasma sintering (SPS) and studied the dosimeter properties against X-rays, in comparison with a MgO single crystal. Generally, synthesis of SPS is done in highly reductive atmosphere; therefore, oxygen vacancies are effectively created and the dosimeter properties are expected to be enhanced. Further, we have report also the optical and scintillation properties because it is pointed out that scintillation and storage luminescence by ionizing radiation are complementarily related in recent study [31, 32].

2. Experiment

A MgO transparent ceramic sample was synthesized by the SPS method using a Sinter Land LabX-100. Here, a reagent grade of MgO powder (99.99 %) was loaded in a graphite die and sintered at 1500 °C for 60 min while applying the pressure of 80 MPa. After the synthesis, wide surfaces of the ceramic sample were polished. The MgO single crystal sample used in this study is a commercial product and was purchased from NEOTRON, Japan. As same for the ceramic sample, the wide surfaces were polished. In the course of study, the following measurements were carried out for these two 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 step [33]. The photoluminescence (PL) emission spectrum was measured with a 265 nm excitation source produced by a combination of xenon lamp (LAX-C100, Asahi Spectra) and a band-pass filter (VPF-25C-10-12-26500, OptoSigma). The consequent emission spectrum was digitized using an optical fiber-coupled CCD spectrometer (QE65Pro, Ocean Optics). 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 sample was excited using the 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 CCD-based spectrometers: Andor (CCD, DU920-BU2NC; grating, SR163i-UV) and Ocean Optics (QE65Pro). The former 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 [34]. 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 the properties of MgO ceramic as a thermally-stimulated luminescent (TSL) dosimetric detector, we have measured a TSL glow curve using a Nanogray TL-2000 [35] after varying X-ray irradiation doses from 0.1 mGy to 1000 mGy. The heating rate used for all the TSL measurements was fixed to 1 °C/s over the temperature range from 50 to 490 °C. The TSL spectrum was measured using Andor spectrometer (CCD, DU920-BU2NC; grating, SR163i-UV) 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 MgO ceramic sample synthesized by the SPS method was visibly transparent. Fig.1 (top) shows a photograph of the MgO ceramic and single crystal samples. The bottom figure in Fig. 1 showed the samples under UV (254 nm) excitation, which are emitting light of yellow-green color. Fig. 2 illustrates an SEM image of the MgO ceramic sample. From the SEM image, it can be confirmed that the sample was properly creamed. The grain size and shape seem to be non-uniform. However, the adjacent grains

are closely attached; therefore, a scattering of light is minimized and it appears to be transparent as also confirmed in Fig. 1 (top).

3. 2 Optical properties

Fig. 3 shows the in-line transmittance spectrum of MgO. The MgO ceramic and single crystal showed a transmittance around 20-70% and 50-80% at wavelengths longer than 300 nm, respectively. At 190 nm and shorter wavelengths, the transmittance is close to zero. This range is, in fact, longer than the wavelength that corresponds to the bandgap energy of MgO (~ 7.8 eV=159 nm) [6]. Therefore, we think that this is due to insufficient sensitivity of the instrument in this spectral range.

Fig. 4 represents the PL spectrum of the MgO ceramic and single crystal samples under 265 nm excitation. Main emission band of both samples appeared at 410 nm, but the emission intensities were largely different despite the fact that the sample sizes are comparable. Moreover, in the ceramic sample, a single small emission was observed at 700 nm (inset of Fig. 4 right). We think that the 700 nm emission band is due to Cr ion because it was previously reported that a broad emission arises in the spectral range around 700 nm by Cr ion [19], which can typically contaminate in MgO. Furthermore, strong emissions of a broad band with sharp lines appeared around near infrared (NIR) wavelength of 750-950 nm in the crystal sample.

PL decay time profiles monitoring at 410 nm are shown in Fig. 5. The decay curves are well approximated by a three exponential function. In the MgO single crystal, the obtained decay time constants are 1.9, 5.6 and 18 ns. In the ceramic sample, decay time constants of 2.1, 7.2 and 47.1 ns were observed. We tentatively attribute the origin of each component as follows. The fastest components (1.9 and 2.1 ns) of both samples would be due to the instrumental response because the timing resolution of the instrument is comparable (around 1 ns). Although we deconvoluted the instrumental response, some residual signals were still present. The second fastest (5.6 and 7.2 ns) and slow (18 and 47 ns) decay time components of both samples are in the typical range for emissions from F^+ center [8-17]. Therefore, the peak at 410 nm was assigned to the emission due to F^+ center. PL decay time profile of crystal sample monitoring 750 nm is shown in Fig. 6. The decay curve showed two decay time components: one was fast 0.3 ms and the other was slow 4.4 ms. Since the decay time scale is considerably long, we suspect that these sharp emission lines of 750-950 nm are due to an unexpected contamination such as rare earth ions included in the synthesis processes because many rare earth ions tend to show such sharp emission lines regardless of the host crystal fields by the inter 4f shell transitions.

3. 3 Scintillation properties

Fig. 7 shows the scintillation spectra of the MgO ceramic and single crystal samples. Since both samples do not intentionally include any luminescent centers, the origins of these emissions must be other types of luminescence mechanisms such as exciton and defect centers, or unexpected impurities. The

emission bands of the MgO ceramic had broad spectral shapes with the peaks at 340, 600 and 760 nm. These peak locations are consistent with the ones seen in the PL spectrum under 265 nm excitation. The 340 nm peak is reasonably consistent with the earlier work [13], and the origin of this emission was attributed to the F^+ center. The origin of 760 nm peak was attributed to the Cr ion, as similarly seen in the PL spectrum. The origin of emission band at 600 nm is currently under investigation. On the other hand, the MgO single crystal showed some scintillation emissions with the peaks at 600 nm and 850-900 nm. Unlike PL, no broad emission was observed around 340 nm. The origin of emission of 600 nm is currently under investigation. In addition, the origins of sharp emissions in the 850-950 nm is ascribed to the unexpected rare earth contamination by the same reasons for the PL discussed above. For the emissions by F^+ center at 340 nm, it is much more pronounced in the ceramic sample than single crystal. The reason can be explained that, since the sample was synthesized in a high reducing atmosphere, the ceramic sample contains more oxygen vacancies, each of which attract a single hole charge to form a F^+ center.

In Fig. 8, the X-ray excited scintillation decay time profiles are shown. As for the PL decay time profiles, the scintillation decay curves are well approximated by a three exponential function. The deduced decay time constants are 0.007, 0.4 and 2.3 μ s for the ceramic, and 0.004, 0.06 and 37 μ s for the single crystal sample. The fastest component is from the instrument since the response time of the PMT (R7400, Hamamatsu) is around 1 ns. The decay lifetimes are much slower than those by PL. This difference arises by the different way of excitation and different emission mechanisms. While the X-ray ionize the host matrix and then the generated charges recombine at the luminescent centers to emit light, the UV excitation directly excites the electronic state of luminescent center followed by the emission. Since it tends to take longer time for charge/energy transfer to the luminescent center in the scintillation process, it is typical to have a longer lifetime in scintillation than PL.

3. 4 Dosimeter properties

Fig. 9 shows TSL glow curves of the ceramic and single crystal samples measured after the samples were irradiated at 1 Gy. Both the samples showed a strong single glow peak around 140 °C. This peak is consistent with previous works reported in literatures [18-24], which is a typical feature of MgO. Further, there are some additional glow peaks observed around 240 and 350°C for the ceramic sample and 320, 400°C for the single crystal sample. This fact indicates that there exist three different trapping centers in both ceramic and single crystal samples. Particularly, the peak at ~400°C in the crystal is related to the thermal decay of H centers as discussed in [23], in which the interstitial anion recombines with a neighboring F^+ center followed by emitting light. Thus, in the ceramic produced by SPS, it is suggested that there exists less anion interstitials, and the latter was also suggested by the scintillation spectrum where the emission by F^+ center is larger for the ceramic sample. Overall, TSL intensity is, in fact, much stronger for the ceramic sample than crystal while, as shown in Fig. 6, the scintillation intensity is much

stronger for the crystal. As discussed by Yanagida et al. [31, 32], these two emission intensities by different radiation-induced emission mechanisms, that is, as a dosimeter or scintillator, are typically in a complementary relationship. In a bright scintillator material, the most of radiation generated charges transfer to the luminescent center to emit light while there are less charges trapped, and vice versa.

Fig. 10 depicts a TSL spectrum of the MgO ceramic around 140 °C. The spectrum had a broad emission band in 300-400, 600 and 750 nm, which approximately coincide with scintillation spectra. However, the emission intensity at 750 nm is the strongest unlike in the case of the PL and scintillation spectra. This indicates that the Cr, even with a contamination content, acts as a very effective luminescent center in TSL. In addition, it should be noted that the intense 750 nm emission is not included in the glow curve (Fig. 9) since the thermal radiation cut filter was equipped in the instrument. If this emission signal were included, a much lower dose would be detected. Furthermore, TSL spectrum of MgO single crystal could not be measured for its weak intensity.

Fig. 11 shows a relationship between the TSL intensity and irradiated X-ray dose, namely the dose response curve, of the MgO transparent ceramic and single crystal samples. The dose response is an important characteristic as dosimeter applications. The TSL signal used here is the integrated signal of the peak at 140 °C shown in Fig. 9. From our experimental results, both the samples have a linear response to the incident X-ray dose over the dose range from 0.1 to 1000 mGy. Dosimeter having a linear response is advantageous because it enables us to easily and accurately calibrate the dose. Furthermore, particularly the MgO ceramic has much higher sensitivity than that of the single crystal. It is an equivalent performance with commercial dosimeters for personal dosimetry and showed much more superior performance for MgO than ever reported.

4. Conclusions

We have synthesized MgO transparent ceramics by an SPS technique. Subsequently, optical, scintillation and dosimeter properties were investigated in comparison with a MgO single crystal. The TSL glow curves of both samples have the main peak around 140 °C. Using this glow peak, both the samples have a dose detection ability at least over the range 0.1-1000 mGy. Furthermore, the response is linearly correlated with the incident dose over the dose range tested.

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References

- [1] T. Yanagida, A. Yoshikawa, Y. Yokota, K. Kamada, Y. Usuki, S. Yamamoto, M. Miyake, M. Baba,

- K. Sasaki and M. Ito, *IEEE Trans. Nucl. Sci.*, **57** 1492 (2010).
- [2] D. Totsuka, T. Yanagida, K. Fukuda, N. Kawaguchi, Y. Fujimoto, Y. Yokota and A. Yoshikawa, *Nucl. Instrum. Methods A.*, **659** 399 (2011).
- [3] M. R. Mayhugh, R. W. Chrisy and N. M. Johnson, *J. Appl. Phys.*, **41** 2968 (1970).
- [4] S.W.S. McKeever, *Radiat. Meas.*, **46** 1336 (2011).
- [5] Y. Miyamoto, Y. Takei, H. Nanto, T. Kurobori, A. Konnai, T. Yanagida, A. Yoshikawa, Y. Shimotsuma, M. Sakakura, K. Miura, K. Hirao, Y. Nagashima and T. Yamamoto, *Radiat. Meas.*, **46** 1480 (2011).
- [6] D.M. Roessler, W.C. Walker, *Phys. Rev.*, **159** 733 (1967).
- [7] C. Klein, C.S. Hurlbut Jr., Manual of Mineralogy, John Wiley & Sons, New York, 1999.
- [8] T. Uchino, D. Okutsu, R. Katayama, S. Sawai, *Phys. Rev. B.*, **79** 165107 (2009)
- [9] H. Soma, Y. Uenaka, A. Asahara, T. Suemoto, T. Uchino, *Appl. Phys. Lett.*, **106** 041116 (2015).
- [10] Y. Yanagisawa, R. Huzimura, *J. Phys. Soc. Jpn.*, **53** 66 (1984).
- [11] G.P. Summers, T.M. Wilson, B.T. Jeffries, H.T. Tohver, Y. Chen, M.M. Abraham, *Phys. Rev. B.*, **27** 1283 (1983).
- [12] C. Martinez-Boubeta, A. Martinez, S. Hernandez, P. Pellegrino, A. Antony, J. Bertomeu, Ll. Balcells, Z. Konstantinovic, B. Martinez, *Solid. State. Commun.*, **151** 751 (2011).
- [13] G.H. Rosenblatt, M.W. Rowe, G.P. Williams Jr., R.T. Williams, Y. Chen, *Phys. Rev. B.*, **39** 10309 (1989).
- [14] Y. Chen, J.L. Kolopus, W.A. Sibley, *Phys. Rev. B.*, **186** 865 (1969).
- [15] L.A. Kappers, R.L. Kroes, E.B. Hensley, *Phys. Rev. B.*, **1** 4151 (1970).
- [16] T. Jeffries, R. Gonzalez, Y. Chen, G.P. Summers, *Phys. Rev. B.*, **25** 2077 (1982).
- [17] Y. Uenaka, T. Uchino, *Phys. Rev. B.*, **83** 195108 (2011).
- [18] H. Nanto, K. Inabe, H. Yamazaki, N. Takeuchi, *J. Phys. Chem. Solids.*, **36** 477 (1975).
- [19] N. Takeuchi, K. Inabe, H. Nanto, *Solid. State. Commun.*, **17** 1267 (1975).
- [20] W.A. Sibley, J.L. Kolopus, W.C. Mallard, *Phys. Status Solidi.*, **31** 223 (1969).
- [21] W.M. Ziniker, J.M. Rusin, T.G. Stoebe, *J. Mater. Sci.*, **8** 407 (1973).
- [22] A. Sathymoorthy, J.M. Luthra, *J. Mater. Sci.*, **13** 2637 (1978).
- [23] W.C. Las, T.G. Stoebe, *Radiat. Prot. Dosim.*, **8** 45 (1984).
- [24] S. Dolgov, T. Karner, A. Lushchik, A. Maaroos, N. Mironova-Ulmane, S. Nakonechnyi, *Radiat. Prot. Dosim.*, **100** 127 (2002).
- [25] C. Soliman, *Radiat. Eff. Defect. S.*, **164** 257 (2009).
- [26] Y. Fang, D. Agrawal, G. Skandan, M. Jain, *Mater. Lett.*, **58** 551 (2004).
- [27] R. Chaim, Z. Shen, M. Nygren, *J. Mater. Res.*, **19** 2527 (2004).
- [28] D. Chen, E.H. Jordan, M. Gell, *Scripta. Mater.*, **59** 757 (2008)
- [29] R. Chaim, R. Marder, C. Estourns, *Scripta. Mater.*, **63** 211 (2010).
- [30] S. Wakahara, T. Yanagida, Y. Yokota, Y. Fujimoto, V. Chani, M. Sugiyama, Y. Futami, A. Yoshikawa, *Opt. Mater.*, **35** 558 (2013).
- [31] T. Yanagida, Y. Fujimoto, K. Watanabe, K. Fukuda, N. Kawaguchi, Y. Miyamoto, H. Nanto, *Radiat. Meas.*, **71** 162 (2014).
- [32] T. Yanagida, *J. Lumin.*, in press, doi:10.1016/j.jlumin.2015.01.006 (2015).
- [33] T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi, T. Yanagitani, *Opt. Mater.*, **35** 2480 (2013).
- [34] T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama, K. Mori, *Appl. Phys. Exp.*, **7** 062401 (2014).
- [35] T. Yanagida, Y. Fujimoto, N. Kawaguchi, S. Yanagida, *J. Ceram. Soc. Jpn.*, **121** 988 (2013).

Fig. 1 Synthesized MgO transparent ceramic (left) and single crystal sample (right) under ambient light (top) and 254 nm UV light (bottom).

Fig. 2 SEM image of MgO ceramic.

Fig. 3 Transmittance spectra of MgO transparent ceramic and single crystal.

Fig. 4 PL emission spectrum of MgO ceramic and single crystal samples when excited at 265 nm in the UV-Vis (left) and NIR ranges (right). The inset in the right figure expands the spectral data around 700 nm.

Fig. 5 PL decay time profiles of MgO ceramic (left) and single crystal (right) samples under 280 nm excitation while monitoring the 410 nm emission.

Fig. 6 PL decay time profiles of MgO single crystal sample under 280 nm excitation while monitoring the 750 nm emission.

Fig. 7 X-ray induced scintillation spectra of the MgO ceramic and the single crystal samples. The inset expands 650-950 nm regions.

Fig. 8 Scintillation decay time profiles of the MgO ceramic (left) and single crystal (right) samples.

Fig. 9 TSL glow curve of the MgO ceramic and the single crystal after 1 Gy X-ray exposure.

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