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Full Length Article

Scintillation, OSL and TSL properties of yttria stabilized zirconia crystal

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ABSTRACT

We investigated the scintillation and dosimeter properties of yttria stabilized zirconia (YSZ, Y_2O_3–ZrO_2) crystal. It showed 70–80% in-line transmittance at wavelength longer than 300 nm. Under excitations around the bandgap energy, several intense photoluminescence (PL) emission peaks appeared at 450, 550, 570 and 600 nm, and the PL decay time constants were 5.5 and 20.7 ns. In the X-ray induced scintillation spectrum, an intense emission peak around 450 nm was observed, and the scintillation decay time constants were 14.4 and 169.8 ns. After irradiations with X-rays, thermally stimulated luminescence (TSL) glow peaks appeared at 100, 200 and 450 °C. Also, after X-ray irradiations, optically stimulated luminescence (OSL) was detected around 500 nm with 650 nm stimulation.

1. Introduction

In order to measure invisible ionizing radiations, luminescent materials have commonly been utilized in radiation detectors. Such materials may be classified into two types such as scintillators and dosimeters. The former is a phosphor which converts ionizing radiation to thousands of visible photons immediately. Scintillators are used in various fields of radiation detections such as medical imaging [1], security system [2], well-logging [3], high energy physics [4] and astrophysics [5]. On the other hand, dosimeters are mainly used for personal dose monitoring. Such materials store and accumulate the absorbed radiation energy, and the accumulated energy is released in a form of light emission during heating (thermally stimulated luminescence: TSL) or optical stimulation (optically stimulated luminescence: OSL). The emission intensity is proportional to the dose accumulated, hence the dose can be indirectly measured.

In this study, we have studied the scintillation, TSL and OSL properties of yttria stabilized zirconia (YSZ, Y_2O_3–ZrO_2) crystal. YSZ is, in general, well-known as a solid state ionic conductor which has a high mechanical strength and chemical stability. With these notable characteristics, YSZ has been used in various applications including gas sensors [6], conductive ceramics [7], thermal barrier coatings [8], and solid fuel cells [9]. In these applications, understanding the behavior of YSZ under excitation is important. The emission by the recombination of the photo-excited electrons with holes is called the photoluminescence (PL), and the PL measurements often give us information towards understanding the nature of electrons and holes in materials. Thus, the PL properties of YSZ show its electronic band structure and indispensable defects in synthesis of bulk forms. To date, the PL properties of non-doped and rare earth doped YSZ have been reported elsewhere [10–16], and YSZ is well known as one of the good phosphors, which has various emission wavelengths. However, as far as we are aware, no studies have been reported on the radiation induced luminescence properties of YSZ. YSZ is an interesting material since it has a high density of 6 g/cm^3 so the radiation stopping power is high and radiation energy is effectively absorbed. Also, in some host materials, an inclusion of zirconium would enhance the detection probability of the double beta decay ($0\nu\beta\beta$) which tests the validity of the grand unification theory [17], and yittria itself acts as a very bright scintillator [18,19]. Moreover, in addition to the scintillation properties, it is of a great importance to comprehensively investigate the dosimeter properties together since these are complementarily related as reported in Ref. [20]. In other words, for example, a bright scintillator material is not a sensitive dosimeter and vice versa. Therefore, such comprehensive study helps reveal a room to improve the performance as a radiation detector.

2. Experimental procedures

The YSZ crystal sample used in this study is a commercial product and was purchased from NEOTRON, Japan. Fig. 1 shows an appearance of the sample. The sample size was $10 \times 10 \times 1$ mm^3. The wide

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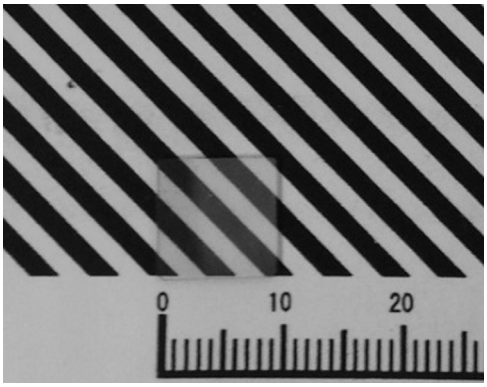

Fig. 1. Picture of YSZ crystal.

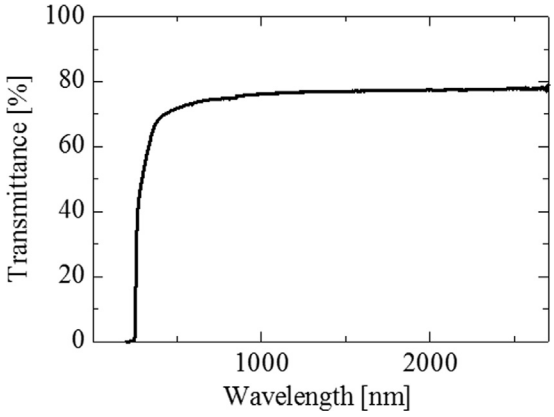

Fig. 2. In-line transmittance of YSZ crystal.

surfaces were polished for optical characterizations, and it was visually colorless. 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 spectra under various excitation wavelengths were measured by using a spectrofluorometer (FP-8600, JASCO). The PL decay time profile monitoring at 450 nm under 280 nm excitation was evaluated by using Hamamatsu Quantaurus-τ (Hamamatsu Photonics). The reason why we used the 280 nm excitation was because it was the shortest and most efficient excitation wavelength available in the instrument.

X-ray induced radioluminescence (RL) spectrum was measured by utilizing our original setup [21]. The irradiation source was X-ray generator equipped with a tungsten anode target (XRB80P&N200X4550, Spellman). During the measurements, the X-ray generator was supplied with the voltage of 80 kV and tube current of 2.5 mA. While the sample was irradiated by X-rays, the scintillation emissions from the sample were fed into the spectrometer through a 2 m optical fiber to measure the scintillation spectrum. The spectrometer (Andor DU-420-BU2 CCD and Shamrock 163 monochromator) was cooled down to 193 K by a Peltier module to reduce the thermal noise. Further, we have measured the scintillation decay time and afterglow profiles using a pulsed X-ray source equipped afterglow characterization system [22]. In order to characterize relatively shallow trapping centers induced by X-ray irradiations, the TSL glow curves were measured by TL-2000 (Nanogray, Japan) with the heating rate of 1 °C/s over the temperature range from 50 to 490 °C [23]. On the other hand, for deeper trapping centers, OSL was also studied under 650 nm stimulation by using FP8600 spectrofluorometer (JASCO). Except the TSL, all the other measurements mentioned above were performed at room temperature unless specified.

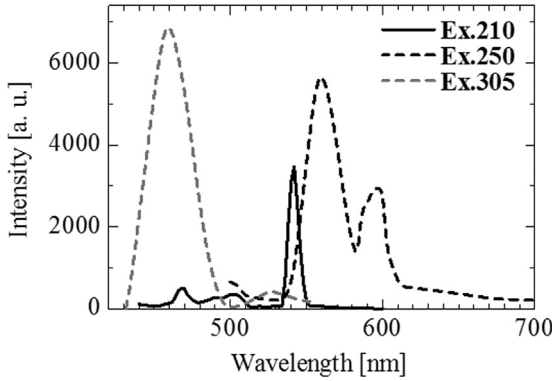

Fig. 3. PL emission spectra upon various excitation wavelengths.

3. Results and discussion

The in-line transmittance spectrum of YSZ crystal is shown in Fig. 2. The transmittance was 70–80% at the wavelengths longer than 300 nm, but a rapid edge was clearly observed around 300 nm due to the bandgap absorption. The observed data was consistent with the bandgap energy (5.0 eV=250 nm) of YSZ [24]. No particular absorption band structures were observed in the wavelength range of our measurement.

The PL emission spectra are shown in Fig. 3. Under excitations with 305, 210 and 250 nm, one intense emission band around 450 nm, one emission band around 550 nm and two emission bands around 570 and 600 nm appeared, respectively. Petrik et al. reported that YSZ has three main defect structures with oxygen vacancies, and they affect the PL spectrum [12]. That is, the emission at 450 nm is due to a defect structure where all the nearest neighbors of Zr^{4+} are in oxygen vacancy, and the emissions at 550 and 600 nm correspond to defect structures where a single oxygen vacancy has one and two neighboring Y^{3+} ions, respectively.

The PL decay time profiles of YSZ monitoring at 450 nm emission band under 280 nm excitation are illustrated in Fig. 4. The obtained decay time constants are 1.1, 5.5 and 20.7 ns. We think that the fastest component (1.1 ns) would be due to the instrumental response because the timing resolution of the instrument was around 1 ns. The 5.5 ns component is caused by some kinds of defects of ZrO_2 because similar results were reported previously [25]. The origin of the 20.7 ns component is under investigation but a similar decay profile with 20 ns of lifetime was previously reported by another research [26]. In this report, it was mentioned that the lifetime of this decay component varies by heat treatment in air; therefore, the origin of this 20 ns component would be due to the oxygen vacancy.

The X-ray induced scintillation spectrum of YSZ is shown in Fig. 5. As it was observed in the PL spectra, an emission band was observed around 450 nm. Although no reports can be found about scintillation properties of both YSZ and ZrO_2, a previous work [18] reported that Y_2O_3 ceramics show scintillation with a broad emission peaking around 350 nm, but the emission peak does not agree with our result. Therefore, we think that the scintillation observed around 450 nm is mainly due to the defect centers surrounded by Zr^{4+} ions as suggested by the PL measurements. The broad structure of the emission suggest that there are some other emissions with different origins, but they overlap each other to have such a broad structure. Additionally, self-trapped excitons (STE) might cause the broad peak since STE is observed in Y_2O_3 [18] and other simple oxides. These minor emission may be due to the other defects observed in our PL measurements above. In addition, we think that a weak sharp peak appeared around 610 nm would be due to an unexpected rare earth