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Scintillation and dosimeter properties of CaF_2 translucent ceramic produced by SPS

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ABSTRACT

We have developed CaF_2 translucent ceramics by spark plasma sintering (SPS) and investigated the scintillation and dosimeter properties, in comparison with a CaF_2 single crystal. Under X-ray irradiation, light emission was observed at 270 and 300 nm, due to self-trapped exciton (STE). The scintillation light yield of CaF_2 translucent ceramic was measured to be about 6000 photons/MeV under ^{137}Cs irradiation, and this value was smaller than that of the single crystal by a factor of approximately 2. The afterglow level, after X-ray irradiation, of the ceramic sample was lower than that of the single crystal. Thermally stimulated luminescence (TSL) glow peaks were observed at 100 and 150 °C in both ceramic and single crystal samples, however the TSL intensity was much stronger than that of the single crystal sample.

1. Introduction

In solid state ionizing radiation detectors, there are mainly two different approaches. One is direct conversion type, and the other is indirect conversion. The former type typically uses semiconductor detectors (e.g., Si photodiode) which directly converts radiations to electronic signals, and the latter utilizes phosphor materials such as scintillator and dosimeter materials, which convert radiations to low energy photons which are then measured by conventional photodetectors. Thus, radiations are converted to electronic signals indirectly. Scintillators have a function to convert the absorbed energy of ionizing radiation into low energy photons almost instantly, and they have been widely used in practical applications such as medicine [1], security [2] and high energy physics [3]. Among scintillation properties, particularly important ones in practical applications are high light yield and short decay time. On the other hand, dosimeters store and accumulate incident radiation energy in a form of carrier trapping at localized centers. The absorbed energy can be read out as a form of photon emissions by external stimulation, which de-capture the trapped charges followed by recombination. When the stimulation is light, the resultant light emission is referred as optically stimulated luminescence (OSL), whereas emitted light stimulated by heat is so-called thermally stimulated luminescence (TSL). It is desirable that the effective atomic number (Z_{eff}) of dosimeter material is close to that of the soft tissue of human body (Z_{eff} = 7.51) because dosimeters are mainly used to measure absorbed dose in human body (or personal dose monitoring applications) [4]. If Z_{eff} of dosimeter is the same as that of human body, no energy dependence is essentially expected, so mathematical calibrations are not needed. In addition, it has been recently clarified that scintillation and dosimeter properties have complementary relationship [5,6].

Raw materials of CaF_2 can be found easily in nature, and CaF_2 can be manufactured in large quantities with low cost. The CaF_2 single crystal is known to show scintillation emission due to self-trapped exciton (STE) at 270 nm [7]. In addition, it has a large band gap energy (12 eV) and relatively high scintillation light yield (13,000 photons/MeV) [8], and CaF_2 has been studied for potential use as a scintillator in astrophysics [9]. On the other hand, CaF_2 has also attracted much attention as dosimeter material [10] because the effective atomic number(Z_{eff} = 17.1)is close to that of soft tissue. Therefore, the CaF_2 would be a favorable candidate for both scintillation and dosimeter materials. There are a number of studies published on a use of CaF_2 in various forms, e.g. single crystals [11] and nanoparticles [12], for indirect radiation detections. Furthermore, impurities such as europium [13], ytterbium [14] and thulium [15] may be added to CaF_2 as emission centers in order to enhance the properties. So far, materials used in ionizing radiation detectors are bulk single crystals mainly because they have a high optical quality. However, the recent advancement of sintering

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techniques has made us possible to synthesize inorganic ceramics with high optical transparency. We have previously shown that, compared with a single crystal form, some luminescence properties of transparent ceramics were modified and improved [16–19]. In spite of the numerous number of studies reported on CaF_2 single crystals and transparent ceramics doped with rare earths [20–25], no reports are found for scintillation and dosimeter properties of non-doped CaF_2 transparent ceramic. For the reasons, in this study, we have synthesized a non-doped CaF_2 translucent ceramic by using spark plasma sintering (SPS). Subsequently, we studied both the scintillation and dosimeter properties, together with those of CaF_2 single crystal.

2. Experiment

CaF_2 translucent ceramic was synthesized by the SPS technique using Sinter Land LabX-100 in a vacuum. The 1.5 g of high purity CaF_2 powder (>99.99%) which was purchased by Tokuyama Corp was introduced into a cylindrical graphite die with a hole of 10.4 mm in diameter, in which the raw powder was held between two graphite punches inserted to the hole. Subsequently, the sintering was performed by applying uniaxial pressure through the assembly while applying pulsed current to sinter. The sintering was carried out by two steps. First, the temperature was increased from 15 °C to 800 °C with a heating rate of 80 °C/min and then kept at 800 °C for 10 min under 10 MPa pressure. Next, the temperature was further increased from 800 °C to 1070 °C with a heating rate of 100 °C/min and then kept at 1070 °C for 15 min under 70 MPa pressure. The temperature was measured by using a thermocouple (K type) attached onto the graphite die. After the SPS sintering treatment, both the flat faces of cylinder-shaped sample were mechanically polished using 0.05 μm alumina polishing suspension. CaF_2 single crystal sample used in this study was prepared by Tokuyama Corp, and the surfaces were also fine-polished as for the ceramic sample. The sizes of single crystal and ceramic samples were comparable, and they were equally characterized by the same manner described below.

Backscattered electron image was observed by using a scanning electron microscope (SEM; Hitachi TM3030). The optical in-line transmittance spectra were measured by using JASCO V670 spectrometer over the spectral range of 190–2700 nm with 1 nm intervals.

In order to investigate scintillation properties, X-ray induced scintillation spectra were measured by using our original setup [26]. The excitation source was an X-ray generator equipped with a tungsten anode target (XRB80P&N200×4550, Spellman), and it was operated with the tube voltage of 40 kV and current of 5.2 mA. The scintillation photons from the sample were collected and guided to the spectrometer (Ander DU-420-BU2 CCD and Shamrock 163 monochromator) through a 2.0 m optical fiber. Here, the spectrometer was placed off the irradiation geometry axis in order to avoid strike the X-rays onto the CCD. The spectrometer was cooled down to 193 K by a Peltier module in order to reduce the thermal noise. X-ray induced scintillation decay and afterglow profiles were evaluated by using a pulse X-ray source equipped afterglow characterization system [27]. The applied voltage to the X-ray source was 30 kV. The scintillation light yield induced by γ-rays was evaluated by conducting pulse height spectroscopy measurements. In the measurements, a sample was firmly placed onto a window of photomultiplier tube (PMT; R877-100, Hamamatsu) by using optical grease (6262A, OKEN), and the sample was covered by several layers of Teflon sheet in order to effectively guide the scintillation photons to the PMT. The PMT output signals was amplified by a pre-amplifier (113, ORTEC) and processed by a shaping amplifier (572, ORTEC) with 3 μs shaping time. The signal output was integrated and registered by a multichannel analyzer (Pocket MCA 8000A, Amptek) and then a pulse height spectrum was constructed on a computer. Here, a sealed radioactive ^{137}Cs γ-ray was used as the radiation source in this measurement.

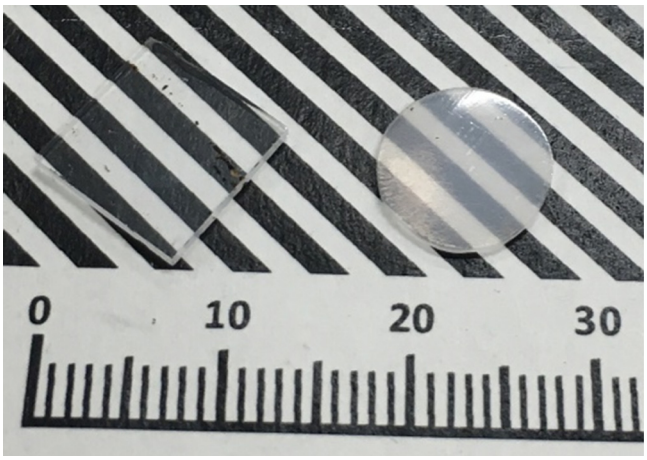

Fig. 1. Synthesized CaF_2 translucent ceramic (right) and single crystal (left) samples.

In order to investigate thermally stimulated luminescence (TSL) properties, a TSL glow curve was measured by using a TSL reader (TL-2000, Nanogray Inc.) [28] after X-ray irradiation. The heating rate was 1 °C/s over, and the measurement temperature range was from 50 to 490 °C.

3. Results and discussion

3.1. Sample

Fig. 1 shows a photograph of CaF_2 ceramic sample synthesized in this research and single crystal sample as a reference. The thickness of the single crystal and ceramic samples were 1.00 and 0.70 mm, respectively. It can be confirmed that the stripe patterns on the back of samples are clearly seen through. An SEM image of the ceramic sample is illustrated in Fig. 2. From the SEM image, an average grain size on the surface of the ceramic sample was estimated to be about 35 μm. Fig. 3 shows the in-line transmittance spectra of the CaF_2 ceramic and single crystal samples. The single crystal showed very high transmittance (~80–90%) in the visible range, and the fundamental absorption edge was beyond the measurable range by the instrument. On the other hand, transmittance of the ceramic sample was much lower and varied ~5–80% over the measurement range. The low transmittance should be due to the contribution of Mie scatterings as also indicated by the appearance that the sample is seen milky in the photograph (Fig. 2). In addition to the visual observation, it is also based on the curve fitting with a Mie-based formula [29], which is plotted together in Fig. 3. The experimental data and the mathematical results reasonably agree each other; however, it is also possible that additional contribution is involved as these curves are not perfectly in agreement. Overall, both samples, no particular absorption bands independent to the host were observed throughout the spectral range of measurement.

3.2. Scintillation properties

X-ray induced scintillation spectra of CaF_2 ceramic and single crystal samples are presented in Fig. 4. Emission peaks at 270 and 300 nm were observed in both the samples. Similar emission peaks were also reported by earlier work [7], in which the origins of these emissions are ascribed to STE. Furthermore, an additional emission peak at 500 nm appeared only in the ceramic sample. A similar

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