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Scintillation and thermoluminescence properties of Ce-doped $Ca_2Al_2SiO_7$ single crystals

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ABSTRACT

Undoped and Ce-doped $Ca_2Al_2SiO_7$ single crystals with different Ce concentrations were prepared by the floating zone method. From the X-ray diffraction patterns, we confirmed that all the grown crystals have no impurity phases. The undoped sample shows scintillation induced by X-rays, and the spectrum consists of two broad emission bands peaking at 350 and 400 nm. The decay curve appeared to consist of only single exponential decay with the decay constant of 51 ns. In contrast, Ce-doped samples show a broad scintillation peaking around 400 nm, in which the decay curve consists of two exponential decay functions with the decay times of approximately 30 and 100 ns. From the pulse height spectra measured using the present samples under ^{241}Am 59.5 keV γ-ray irradiation, we confirmed that the 0.3% Ce-doped sample exhibits the highest absolute scintillation light yield of 16,000 ph/MeV. The samples also exhibit thermoluminescence (TL). The glow curves appear to have a broad feature with the peak temperature from 100 to 500 °C for undoped and from 50 to 400 °C for Ce-doped samples. Among the present samples, the 0.3% Ce-doped sample shows the highest sensitivity, and a linear response to the irradiation dose was confirmed in the dose range of 0.01–100 mGy.

1. Introduction

Ionizing radiation detectors using solid-state phosphors have been widely used in industrial and scientific fields such as medical imaging [1], security system [2], well-logging [3], personal dose monitoring [4] and astrophysics [5]. Such phosphors used in radiation measurement applications can be categorized to two types: scintillators and dosimeters. The former immediately converts the absorbed energy of ionizing radiation into a large number of low-energy photons such as UV, visible and near-infrared [6] while the latter stores the radiation energy and emits photons by an external stimulation [7]. As the common scintillation mechanism, interactions of ionizing radiations and materials generate many secondary electrons in the host lattice, and some of them reach to emission centers. Finally, scintillation photons are emitted via electron-hole recombinations at the emission centers. Because interactions of radiation with matter depends on the chemical composition and radiation type, there are many different scintillator materials used today which are designed and developed for each application of interest. Typically, heavy materials are preferred to detect X- and gamma-rays. In contrast, light materials containing ^{6}Li and ^{10}B are used to detect neutrons. And materials of intermediate density are used to detect charged particles [8].

Melilite compounds, which has the tetragonal structure, has high chemical stability and is non-hygroscopic, which are preferable properties for scintillators and dosimeters [9]. Although the melilite compounds have many kinds of chemical compositions, one of the common compositions is expressed as $AE_2Al_2SiO_7$ where *AE* stands for alkali metal elements. $Ca_2Al_2SiO_7$ (CASM), whose density is 3.038 g/cm^3, also has a melilite structure and belongs to the family of $AE_2Al_2SiO_7$. The luminescence properties of rare-earth-doped CASM have been studied intensively in various fields including laser [10], thermoluminescence (TL) [11] and mechanoluminescence applications [12]. To the best of our knowledge, only a few studies on scintillation properties of CASM have been reported. However, the material form was in powder [9], and no studies in a bulk crystalline form have been reported yet. A bulk crystalline form is essentially important for scintillators. This is because single crystalline materials generally have a high density which leads to high interaction probabilities with radiations. In addition, single crystals have high optical transparency which can effectively deliver the scintillation photons to photodetectors to detect the signal [13]. In addition to the host material, emission centers are also important in scintillators. Today, Ce-doped materials are the most common choice of scintillator materials owing to the strong emission in the near-ultraviolet and visible regions [14] with a fast decay time of several tens of

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nanoseconds due to the 5d-4f transitions. Typical examples of the Ce-doped scintillator materials in practice are Gd_2SiO_5 [15], $Gd_2Si_2O_7$ [16], $Lu_{2(1-x)}Y_2xSiO_5$ [17], Lu_2SiO_5 [18], $LaBr_3$ [19] and $Gd_3Al_2Ga_3O_{12}$ [20,21]. Such a fast scintillation response is favorable particularly for high counting rate applications such as the positron emission tomography (PET) [22].

In this work, for the reasons above, we studied Ce:CASM single crystals for scintillator and dosimeter applications. The Ce:CASM single crystals with various concentrations of Ce were synthesized by the floating zone (FZ) method. Then, we evaluated the photoluminescence (PL), scintillation and TL properties. In addition to scintillation properties, we also study the TL as dosimetric properties to comprehensively evaluate radiation-induced luminescence properties since scintillation and dosimetric properties are complementary related [6,23]. Since the effective atomic number of CASM (15.2) is close to that of human soft tissue (7.29), CASM is suitable as dosimeter material.

2. Experimental

We used CaO (99.99%), Al_2O_3 (99.99%), SiO_2 (99.99%) and CeO_2 (99.99%) powders as raw materials. They were mixed in a stoichiometric ratio homogeneously, and the mixture was formed to a cylinder rod by applying a hydrostatic pressure. The rod was then sintered at 1200 °C for 6 h to obtain a ceramic rod. The sintered rod was loaded into the FZ furnace, and the crystal growth was conducted with the pull-down rate of 5 mm/h. To identify the crystalline phase, X-ray diffraction (XRD) pattern was measured using a diffractometer (MiniFlex600, Rigaku). The X-ray tube (CuKα) was operated at 40 kV and 15 mA, and the scanning 2θ range was 5–90°. After cutting the samples to adjust size, the prepared samples were characterized as below.

The PL excitation and emission spectra was measured by a spectrofluorometer (FP-8600, JASCO). The excitation and emission spectral ranges were from 220 to 410 nm and from 350 to 510 nm, respectively. PL quantum yield (*QY*) were measured by using Quantaurus-QY (C11347, Hamamatsu). The spectral range measured for the excitation and emission were 250–400 nm and 200–950 nm, respectively. The absolute *QY* was defined as $QY = N_{emit}/N_{absorb}$ where N_{emit} and N_{absorb} are the numbers of emitted and absorbed photons, respectively. In this evaluation, N_{emit} is the integrated number of emitted photons from 360 to 550 nm, and N_{absorb} is that of absorbed photons of 350 ± 10 nm.

PL decay time profiles were evaluated using Quantaurus-τ (C11367, Hamamatsu). Here, the equipped excitation source was a pulse LED. The excitation wavelengths were 340 and 280 nm for the undoped CASM and Ce:CASM samples, respectively, while the monitoring wavelengths for the undoped and Ce-doped CASM were 410 and 420 nm, respectively. The pulse repetition rate was 500 kHz and the decay profile was recorded over the range of 500 ns.

As a scintillation property, X-ray-induced scintillation spectrum was measured by utilizing our original setup [21]. The irradiation source was an X-ray generator (XRB80N100/CB, Spellman) equipped with a conventional X-ray tube (tungsten anode target) and beryllium window. During the measurements, the X-ray tube was supplied with a bias voltage of 60 kV and tube current of 1.2 mA. While the sample was irradiated by X-rays, the scintillation from the sample was fed into a CCD-based spectrometer (Andor DU-420-BU2 CCD with Shamrock SR163 monochromator) through a 2 m optical fiber to measure the spectrum. The CCD was cooled down to 188 K by a Peltier module to reduce the thermal noise. Further, we have measured the scintillation decay time using an afterglow characterization system equipped with a pulse X-ray source [24,25]. The pulse height spectroscopy measurement was performed in order to characterize the absolute scintillation light yield (*LY*: number of emission photons per incident radiation energy). For the measurements, we placed a sample on a window of photomultiplier tube (PMT; R7600U-100, Hamamatsu) with optical grease (OKEN 6262A), and the sample was covered by a Teflon tape. A bias voltage of 600 V was applied to the PMT by a DC power supply (ORTEC 556), and the electrical signal from the anode of the PMT was amplified by a pre-amplifier (ORTEC 113). Further, the amplified signal was processed by a shaping amplifier (ORTEC 570) with 500 ns shaping time to obtain the light output upon a single γ-ray event, which was then processed by a multichannel analyzer (Pocket MCA 8000A, Amptek). Finally, the pulse height spectrum was constructed on the computer. We used a sealed radioactive ^{241}Am γ-ray source (59.5 keV) as a radiation source in this measurement. We used the Tl-doped NaI single crystal (40,000 ph/MeV) [26] as a reference to derive *LY* of present samples. The scintillation spectra of a Tl-doped NaI and Ce:CASM single crystals were similar; therefore, the uncertainty arose by the spectral response of PMT was negligible.

As dosimetric properties, the TL glow curve and the TL intensity as a function of irradiation dose, namely dose response function, were evaluated. The sample sizes of undoped, 0.3%, 1.0% and 3.0% Ce-doped CASM single crystals used in TL properties are 75, 85, 50 and 70 mm^3, respectively. The TL glow curve was measured by using TL-2000 (Nanogray). In this instrument, TL photons from 300 nm to 500 nm were integrated, and a heating rate was 1 °C/s. The irradiation was performed by using the same X-ray generator as the one used for the scintillation spectrum measurements. The irradiation dose was calibrated by an ionization chamber (TN30013, PTW). All the characterizations were performed at room temperature unless stated.

3. Results and discussion

3.1. Sample synthesis and structure

Undoped and Ce-doped CASM crystal samples were successfully grown by the FZ method. Photographs of the grown crystals are shown in Fig. 1. The typical size of the obtained crystal rods was ~4 mm in diameter and ~30 mm in length. The undoped sample and the 0.3% and 1.0% Ce-doped samples look colorless and transparent, and the 3.0% Ce-doped sample looks white and translucent. These samples were cut into small pieces for characterizations.

The XRD patterns of undoped and Ce-doped CASM are shown in Fig. 2. The standard diffraction pattern (COD card No. 1000048) is also provided as a reference. All the diffraction peaks measured are identified as CASM, and no impurity phase was observed. The CASM has tetragonal structure with space group of $P42_1m$.

3.2. PL properties

The excitation and emission spectra of the 0.3% Ce-doped CASM single crystal is demonstrated in Fig. 3 as a representative. The excitation spectrum was measured by monitoring the emission at 420 nm while the emission spectrum was measured by 280 nm excitation. A broad emission is observed from 380 to 500 nm, and the origin is ascribed to the 5d-4f transitions of Ce^{3+} which is often seen in Ce^{3+}-doped materials [27,28]. The excitation bands around 260 and 360 nm are due to the 4f-$5d_2$ and 4f-$5d_1$ transitions of Ce^{3+}, respectively. All the Ce-doped samples show similar excitation and emission features. The *QY*s of 0.3%, 1.0% and 3.0% Ce-doped CASM are 23%, 21% and 13%, respectively. The signal from the undoped sample was too small to measure. The measured excitation-emission features are similar to those reported in the previous work on Ce-doped CASM single crystal [29].

The PL decay time profiles of the Ce-doped CASM single crystals are

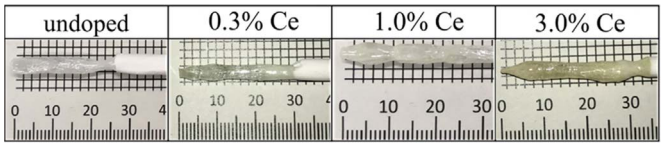

Fig. 1. Photographs of the synthesized CASM single crystals undoped and doped with Ce.