Luminescence and scintillation properties of Ce doped SrHfO₃ based eutectics

Kei Kamada^{a,b,*}, Shunsuke Kurosawa^{b,c}, Yasuhiro Shoji^{a,c}, Jan Pejchal^{b,d}, Yuji Ohashi^c, Yuui Yokota^a, Akira Yoshikawa^{a,b,c}

^a C&A Corporation, T-Biz, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

^b Tohoku University, New Industry Creation Hatchery Center, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

^c Tohoku University, Institute for Material Research, 2-1-1 Katahira Aoba-ku, Sendai, Miyagi 980-8577, Japan

^d Institute of Physics AS CR, Cukrovarnicka 10, 16253 Prague, Czech Republic

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ABSTRACT

Ce doped SrHfO₃/SrAl₁₂O₁₉ eutectics were grown by the micro pulling down (μ -PD) method and their directionally solidified eutectic system has been investigated. Investigations of obtained eutectic structure, luminescence and scintillation performances were also performed. Eutectics were grown at the speed of 0.60–0.90 mm/min. In the eutectics, Ce³⁺ 4f–5d emission was observed at 410 nm. The eutectics showed light yield of around 300 photon/5.5 MeV alpha-ray by ²⁴¹Am excitation. Scintillation decay time was 26.4 ns (45%) with slower decay component of 263 ns (55%).

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1. Introduction

A number of halide and oxide scintillator materials have been developed and they are applied to various fields such as astronomy, medical imaging, and homeland security. Although halide scintillators, such as Tl:Nal, Tl:Csl and Ce:LaBr₃ [1], have high light outputs of more than 30,000 photons/MeV, they have hygroscopic nature. In the X-ray imaging, indirect flat panel detector (FPD) composed of a scintillator layer such as Csl:Tl and photo-sensor array requires improvements in their spatial resolution and sensitivity. But the spatial resolution is degraded by the light scattering in the columnar films with increasing the film thickness [2]. Recently submicron-diameter phase-separated scintillator fibers (PSSFs) were reported and they possessed both the properties of an optical fiber and a radiation-to-light conversion. The PSSFs were fabricated using a directionally solidified eutectic (DSE) system. The DSE systems have been discovered in various materials for many applications [3–6]. In PSSFs, the light emitted from the scintillator fibers is confined and transported along the fiber direction by a total reflection mode as shown in Fig. 1, so that high-resolution radiation imaging can be achieved. Csl/NaCl [7] and Ce:GdAlO₃(GAP)/Al₂O₃ [8] have been already reported as PSSFs.

Recently, SrHfO₃ doped with Ce (Ce:SHO) has attracted attention due to its high density of 7.65 g/cm³, a high effective atomic number of 64 and negligible intrinsic-background. [9]. However, hafnium

itself and hafnium compounds have generally high melting temperatures of more than 2300 °C, and that of SHO is approximately 2700 °C. Due to the high melting-temperature, it is difficult to grow the crystal from the melt in a crucible using conventional crystal growth methods such as Czochralski, Bridgman, and micro-pulling down (μ -PD) method. Therefore, Ce:SHO scintillators were investigated in the form of nano-crystals and ceramics obtained from crystalline powders prepared by solid-state synthesis (Ji et al., 2005; Nikl et al., 2011; therefore, Ce:SHO scintillators were investigated in the form of nano-crystals and ceramics obtained from crystalline powders prepared by solid-state synthesis [10,11]. Scintillation properties of the Ce:SHO ceramics have been investigated by some groups [11–13]. Maximum emission wavelength, light output and decay time under X-ray excitation of Ce:SHO prepared by a vacuum hot pressing or a hot isostatic pressing were determined to be 410 nm, 40,000 photons/MeV and 42 ns, respectively. In addition, timing resolution of ceramics Ce:SHO was 276 ps [11].

In this study, Ce:SHO/SrAl₁₂O₁₉ (SAO) eutectics were grown by the micro pulling down method and their DSE system has been investigated. Investigations of obtained eutectic structure, luminescence and scintillation performances were performed.

2. Experimental

2.1. Crystal growth

A stoichiometric mixture of 4 N CeO₂, SrCO₂, HfO₂ and α -Al₂O₃ powders (Kanto Chemicals Co.) was used as starting material.

* Corresponding author at: Tohoku University, New Industry Creation Hatchery Center, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan.

Fig. 1. Schematic view of directionally solidified eutectic (DSE) scintillator.

Ce:SHO/SAO eutectics were grown by the μ -PD method with a RF heating system at the composition of 0.21 mol% CeO₂, 20.79 mol% SrCO₃, 25 mol% HfO₂, 50 mol% Al₂O₃ (see Fig. 2, [14]). A schematic of the μ -PD growth apparatus is given in Ref. [15]. Typical pulling rates were 0.6–0.9 mm/min and the diameter was around 3 mm. Crystals were grown from an Ir crucible under the N₂ atmosphere. An Ir rod was used as a seed for crystal growth. Plates of ϕ^3 mm $\times$ 1 mm were cut and polished for luminescence spectra and scintillation properties measurements, while the rest of the rods were used for the crystal structure analyses. The eutectic phase structure was observed by back scattered electron image (BEI) using Hitachi S3400N and their chemical compositions were observed by electron probe microanalysis (EPMA; JXA-8621MX, JEOL). Pieces of the grown crystals were crushed and ground into powders in a mortar. Powder X-ray diffraction analysis was carried out in the 2θ range 15–75° using RINT Ultima (RIGAKU) diffractometer. The Cu K α X-ray source was used, and the accelerating voltage and current were of 40 kV and 40 mA, respectively.

2.2. Optical, luminescence and gamma-ray response measurement procedure

Excitation and emission spectra were measured with Spectrofluorometer 199S (Edinburgh Instrument) using a Xenon lamp.

Radio-luminescence spectrum at room temperature was measured with the spectrometer (EI FLS920) under an X-ray (Cu K α 40 kV, 30 mA). Light output measurements were performed by using photomultiplier tube (PMT Hamamatsu R7600U). Sample pieces with 3 mm in diameter and 1 mm in thickness were cut from the grown single crystal, ϕ^3 mm surfaces were mechanically polished. The samples were coupled by the PMT using silicone grease (OKEN, 6262A). The pieces were covered by using Teflon-tape. To determine the light yield, the energy spectra were collected under 662 keV γ -ray excitation (¹³⁷Cs source) by using a PMT (Hamamatsu H7600, bialkali photocathode, quartz window). The signal was fed into a shaping amplifier (ORTEC 572A), a multichannel analyzer (MCA) (ORTEC 926), and finally to a personal computer. The shaping time was set as 2 μ s. The bias for the PMT was supplied by an ORTEC 556. For the decay time measurement the same setup with the PMT and digital oscilloscope TD5032B were used.

3. Result and discussion

3.1. Crystal growth

Eutectic crystals were grown at various growth speeds in an attempt to generate rod-like microstructure. An photograph of the grown eutectic is shown in Fig. 3a. White rod with 3 mm in diameter and 13 mm in length was obtained. BEI of grown crystals in vertical and transverse cross-section are shown in Fig. 3b and c. Rod phases with around 3–4 μ m diameter were observed on the transverse cross-section. Fiber-like structure with around 100–150 μ m length was observed on the vertical cross-section along the growth direction as shown in Fig. 3c. The result of powder XRD of the grown eutectic was shown in Fig. 4. The grown eutectic showed two phases of SHO and SAO. The results of powder XRD and EPMA indicated that the white rod phase was SHO and black matrix phase was SAO.

Fig. 2. The phase diagram of SrO–HfO₂–Al₂O₃ system.

Fig. 3. (a) Example photos of the grown Ce-doped SHO/SAO eutectic, and BEI image of (b) transverse cross-section and (c) vertical cross-section.

Fig. 4. Powder X-ray diffraction pattern for the eutectic.

3.2. Luminescence properties

Fig. 5 shows radioluminescence spectra of the Ce doped SHO/SAO eutectic sample. The peaks in the wavelengths of 410 nm are attributed to Ce^{3+} 5d–4f transitions in SHO according to the previous reports [11–13]. Ce^{3+} 5d–4f emission of Ce doped SAO at 310 nm reported by other groups [16,17] was not detected. Fig. 6 shows excitation and emission spectra of the eutectic sample. Excitation peak of 310 nm attributed to Ce^{3+} 5d–4f transitions

Fig. 5. Radioluminescence spectra of the Ce-doped SHO/SAO eutectic. Excitation by X-rays, 40 kV, 30 mA.

Fig. 6. Excitation and emission spectra of the Ce-doped SHO/SAO eutectic. (Excitation@330 nm, Emission@400 nm). Intensities were normalized at each peaks of Ce^{3+} 4f5d transition in SHO.

in SHO was observed with a trace of excitation peak of Ce^{3+} 5d–4f transitions in SAO in 260 nm. There are possibility that Ce^{3+} 5d–4f emission of Ce:SAO matrix was absorbed by Ce:SHO rod and only the 410 nm emission of Ce:SHO was generated from surface of the eutectics.

3.3. Gamma-ray response

The typical energy spectra of the Ce doped SHO/SAO eutectic sample excited by ^{137}Cs gamma-ray and ^{241}Am alpha-ray at room temperature using the PMT are shown in Fig. 7. The pulse height of Ce:(Lu,Y) $_2\text{SiO}_5$ (LYSO) crystal, which has a light output of 28,000 photons/MeV [18] was also measured as a reference. Light yield was corrected by a quantum efficiency (QE) of the PMT at the emission wavelength of LYSO (QE = 38%@420 nm) and Ce doped SHO/SAO eutectic (QE = 39%@410 nm). 5.5 MeV alpha-ray peak was observed by ^{241}Am excitation and light yield of the eutectic sample was around 300 photon/5.5 MeV alpha-ray. Photo-absorption peak was not clearly observed by ^{137}Cs gamma-ray excitation. Scintillation decay curves were obtained by using the PMT and digital oscilloscope and the sample was irradiated by ^{137}Cs (Fig. 8). Scintillation decay is approximated by the sum of two exponentials according to Eq. (1).

$$I(t) = \sum A_i \exp[-t/\tau_i], \quad i = 1, 2. \quad (1)$$

Ratio (%) is calculated by $\tau_1/(A_1\tau_1 + A_2\tau_2) \times 100\%$. Scintillation decay time of Ce doped SHO/SAO eutectic was 26.4 ns (45%) with

Fig. 7. Energy spectra of the Ce-doped SHO/SAO eutectic. Excitation by ^{137}Cs radioisotope (662 keV gamma-ray) and ^{241}Am radioisotope (5.5 MeV alpha-ray).

Fig. 8. Scintillation decay curves of the Ce-doped SHO/SAO eutectic. Excitation by ^{137}Cs radioisotope (662 keV).

slower decay component of 263 ns (55%). Observed decay time is comparable value with previous reports [11–13].

4. Conclusion

Ce:SHO/SAO eutectics were grown by the μ -PD method at the composition of 0.21 mol% CeO_2 , 20.79 mol% SrCO_2 , 25 mol% HfO_2 , 50 mol% Al_2O_3 . Rod phases with around 3–4 μm diameter were observed on the transverse cross-section. PSSFs structure with fibers of around 3–4 μm diameter and 100–150 μm length was observed. The 410 nm emission of Ce^{3+} 5d–4f transitions from the Ce doped SHO phase was observed. The light yield of the eutectic sample was around 300 photon/5.5 MeV alpha-ray and scintillation decay time was 26.4 ns (45%) with slower decay component of 263 ns (55%). The light yield of the grown eutectics were much less than that of Ce:SHO ceramics. It is guess that light yield will be improved if the Ce:SHO/SAO eutectic can be grown with well aligned PSSFs structure and show good transparency. High quality bulk eutectic growth of SHO/SAO eutectic is now in investigated and the result will be reported in the future.

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