Luminescence Properties of the Mg co-doped Ce:SrHfO₃ Ceramics Prepared by the Spark Plasma Sintering Method

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HIGHLIGHTS

- ▶ Luminescence Properties of Al/Ce/Mg:SrHfO₃ ceramics scintillator investigated
- ▶ The ceramics prepared by the Spark Plasma Sintering Method
- ▶ Light output of the Al/Ce/ Mg:SrHfO₃ ceramics of approx. 5,000 ph/MeV achieved.

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ABSTRACT

1,300 or 1,400°C pre-sintered Al/Ce/Mg:SrHfO₃ and Al/Ce:SrHfO₃ ceramics were prepared by the Spark Plasma Sintering (SPS) in order to search for a new scintillation material with a high-effective atomic number (Z_{eff}) and good light output. The SrHfO₃ has a high Z_{eff} of 60, and high gamma-ray detection efficiency is expected. Meanwhile it has a high melting point of over 2,500°C, and single crystal is hard to be grown. On the other hand, high melting materials can be prepared as ceramics, and the SPS method is a simple process to fabricate the ceramics within a few hours. Thus, we prepared the samples using the SPS method, and their optical and scintillation properties were investigated. We found that Al/Ce/Mg:SrHfO₃ and Al/Ce:SrHfO₃ ceramics had an emission wavelength at around 400 nm originating from 5d–4f transition of Ce³⁺. Moreover, Al/Ce/Mg:SrHfO₃ pre-sintered at a temperature of 1,400°C had a light output of approximately 5,000 ph/MeV. In this paper, the light output of Mg-co-doped samples was improved compared with the Mg-free ones. The light output also depends on the pre-sintering temperature. © 2015 Elsevier Ltd. All rights reserved

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1. Introduction

Positron emission tomography (PET) is a medical diagnostic technique which usually uses the Lu-based scintillators due to their

favorable properties such as high effective atomic number and fast decay time (Melcher and Schweitzer, 1992, Ogino et al., 2006, Yao, et al., 2008). Generally, thin scintillator is required to suppress the error of depth of information in the pixel scintillator for the PET camera. On the other hand, thin scintillator has lower gamma-ray

detection efficiency when compared to a thick one. The stopping power is related to the effective atomic number according to following equation

$$\sigma_{\text{photo}} \propto Z_{\text{eff}}^n \rho, \quad (1)$$

where, σ_{photo} , Z_{eff} and ρ denote cross section of photo-absorption, effective atomic number and density, respectively. Moreover, n is approximately 4–5. Thus, high effective atomic number is an important factor to realize the thin scintillator with high stopping power. Here, Lu based scintillators are supposed to have high effective atomic number (Z_{eff}).

However, Lu-containing scintillators have gamma-ray intrinsic background of the order of 100 counts/s/cm³ because of 2.59% natural abundance of ¹⁷⁶Lu radioisotope. Thus, presence of Lu may deteriorate the scintillator sensitivity and signal/noise ratio so that new Lu-free scintillators are required. In this study, we focus on the Hf-based scintillator, because Hf has high atomic number of 72 (higher compared to that of Lu). Moreover, the radioactive ¹⁷⁴Hf, which is the most abundant of the Hf radioisotope, has natural abundance as low as 0.162%. Its half-life is as long as 2×10^5 years, which makes the intrinsic background negligible in Hf-based materials.

SrHfO₃ (SHO) ceramics scintillator has been already studied (Loef et al., 2007, Nikl et al., 2011, Mihóková, et al, 2013), and this material is one of the candidates for the next generation scintillator. We have also studied SHO prepared by the spark plasma sintering (SPS) method. The SPS process takes only a few hours and a little raw material (Chaim and Margulis, 2005, Mishra et al., 1995). Moreover, the SPS setup is easy to operate and control. Up to now, optical and scintillation properties of Al/Ce:SHO have been studied (Kurosawa et al., 2013). It was reported that Al/Ce:SHO has a high density of 7.65g/cm³ and fast decay time of 21.6 ± 0.9 ns. However, photo absorption peak was not observed in the pulse height spectrum using single photon counting method, and its light output was estimated to be less than 4,000 ph/MeV. Since the light output of Al/Ce:SHO is much less than that of Lu based scintillators, its improvement is necessary to obtain a competitive scintillator.

For a ceramics scintillator, scintillation light output can be suppressed by pores among grains causing light scattering as shown in Fig. 1. Thus, in this work we tried to reduce the pore concentration to improve the light yield. Mg is sometimes used as sintering aid, and pre-sintered Mg co-doped sample is expected to be better densified. Moreover, grain boundary diffusion is expected to be promoted by Mg-codoping. As a consequence, grain sizes are changed, and concentration of pores can be diminished (Lee et al., 2006)

Moreover, pre-sintering temperature can also influence the light output. Change of pre-sintering temperature has an effect on grain size and shape, and their optimization may also cause a reduction of pore concentration and lead to the improvement of scintillation and optical properties. Therefore, we studied the optical and scintillation properties of Mg co-doped Al/Ce:SHO and Mg-free Al/Ce:SHO prepared under different pre-sintering temperatures.

50 2. Materials and methods

Using the SPS method, we fabricated several SrHfO₃ ceramics listed in Table 1. For starting materials, HfO₂ (99.95% pure), SrCO₃ (99.99% pure), α -Al₂O₃ (99.99% pure), CeO₂ (99.99% pure) and MgCO₃ (99.9% pure) powders were used. SHO ceramic samples were pre-sintered; the above powders were well wet-blended and put into the Al₂O₃ crucible, which was heated at 1,300 or 1,400 °C for 12 hours in a chamber filled with air.

SHO ceramic samples were prepared from the SHO powder with a 10-mm-diameter punch, 30-mm-diameter dies and a SPS chamber (DR.SINTER, Fuji Denpa) by multi-step process as follows: (i) the SHO material was heated up to 600°C under the pressure of 100 MPa within 3 min, (ii) then it was heated up to 1,100°C with rate of

17 °C/min. (iii) the temperature was hold at 1,100°C for 30 min. (iv) the temperature was raised to the sintering temperatures up to 1,700°C with the heating rate of 50 °C/min. (v) After keeping the temperature for 45 min, the carbon punch and dies were cooled down.

The sintered samples with a diameter of 10 mm and 1 mm thickness were mirror-polished. The grain size and the pores in the samples were observed using a Scanning Electron Microscopy (SEM, JXA-8621MX, JEOL) with a voltage of 15 kV and a current of 6.2×10^{-5} A.

Transmittance and photo-luminescence of the all samples were measured with a spectrophotometer (V-550, JASCO) and an absolute PL quantum yields measurement system with an integrating sphere (C9920-02G, Hamamatsu) under Xe Lamp (L10092, Hamamatsu) excitation (Kurosawa et al., 2014)..

To determine the light output, we measured the pulse height spectra of these samples under excitation of 662 keV gamma photons from a ¹³⁷Cs radioisotope. Scintillation photons were detected by a photomultiplier tube (PMT, R7600U-200, Hamamatsu), and then the signals from the PMT were amplified (model 113, ORTEC), shaped with a shaping time of 0.5 μ s (572A, ORTEC), and readout with a multi-channel analyzer (MCA, 8000A, Amptek). The pulse height spectrum of 1.0-mol%-Ce-doped Gd₂SiO₅ (GSO) crystal which has a light output of about 12,500 ph/MeV was also measured as a reference (Melcher et al., 1996). We evaluated the light outputs of the samples as follows: we compared MCA channel of the 662 keV photo absorption peaks with that of Ce:GSO, and considered the correction of the PMT quantum efficiency at emission band peak.

90 3. Results and discussions

Prepared samples were polished to 1 mm thickness as shown in Fig. 2. Visually, pure SrHfO₃, Al/Ce:SrHfO₃ and Al/Ce/Mg:SrHfO₃ samples pre-sintered at 1300 and 1400°C had good transparency compared with the other samples. The Back Scattered Electron (BSE) images of 1400°C pre-sintered Al/Ce:SHO and Al/Ce/Mg:SHO are shown in Fig. 3. The Mg co-doped samples had larger grains, see Table 2, where the grain size is estimated by Thompson equation (Thompson 1972). Additionally, the concentration of pores among the grains was reduced in the Mg co-doped samples compared with the Mg-free ones (Al/Ce:SHO). It suggested that larger grain size is an important factor to remove the pores, and Mg(CO₃) was supposed to play a role of sintering aid.

Fig. 4 shows the transmittance spectra of Al/Ce:SHO and Al/Ce/Mg:SHO. Mg co-doped samples had no absorption peak at around 450 nm, while the Mg-free ones had such peaks which might be due to a color center based on the oxygen vacancy. However, the transmittance values at the Ce³⁺ emission wavelength (400 nm) are not very different for all the samples. Thus, we found no correlation between Mg-co-doping and transmittance at 400 nm.

Fig. 5 shows the photoluminescence spectra of Al/Ce:SHO and Al/Ce/Mg:SHO samples excited with 310 nm photons using a Xe lamp. No remarkable differences were observed among the spectra for all samples which are dominated by a broad peak around 400 nm originating from the Ce³⁺ 5d–4f transition. The quantum yields (QY) of Al/Ce/Mg:SHO pre-sintered at 1,300 and 1,400°C were 0.127 and 0.176, respectively. On the other hand, Mg-free samples (Al/Ce:SHO) pre-sintered at 1,300 and 1,400°C had as smaller QYs as 0.054 and 0.043, respectively, compared with Mg-co-doped ones. This result can be explained by decrease of pore concentration in the latter samples as the grain size increases. Consequently, the suppression of light scattering in the Mg-co-doped ceramics was achieved.

Pulse height spectra of Al/Ce:SHO and Al/Ce/Mg:SHO are shown in Fig. 6, and the light output and energy resolution values at 662 keV (FWHM of photopeak) are listed in Table 2. The Al/Ce/Mg:SHO pre-sintered at 1,400°C had the highest light output of approximately 5,000

ph/MeV and best energy resolution among the studied samples. Thus, we found the Mg-co-doping made grain size larger, and improved the light output and the energy resolution in the SHO sample set. This improvement of the scintillation properties resulted mainly from the improvement of QY due to reduction of the pore concentration. In other words, light emission efficiency was improved due to suppression of the light scattering at the pores.

4. Conclusion

1% Ce doped SrHfO₃ (SHO) ceramics, co-doped with Al or with Al and Mg, pre-sintered at temperatures of 1,300°C and 1,400°C were prepared by the SPS method. Emission band of Ce³⁺ at 400 nm was found to be independent on Mg co-dopant and pre-sintering temperature. However, their quantum yield under 310 nm excitation was increased by Mg co-doping. The pulse-height spectra of the Al/Ce/Mg:SHO samples did show photo absorption peak upon excitation by 662 keV gamma photons from a ¹³⁷Cs source, while those of the Mg-free samples did not. The highest light output was estimated to be ~5,000 ph/MeV for the Al/Ce/Mg:SHO pre-sintered at a temperature of 1,400°C. Mg admixture was suggested to play a role of sintering aid that stimulated the grains growth leading to the decrease of pore concentration and light scattering in the ceramics.

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Figure Caption

Fig. 1: Schematic view of light scattering at pore.

Fig. 2: Photographs of 1400°C–SrHfO₃ (a), 1400°C–Ce:SrHfO₃ (b), 1400°C–Al/Ce:SrHfO₃ (c), 1400°C–Al/Ce/Mg:SrHfO₃ (d), 1300°C–SrHfO₃ (e), 1300°C–Ce:SrHfO₃ (f), 1300°C–Al/Ce:SrHfO₃ (g) and 1300°C–Al/Ce/Mg:SrHfO₃ (h).

Fig. 3: BSE images of 1400°C–Al/Ce:SrHfO₃ (a) and 1400°C–Al/Ce/Mg:SrHfO₃ (b).

Fig. 4: Transmittances of 1300°C–Al/Ce:SrHfO₃, 1300°C–Al/Ce/Mg:SrHfO₃, 1400°C–Al/Ce:SrHfO₃ and 1400°C–Al/Ce/Mg:SrHfO₃.

Fig. 5: Photoluminescence spectra of 1300°C–Al/Ce:SrHfO₃, 1300°C–Al/Ce/Mg:SrHfO₃, 1400°C–Al/Ce:SrHfO₃ and 1400°C–Al/Ce/Mg:SrHfO₃, respectively, excited with 310-nm photons.

Fig. 6: Pulse height spectra of 1300°C–Al/Ce:SrHfO₃, 1300°C–Al/Ce/Mg:SrHfO₃, 1400°C–Al/Ce:SrHfO₃ and 1400°C–Al/Ce/Mg:SrHfO₃ and Ce:GSO as a reference, respectively, irradiated with gamma rays from a ¹³⁷Cs source.

Table Caption

Table 1: Composition and abbreviations of all samples

1
2 Table 2: Average of grain sizes, light outputs and energy resolutions
3 (662 keV, FWHM) of 1300°C–Al/Ce:SrHfO₃, 1300°C–
4 Al/Ce/Mg:SrHfO₃, 1400°C–Al/Ce: SrHfO₃ and 1400°C –Al/Ce/Mg:
5 SrHfO₃
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Pre-sintering temperature	Abbreviations	Composition
1300°C	1300°C–SrHfO ₃ or 1300°C–SHO	SrHfO ₃
1300°C	1300°C–Ce:SrHfO ₃ or 1300°C–Ce:SHO	Ce _{0.01} :Sr _{0.99} HfO ₃
1300°C	1300°C–Al/Ce:SrHfO ₃ or 1300°C–Al/Ce:SHO	Al _{0.01} /Ce _{0.01} :Sr _{0.99} Hf _{0.99} O ₃
1300°C	1300°C– Al/Ce/Mg:SrHfO ₃ or 1300°C– Al/Ce/Mg:SHO	Al _{0.01} /Ce _{0.01} /Mg _{0.005} :Sr _{0.985} Hf _{0.99} O ₃
1400°C	1400°C–SrHfO ₃ or 1400°C–SHO	SrHfO ₃
1400°C	1400°C–Ce:SrHfO ₃ or 1400°C–Ce:SHO	Ce _{0.01} :Sr _{0.99} HfO ₃
1400°C	1400°C–Al/Ce:SrHfO ₃ or 1400°C–Al/Ce:SHO	Al _{0.01} /Ce _{0.01} :Sr _{0.99} Hf _{0.99} O ₃
1400°C	1400°C– Al/Ce/Mg:SrHfO ₃ or 1400°C– Al/Ce/Mg:SHO	Al _{0.01} /Ce _{0.01} /Mg _{0.005} :Sr _{0.985} Hf _{0.99} O ₃

Samples	Average grain size (μm)	Light output (ph/MeV)	Energy resolution (%) (662 keV FWHM)
1300°C– Al/Ce:SrHfO ₃	~26	~2,000	N/A
1300°C– Al/Ce/Mg:SrHfO ₃	~240	~3,000	27.76
1400°C– Al/Ce:SrHfO ₃	~15	~1,000	N/A
1400°C– Al/Ce/Mg:SrHfO ₃	~190	~5,000	20.75

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6