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Synthesis of transparent $CaHfO_3$ crystals by the CH method and its optical properties

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Abstract

Hf containing oxides like $SrHfO_3$ and $CaHfO_3$ are attractive scintillation materials with relatively high gamma-ray stopping power than conventional scintillators (i.e. Gd_2SiO_5). Although the crystal growth of Hf compounds are hard due to extremely high melting points, we succeeded in synthesis of transparent Ce doped $CaHfO_3$ crystals by the Core Heating (CH) method. The CH method is a novel crystal growth method for optical materials with high melting points. The optical and scintillation properties of Ce doped $CaHfO_3$ were evaluated in this study and light output was estimated to be approximately 1300 ph./5.5MeV.

1. Introduction

Scintillators are one of the optical materials to detect radiations used in various fields such as medical imaging, radiation detector, and positron emission tomography (PET) camera. Gamma-ray stopping power is an important property for the PET camera, and this stopping power is proportional to density and $(Z_{eff})^a$, where Z_{eff} is an effective atomic number and a=4-5.

Hf compounds, like $SrHfO_3$ and $CaHfO_3$ [1,2], are attractive materials for the PET camera due to high effective atomic number and no intrinsic noise.

However, conventional melt growth techniques with a crucible such as the Czochralski method and micro-pulling down method [3] are not able to grow such Hf-containing materials due to the higher melting points than the softening or melting points of the crucibles. Here, the melting points of $SrHfO_3$ and Ir (the crucible material) are, for example, 2730 °C and 2447°C , respectively.

Some groups have reported the scintillation properties of Ce: SrHfO and SrHfO-based materials as transparent ceramics [1]. Although these ceramics samples had lower line transmittances of less than a few % and small light outputs (less than 1000 photons/MeV gamma or 5.5 MeV alpha), the decay times were determined to be less than 30 ns [1]. PET scintillators are also required fast decay times and good light output, and the conventional scintillation materials for the PET camera such as Ce-doped Gd_2SiO_5 or (Lu, Y)$_2SiO_5$ have decay times of 30 -60 ns. Thus, we expected to obtain better light outputs for highly transparent single crystals than that for the ceramic samples reportrd in Ref. [1].

We have developed a novel crystal growth method “Core Heating (CH) method” [4] to search for such materials with extremely high melting points. The CH method can be applied for material search of such high melting point materials, because the crucibles are not required. The purpose of this study is to synthesize transparent crystals of Hf compounds using the CH method, and measure the optical and scintillation properties. As a first demonstration of crystal growth of a scintillation material by the CH method, we selected Ce doped $CaHfO_3$, because $CaHfO_3$ has relatively high effective atomic number of 65 compared with conventional materials like Gd_2SiO_5. Moreover, $CaHfO_3$ has lower melting point than that of Hf-containing materials like $SrHfO_3$.

2. Experiments

Ce-doped $CaHfO_3$ samples were synthesized by the CH method, where $CaCO_3$, HfO_2, CeO_2 powder were used as starting materials. After weighing and mixing, a Ce-doped $CaHfO_3$ pellet and powder were prepared by the solid-state reaction. Figure 1 shows a schematic view of the CH method We set in the order of Ce doped $CaHfO_3$ powder, the pellet and an Ir tablet from the bottom of the Cu hearth, whose inner diameter is 20 mm and inner height is 10 mm. Then only the Ir tablet was irradiated with electric arc. The Ir tablet was melted by the electric arc, and the $CaHfO_3$ pellet was melted due to heating from the Ir-melt. After that, we gradually weakened the output of the electric arc and transparent crystals were synthesized.

The grown crystals were cut and mirror polished. We confirmed the single phase for each crystal using powder X-ray diffraction analysis. Optical and scintillation properties were measured. Photoluminescence spectra were measured with a spectrofluorometer FP-8300 (JASCO) using a Xenon lamp. To determine the light output, the photons from $CaHfO_3$ crystals irradiated with alpha rays from an ^{241}Am source were detected with a photomultiplier tube (PMT). Scintillation decay times were measured at room temperature with the same PMT as that for the light output measurement.

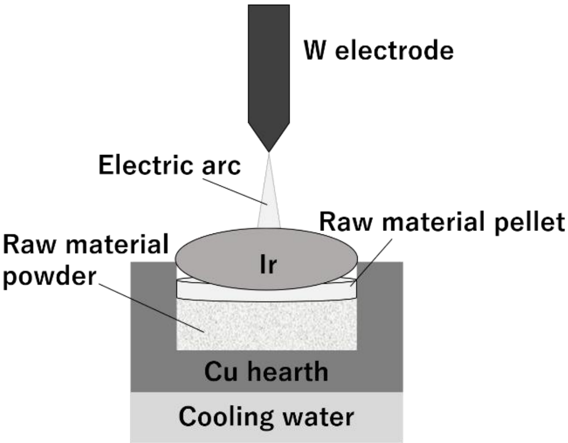

Fig. 1 Schematic of the CH method

3. Results

The synthesized crystals were cut and polished. Figure 2 shows a photograph of Ce doped $CaHfO_3$ synthesized by the CH method. The powder X-ray diffraction pattern revealed that the synthesized crystal has a single phase of $CaHfO_3$ (orthohormbic) as shown in Fig. 3.

Moreover, we measured optical and scintillation properties such as photoluminescence emission, excitation spectra, decay time, and pulse height spectra. Figure 4 shows the scintillation decay-time profile of Ce doped $CaHfO_3$. The decay time of the main component was determined to be approximately 35 ns, which is much faster than that of typical oxide scintillators. Pulse height spectra of Ce doped $CaHfO_3$ irradiated with alpha rays from an ^{241}Am source are shown in Fig. 5. The light output estimated from the spectra was approximately 1300 ph./5.5MeV.

Fig. 2 Photograph of Ce doped $CaHfO_3$ synthesized by CH method

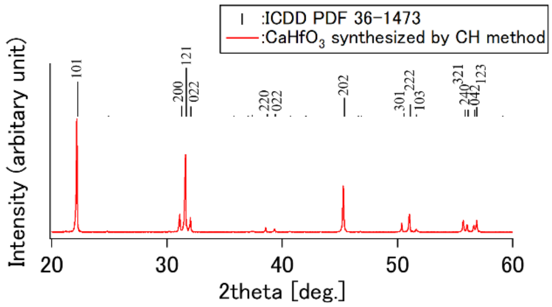

Fig. 3 Powder X-ray diffraction pattern of Ce doped $CaHfO_3$ synthesized by CH method

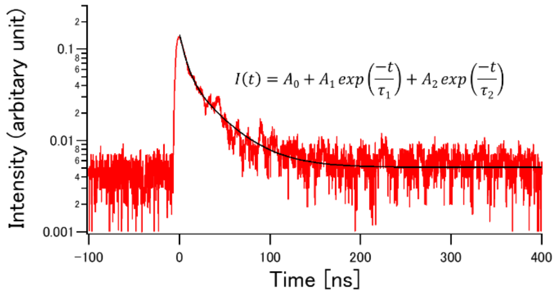

Fig. 4 Decay time profile of Ce doped $CaHfO_3$

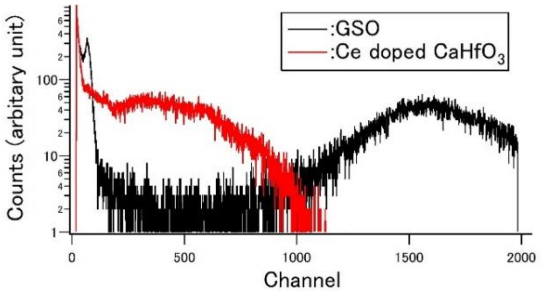

Fig. 5 Pulse height spectra of Ce doped $CaHfO_3$ excited by a ^{241}Am source

4. Conclusions

Transparent Ce doped $CaHfO_3$ crystals were synthesized by the CH method. Although the growth of large transparent $CaHfO_3$ crystals from the melt was hard due to the higher melting point, we fabricated Ce doped $CaHfO_3$ by the CH method. The decay component and light output were determined to be approximately 35 ns and 1300 ph./5.5MeV, respectively. The details of the scintillation properties for Ce doped $CaHfO_3$ has been presented in this paper.

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