Crystal growth and scintillation properties of Lu substituted CeBr₃ single crystals

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Abstract:

We grew Lu substituted CeBr₃ [(Ce_{1-x}Lu_x)Br₃] crystals by a modified micro-pulling-down method to increase the effective atomic number to investigate effects of the Lu substitution on the crystal growth, phase generation, chemical composition, and optical and scintillation properties. The (Ce_{1-x}Lu_x)Br₃ crystals with $x = 0$ and 0.01 had high transparency while the milky parts were generated in the crystals with $x = 0.05$ and 0.20. By the analysis of chemical composition, the estimated Z_{eff} increased to 47.9. On the other hand, the light yields were systematically decreased and decay times were increased with increasing Lu concentration.

Keywords: A1. Radiation, A2. Single crystal growth, A2. Growth from melt, B1. Halides, B2. Scintillator materials, B3. Scintillators

1. Introduction

Most of halide single crystals indicate relatively high light yield and energy resolution under radiation excitation due to the small band-gap and these single crystals are expected to be applied for a scintillator in next-generation radiation detectors. Among these halide scintillator crystals, CeBr_3 with hexagonal structure (UCl_3 type) and $\text{P6}/3\text{m}$ space group shows fast decay time of ~ 22 ns in addition to the high light yield of $\sim 60,000$ ph/MeV and high energy resolution of $\sim 3\%$ [1,2]. The melting point of CeBr_3 is 732°C and the density is 5.18 g/cm^3 as reported by Higgins et al. [3], where the bulk single crystal of the CeBr_3 was grown by the Vertical Bridgman method using a sealed quartz ampoule. The CeBr_3 single crystal under X-ray irradiation indicated an emission peak around 380 nm originated from the $5\text{d}-4\text{f}$ transition of Ce^{3+} ion.

The CeBr_3 crystal is expected to be applied in a Time-of-flight Positron Emission Tomography [TOF-PET] with higher position resolution than previous PET. The TOF-PET is a new-generation PET system that can detect arrival times of γ -ray from a positron with high timing resolution to achieve the high position resolution. Therefore, the TOF-PET needs a scintillator with high light yield and 10 nanosecond-level short decay time for the intended timing resolution [4]. In addition, a reactive cross section of scintillator to γ -ray is in proportion to 4-5 th power of an effective atomic number [Z_{eff}] and the large Z_{eff} is required for large stopping power for γ -rays. Present scintillators such as $\text{Ce:Lu}_{1.8}\text{Y}_{0.2}\text{SiO}_5$ [LYSO][5], $\text{Ce:Lu}_2\text{SiO}_5$ [LSO][6] and $\text{Ce:Gd}_2\text{SiO}_5$ [GSO][7] do not have sufficient light yield and decay time for the TOF-PET.

CeBr_3 scintillator has approximately twice higher light yield (68,000 ph/MeV) and shorter decay time (~ 22 ns) than the LYSO [1,5]. However, the Z_{eff} of CeBr_3 (~ 46) is lower than that of LYSO and GSO.

In this study, we grew Lu substituted CeBr_3 [$(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$] crystals in order to increase the Z_{eff} . The Lu^{3+} ion with large atomic number (71) is one of the most suitable candidate elements for the substitution on the Ce^{3+} site of CeBr_3 crystal. $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals are expected to achieve the increase of Z_{eff} with maintenance of high light yield and short decay time.

2. Experimental procedure

The $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals were grown by a modified micro-pulling-down [μ -PD] method with approximately ten times faster growth rate than conventional methods without exposure to air atmosphere using a removable chamber [8-13]. Mixed powders with nominal compositions of $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ ($x = 0.00, 0.01, 0.05, 0.10, \text{ and } 0.20$) were prepared from starting materials of CeBr_3 (3N), LuBr_3 (4N) in a glove box. The glove box was filled with Ar gas and the concentrations of oxygen and moisture in the glove box were held below 1 ppm. The mixed powder was set in a carbon crucible with a die at the bottom, and the die had a $\phi 1$ mm hole at the center. The carbon crucible and aluminum insulator were set in the removable chamber that was taken out of the glove

box. Then, the interior of the chamber was evacuated up to $\sim 10^{-4}$ Pa by a turbo molecular pump at 100~200°C to remove moisture rested on the surfaces of instruments, the crucible, and mixed powders. After the baking process, $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ fiber crystals were grown in high-purity Ar atmosphere (99.9999%) at ~ 0.05 mm/min growth rate using tungsten wire ($\phi 0.1$ mm) as a seed. Specimens with ~ 1 mm thickness, 1~2 mm width and 5~10 mm length were prepared from the as-grown $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ fiber crystals by their cutting and polishing in air using a mineral oil for measurements of optical and scintillation properties. The mineral oil covered the surface of the crystals during the cutting and polishing processes and the $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ fiber crystals could be cut and polished without any visible degradation of the surface on the surface. The specimens for the measurements were obtained from the middle parts of the grown fiber crystals.

Parts of the grown crystals were dispersed in the globe box for the measurements of the X-ray diffraction (XRD), which was carried out in 2theta range 20-70 degrees with 0.02 degree step using the X-ray diffractometer (BRUKER, D8 DISCOVER) equipped with sealed chamber with no influence on the measured XRD pattern. The configuration of the sealed sample chamber was a 51.5 mm outer diameter half-sphere made of polystyrol and polymethyl methacrylate. The X-ray source was Cu- K_α (accelerating voltage: 40 kV and beam current: 40 mA). The Inductively Coupled Plasma [ICP] analysis (Thermo Fisher Scientific, IRIS Advantage DIO) of the as-grown crystals was performed to identify the actual chemical compositions.

Emission spectra of the polished specimens were measured under monochromatic Ultra-Violet photons excitation from Xenon lamp (150 W). In addition, emission spectra excited by X-ray (40 kV, 40 mA) were measured using spectrofluorometer (HAMAMATSU, integration snit A10094) and CCD camera (ORIEL, Thermo). Pulse-height spectra and the scintillation decay curves of the specimens under γ -ray excitation from ^{137}Cs radiation source were also examined to estimate their light yields and decay times using photomultiplier [PMT](HAMAMASTU, R7600U-200), multi-channel analyzer (AMPTEK CO. Pocket MCA 8000A) and an oscilloscope (TEKTRONIX, TBS1102) at the inside of the grove box filled in N_2 gas which atmosphere of the humidity was controlled within less than 10%. Ce 1 mol% doped Gd_2SiO_5 [Ce:GSO] single crystal with the light yield of 11,000 ph/MeV was used as a reference.

To remove effects in the grown crystals on the measurements, same specimens were used for the powder XRD measurements and ICP analysis after the measurements of optical and scintillation properties were performed.

3. Results and discussions

Figure 1 shows the as-grown and polished $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals produced by the modified μ -PD method. Fiber crystals with approximately $\phi 3$ mm diameter and over 15 mm length were obtained for all Lu concentration. There were some cracks in all as-grown crystals and milky parts were

observed for the crystals with $x = 0.05$ and 0.20 while no visible inclusions were detected in the as-grown crystals with $x = 0$ and 0.01 . Polished specimens used for the measurements of XRD, ICP, and optical and scintillation properties were prepared from crack-free parts.

To identify the phases and change of the lattice parameters for the grown $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals, the powder XRD patterns were measured as it is illustrated in Fig.2(left). Almost all diffraction peaks were identified according to the CeBr_3 crystal structure (hexagonal, $P6/3m$). Some of the peaks corresponded to hydrate compounds ($\text{CeBr}_3 \cdot 7\text{H}_2\text{O}$) in addition to the main phase that was associated with insufficient sealing during the XRD measurement. Some additional peaks were observed in the x range of $x \geq 0.05$ that was associated with formation of impurity phase(s) and appearance of milky parts in the grown crystals. Figure 2(right) demonstrates diffraction peaks from (111) plane, and it seems that the peaks were shifted for 0.02 degree right to greater angles in $(\text{Ce}_{0.8}\text{Lu}_{0.2})\text{Br}_3$ crystal. This result suggests that lattice parameters of the CeBr_3 crystal decreased with substitution of relatively large Ce^{3+} cation with relatively small Lu^{3+} .

Actual chemical compositions of the grown $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals were investigated by the ICP analysis and the Z_{eff} of the grown crystals were estimated using actual Lu concentration. Unfortunately, actual Lu concentrations in the crystal with $x = 0.01$ was below limit of detection (LOD) in the ICP analysis. Actual Lu concentrations of the grown crystals with $x = 0.05$ and 0.20 were 1.7 ($\text{Ce}_{0.983}\text{Lu}_{0.017}\text{Br}_3$, $x = 0.017$) and 17.5% ($\text{Ce}_{0.825}\text{Lu}_{0.175}\text{Br}_3$, $x = 0.175$). Therefore, actual Lu concentrations in the crystals were lower than the nominal Lu concentration. The decreases of the actual Lu concentrations in the grown crystals were considered to be due to the differences of the ionic radii between Ce^{3+} and Lu^{3+} . The estimated Z_{eff} 's of Lu 5% and 20%: CeBr_3 crystals were 46.1 and 47.9 , respectively and they are larger than Z_{eff} of CeBr_3 (45.8).

The photoluminescence [PL] and radioluminescence [RL] spectra of the $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals under 340 nm and X-ray excitation are demonstrated in Fig.3(a) and (b), respectively. Emission peaks around $380\sim 400$ nm originated from $5d-4f$ transitions of Ce^{3+} ion were observed for all crystals in both PL and RL spectra. The wavelength of the emission peak for non-doped CeBr_3 crystal (~ 380 nm) was consistent with the previous report [1]. The wavelengths of the emission peaks were systematically shifted to larger wavelength with increasing Lu concentration. In the previous report about the Ce doped LuBr_3 crystals (Ce 2.5 and 8%: LuBr_3), the wavelengths of the emission peaks originated from the Ce^{3+} ion were more than 400 nm [14]. The result suggests that the wavelength of the emission peak was shifted by the change of the band-gap by Lu substitution. As for the shift of the emission peak to longer wavelength by the Lu substitution, we suggest two possibilities which explain the phenomenon. One possibility is that the band-gap was changed by the Lu substitution. In the previous report about the Ce: LuBr_3 [14], the emission peak of Ce^{3+} ion in the Ce: LuBr_3 is longer wavelength than that of the CeBr_3 . Another possibility is the self-absorption of the grown crystals. Lu substitution generated the milky parts including the

secondary phase. Therefore, the emission light could be absorbed by the milky parts. In addition, there was a broad peak around 480-500 nm in the crystals with $x = 0.05$ and 0.20 . There is no clear explanation of the phenomenon right now. However, there is a possibility that the secondary phase affected formation of this peak.

Figure 4 shows the pulse-height spectra and decay curves of the $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals observed under γ -ray irradiation. Estimated Z_{eff} , light yield and decay time are summarized in table 1 with the actual Lu concentration and the emission wavelength of Ce^{3+} ion. The light yields of the specimens were estimated using the Ce:GSO (11,000 ph/MeV) as a reference (Fig.4(a)). The estimated light yields of the specimens with $x = 0, 0.01, 0.05$ and 0.2 were 65,500, 64,500, 55,500 and 42,000 ph/MeV, respectively, and they were decreased with increasing Lu concentration. The estimated energy resolutions of the specimens with $x = 0, 0.01, 0.05$ were 7.0, 6.2 and 11.2%, respectively. The scintillation decay curves were fitted with the single exponential decay function, $f(x) = A\exp(-x/\tau) + y$ (Fig.4(b)) to estimate the decay time (τ_1). Obtained decay times of the specimens with $x = 0, 0.01, 0.05$ and 0.20 were 20.6, 22.1, 34.1 and 42.8 ns, respectively and the decay times were systematically increased with increasing Lu concentration. According to the relation between the decay time and emission wavelength [15], the increase of the decay time is considered to be due to the increase of the emission wavelength. However, in the case of the specimens with $x = 0.05$ and 0.20 , the crystals included milky parts and therefore the increased amounts of the decay times by Lu substitution were suggested to be inconsistent with the relation between decay time and emission wavelength.

4. Conclusions

Lu substituted CeBr_3 crystals were grown by the modified μ -PD method, and their phase identifications, analyses of chemical compositions, and measurements of optical and scintillation properties were performed. Some milky parts were observed in the crystals with $x = 0.05$ and 0.20 . These crystal contained secondary phase(s) according to XRD analysis. Alternatively, the crystals with $x = 0$ and 0.01 were transparent single phase materials. The emission peak originated from the 5d-4f transitions of Ce^{3+} ion was shifted to larger wavelength with Lu substitution. The light yields were systematically decreased with increasing Lu concentration. On the other hand, the decay times were systematically increased with increasing Lu concentration and the increase of decay time is considered to be result of emission wavelength. Consequently, the $(\text{Ce}_{0.8}\text{Lu}_{0.2})\text{Br}_3$ crystal with the $Z_{\text{eff}} = 47.9$, the light yield = 42,000 ph/MeV and the decay time = 42.8 ns was produced.

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Figure Captions

Figure 1 As-grown and polished $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals grown by the modified μ -PD method.

Figure 2 Powder XRD patterns for $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals.

Figure 3 (a) Photoluminescence and (b) radioluminescence under X-ray excitation of $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals.

Figure 4 (a) Pulse height spectra and (b) decay curves of $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals under γ -ray excitation.

Table 1 Effective atomic number and scintillation properties of $(\text{Ce}_{1-x}\text{Lu}_x)\text{Br}_3$ crystals.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

$\text{Ce}_{1-x}\text{Lu}_x\text{Br}_3$ (Nominal compositions)	Actual Lu concentrations /%	Z_{eff}	Emission wavelength /nm	Light yield /photon $\cdot$ MeV^{-1}	Energy resolution / %	Decay time /ns
$x = 0.00$	< LOD	45.8	365	65,500	7.0	20.6
$x = 0.01$	< LOD	45.8	380	64,500	6.2	22.1
$x = 0.05$	1.70	46.1	390	55,500	11.2	34.1
$x = 0.20$	17.5	47.9	400	42,000	-	42.8

TABLE 1