# Effects of Pr Doping on the Scintillation Properties of CeBr<sub>3</sub> Crystals Grown by the Modified Micro-Pulling-Down Method

Tomoki Ito<sup>1</sup>, Yuui Yokota<sup>2</sup>, Shunsuke Kurosawa<sup>1,2</sup>, Kei Kamada<sup>2,3</sup> Jan Pejchal<sup>2,4</sup>, Yuji Ohashi<sup>1</sup>, Akira Yoshikawa<sup>1,2,3</sup>

<sup>1</sup>Institute for Materials Research, Tohoku University 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, JAPAN Phone: +81-2-2215-2214 E-mail: tomoki@imr.tohoku.ac.jp <sup>2</sup>New Industry Creation Hatchery Center (NICHe), Tohoku University 6-6-10, Aramaki, Aoba, Aoba-ku, Sendai, Miyagi, 980-8579, JAPAN <sup>3</sup>C&A Corporation 6-6-40, Aramaki, Aoba, Aoba-ku, Sendai, Miyagi, 980-8577, JAPAN

<sup>4</sup>Institute of Physics AS CR, 10 Cukrovarnicka, Prague 6, 16200 Czech Republic

### Abstract

Halide single crystals with relatively small band-gap show favorable scintillation properties. We grew undoped and Pr doped CeBr<sub>3</sub> crystals by a modified micro-pulling-down (µ-PD) method. Crystals of approximately 10 mm in length and \$\$mm in diameter were obtained. Fast scintillation decay components observed both for the undoped and Pr doped crystals were characterized by a decay time of approximately 16 ns. From the emission spectra excited by 260 nm light, emission peaks originating from Pr 4f-4f transitions were observed at 490, 620 and 650 nm in the Pr-doped sample. In excitation spectra for the 400 nm emission wavelength, the excitation peak observed around 340 nm in the undoped sample was shifted to shorter wavelengths in the Pr-doped one.

# 1. Introduction

Micro-pulling-down ( $\mu$ -PD) method [1] is the one of the methods of crystal growth from the melt. The  $\mu$ -PD method can grow a crystal approximately ten times faster than conventional methods and it is suitable for fast search of functional single crystals with. However, conventional the halide crystals cannot be usually grown with this method because of their hygroscopicity. Therefore, we have developed a modified  $\mu$ -PD method for growth of halide crystals and we have reported the growth and properties of halide scintillator single crystals such as CeCl<sub>3</sub>, Ce:LaBr<sub>3</sub> and Eu:SrI<sub>2</sub> [2,3].

Halide crystals with relatively small band-gap are sxpected to show high light yield and energy resolution [4], which makes them attractive candidates for scintillation materials for many applications [5]. The scintillation properties of Ce:LaBr<sub>3</sub> have been studied recently [6,7] and particularly high light yield (80,000 ph/MeV), short decay time (< 30 ns) and high density (5.1 g/cm<sup>3</sup>) were reported [8]. Other bromides are also expected to be good candidates for new scintillator materials with high performance. Rare earth (RE) ion doping might contribute to improvement of scintillation properties by facilitating the energy transfer from the host matrix to the luminescence centers. For the

CeBr<sub>3</sub> host material, trivalent RE dopant similar ionic radius, such as  $Pr^{3+}$  can be substituted. However, its influence on the scintillation properties of CeBr<sub>3</sub> has not been reported so far.

Based on the above background, the purpose of this study is to prepare Pr doped CeBr<sub>3</sub> by the modified  $\mu$ -PD method and to evaluate the scintillation properties.

## 2. Experimental

In order to prepare Pr doped CeBr<sub>3</sub> crystals, mixed powders with nominal components of  $(Ce_{1-x}Pr_x)Br_3$ , x = 0, 0.01, 0.03, 0.05 and 0.10 were prepared from starting materials of CeBr<sub>3</sub> (>3N) and PrBr<sub>3</sub> (>4N) in a glove box. To remove moisture on the surface of instruments and mixed powders a baking precedure under high vacuum state (~10<sup>-4</sup> Pa) was performed. The crystals were grown in high-purity Ar gas (99.9999%) atmosphere. The carbon crucible was selected considering the wettability of CeBr<sub>3</sub> melt. The crystal growth was performed at pulling-rate of approximately 0.05 mm/min. In order to study properties of the grown crystals, specimens with approximately 1 mm thickness were prepared by cutting and polishing the grown crystals.

The decay curves under  $\gamma$ -ray excitation from <sup>137</sup>Cs radiation source were evaluated to investigate the decay time.

Emission and absorption spectra of the polished crystals were measured. Samples were excited by monochromatic UV photons using Xenon lamp (150W) and a monochromator (SP2150i, Princeton Instruments) controlled by a computer. [9].

# 3. Results and Discussions

To perform a stable crystal growth of CeBr<sub>3</sub> and Pr:CeBr<sub>3</sub> crystals by the modified  $\mu$ -PD method, a carbon crucible with a die with a hole at the bottom was used because melt of CeBr<sub>3</sub> showed a good wettability for the carbon crucible. Figure 1 shows the undoped and Pr5mol% doped CeBr<sub>3</sub> grown crystals. The crystals of, approximately 10 mm in length and  $\phi$ 3mm in diameter were obtained. Both transparent and cracky parts were observed in the polished undoped and Pr doped crystals.

Figure 2 shows decay curves of undoped and Pr 5mol%

doped CeBr<sub>3</sub> crystals under  $\gamma$ -ray excitation. Fast decay components for the undoped and Pr doped crystals were approximately 16 ns. In contrast, Pr doped crystal showed additional slower decay component when compared to the undoped one. The reason of generation of slower decay component is not clear now and further research is required to clarify the effects of Pr doping on decay time of CeBr<sub>3</sub> crystal.

Figure 3 shows emission spectra of the undoped and Pr doped CeBr<sub>3</sub> crystals excited by 260 nm light. Both crystals indicated emission peaks around 380 nm which were attributable to Ce<sup>3+</sup> 5d-4f transition. In addition, emission peaks originating from Pr<sup>3+</sup> 4f-4f transitions were observed at 490, 620 and 650 nm for the Pr doped crystal. In the excitation spectra for the 400 nm emission wavelength, the excitation peak found around 340 nm in the undoped sample was shifted to shorter wavelength in the Pr doped one. On the other hand, the excitation peak around 280 nm was shifted to longer wavelength.

The details of results about crystal growth and their scintillation properties will be reported in our presentation.

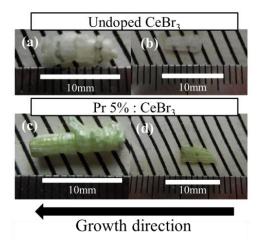


Fig.1 As grown and polished undoped  $CeBr_3$  (a,c) and Pr doped  $CeBr_3$  (c,d) crystals.

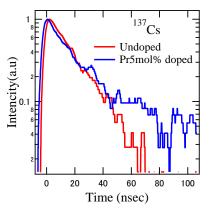


Fig.2 Decay curves of undoped and Pr 5mol% doped  $CeBr_3$  crystals irradiated by  $\gamma\text{-ray.}$ 

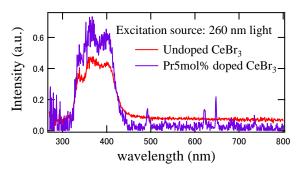


Fig.3 Emission spectra of the undoped and Pr 5mol% doped CeBr<sub>3</sub> crystals excited with 260 nm.

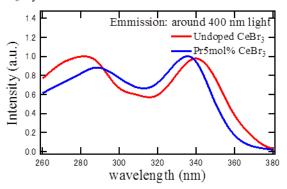


Fig.4 Excitation spectra of undoped and Pr 5mol% doped CeBr<sub>3</sub> crystals at 400 nm emission wavelength

#### Acknowledgements

This work was partially supported by the Japan Society for the Promotion of Science (JSPS) Research Fellowships for Young-Scientists and Grant-in-Aid for Exploratory Research (25600130). In addition, this work was supported by the Japan Science and Technology Agency (JST) for Development of Systems and Technology for Advanced Measurement and Analysis.

#### References

- [1] A. Yoshikawa, et. al., Opt. Mater 30 (2007) 6.
- [2] Y. Yokota, A. Yoshikawa, et. al., J. Cryst. Growth 318 (2011) 908.
- [3] K. Nishimoto, A. Yoshikawa, et. al., Opt. Mater. (2014)
- http://dx.doi.org/10.1016/j.optmat.2014.02.026

[4] P. Dorenbos, Nucl. Instrum. Meth. in Phys. Res. A486 (2002) 208.

[5] N.J. Cherepy, Appl. Phys. Lett. 92 (2008) 083508.

[6] P. Dorenbos, IEEE Tran. Nucl. Sci., 57 (2010).

[7] F.G.A. Quarati, Nucl. Instrum. Meth. in Phys. Res. A 735 (2014) 655.

[8]W.M. Higgins, K.S. Shah, et. al., J. Cryst. Growth 287(2006)239-242

[9] S. Kurosawa, A. Yoshikawa, et. al., J. Cryst. Growth 393(2014) 163-166.