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Crystal Growth and Luminescence Properties of Cs_3LuBr_6:Ce^{3+}

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Crystal growth, and luminescence properties of Ce doped Cs_3LuBr_6 crystal are presented. The CsBr powder (99.99%, Aldrich), $LuBr_3$ powder (99.99%, Aldrich) and $CeBr_3$ (99.99%, Aldrich) were prepared and the mole ratio between CsBr, and $LuBr_3$ was 3 : 1. The Ce doped Cs_3LuBr_6 crystals were grown with the Bridgman method using a two zone vertical furnace, and the materials were synthesized using the reaction $3CsBr + LuBr_3 \rightarrow Cs_3LuBr_6$. The investigation of the luminescence properties of the Cs_3LuBr_6 crystal was performed under the excitation by UV, X-rays and γ -rays at room temperature.

KEYWORDS: bromo-elapasolite, Bridgman, Cerium, Cs3LuBr6, scintillator

I. Introduction

Development of good performance crystals is important for the high energy physics, the nuclear instrumentation, radiation measurement and the medical imaging. In general, our crystal growth program includes studies of starting material preparation, growth procedures and characterization of grown crystals. Since the discovery of NaI(Tl) scintillator in 1948 by Hofstadter[1], many efforts have been made to improve the characteristics of scintillators such as light yield, fluorescence decay time, energy resolution, detection efficiency, and radiation hardness[2,3].

A Ce^{3+} ion is one of the most interesting luminescent materials used in scintillation materials for many applications. Many scintillation materials doped with the Ce^{3+} show high light yield, favorable emission wavelength, and fast fluorescence decay time[4,5]. Recently, Ce^{3+} doped elpasolite structure scintillators are studied because of their good scintillation properties such as high light yield, and fast decay time[6-8]. As shown in **Table 1**, some Lu contained bromo-elpasolite structure crystals show useful scintillation properties.

In this paper, we grew Cs_3LuBr_6:Ce^{3+} crystal as a bromo-epasolite structure crystal by using Bridgman method. And, we measured the luminescence properties of the grown crystal such as excitation and emission spectrum, fluorescence decay time.

II. Experiments

Fig. 1 A photograph of the two-zone vertical furnace.

TABLE 1
LUTATIUM CONTAINED BROMO-ELPASOLTE SCINTILLATORS

Scintillator	Light Yield (phs/MeV)	Decay Time (ns)	Peak Wavelength (nm)
Cs_2LiYCl_6:Ce [9]	22,000	~1,000	380
Cs_2LiYBr_6:Ce [10]	23,000	89/2, 500	389, 423
$Cs_2LiLuCl_6$:Ce [11]	7,000	30.4	372, 405
$Cs_2LiLaCl_6$:Ce [8]	-	36	375
Li_3YCl_6:Ce [12]	6,000	250, 2,300	360, 385
$Cs_2LiLuBr_6$:Ce [13]	-	37, 337, 1,700	394, 424
Cs_3LuCl_6:Ce [14]	7,500	-	375, 405

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A $Cs_3LuBr_6:Ce^{3+}$ crystal was grown by Bridgman method using two-zone vertical furnace as shown in **Figure 1**. The CsBr (99.99%, Aldrich), $LuBr_3$ (99.99%, Aldrich), and $CeBr_3$ (99.99%, Aldrich) powder were prepared and put into a quartz ampoule size of $\phi12$ mm × 70 mm in an Ar-purged glove box. The ampoule was cleaned with 10% nitrogen acid, acetone, ethanol, and de-ionized water and was sealed under 10^{-6} torr. The mole ratio between CsBr, and $LuBr_3$ was 3 : 1, respectively. The material was synthesized using the reaction $3CsBr + LuBr_3 \rightarrow Cs_3LuBr_6$. During the crystal growth, the temperature gradient of the furnace was 20 K/cm and the lowering rate of the quartz ampoule was 0.1 mm/hr. The $Cs_3LuBr_6:Ce^{3+}$ crystal was cut to a disc shape and was polished by using mixed Al_2O_3 powder (grain size 0.02 μm) in mineral oil on a polishing cloth (No.40-7218, Buehler) because of its hygroscopic property. After polishing, the $Cs_3LuBr_6:Ce^{3+}$ crystal (Ø 8 mm × 2 mm) was then coupled to a SbCs photomultiplier tube (9205B, Electron tube Ltd.) and the scintillation properties of the $Cs_3LuBr_6:Ce^{3+}$ crystals were measured by a pulse height analysis system. Signals from the PMT were fed directly into a 400 MHz FADC (flash analog-to-digital converter) [15], as shown in **Figure 2**. The FADC module was designed to sample the pulse every 40 ns for the duration up to 40 μs so that one can fully reconstruct each photoelectron pulse. The trigger was formed in the FPGA (field programmable gate array) chip on the FADC board as a self-trigger [16]. The FADC was located in a VME (versa module eurocard) crate and was read out by the Linux-operating personal computer through the VME-USB2 (universal serial bus) interface with a maximum data transfer rate of 10 Mbytes/s. The DAQ (data acquisition) system and the analysis program were written in the framework of ROOT package [17].
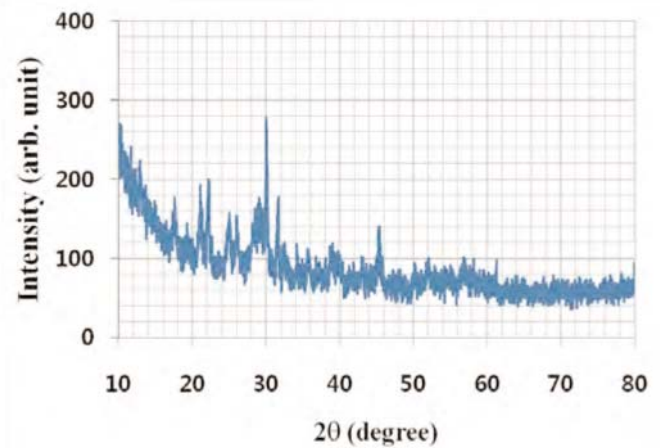
Fig. 2. Scheme of data acquisition system with 9205B PMT.
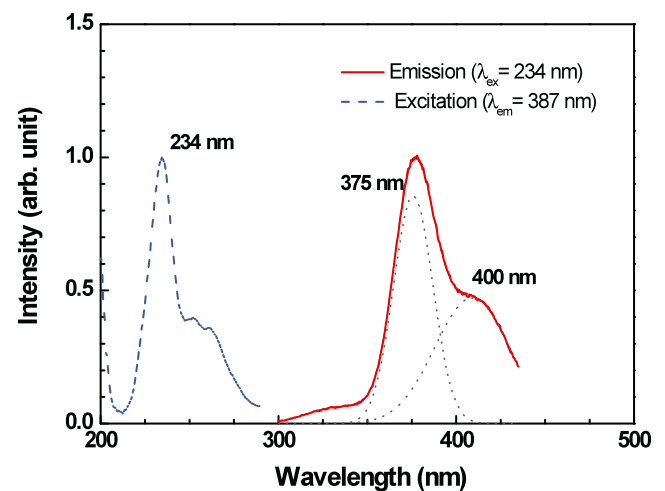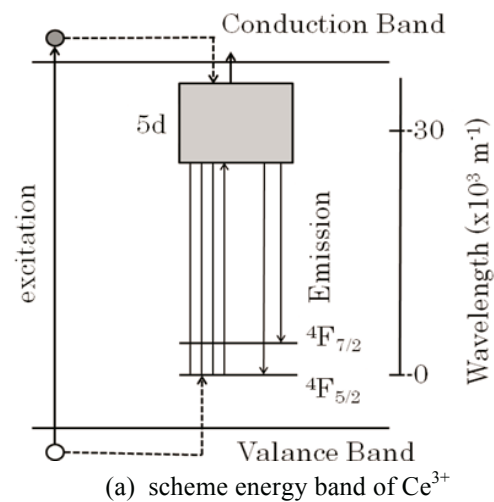
III. Results and Discussion
1. X-ray Diffraction Pattern
The crystal structure of $Cs_3LuBr_6:Ce^{3+}$ was examined by

Fig. 3. X-ray diffraction pattern of the grown $Cs_3LuBr_6:Ce^{3+}$.

using an X-ray diffractometer (X'pert Pro, PANalytical). The X-ray diffraction pattern of the $Cs_2LiLuBr_6:Ce^{3+}$ is shown in **Figure 3**.

(a) scheme energy band of Ce^{3+}
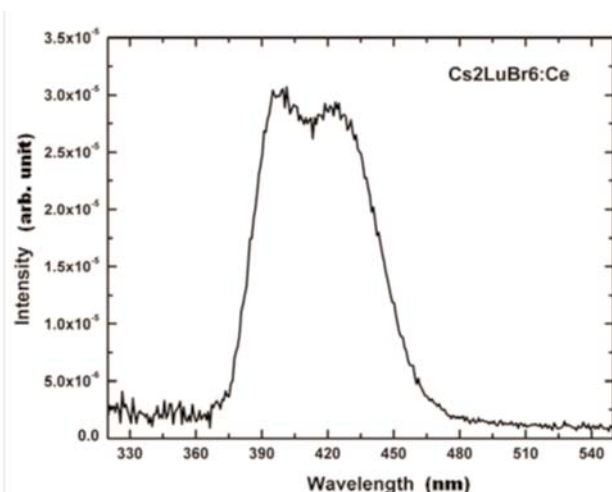
(b) excitation and emission spectra

Fig. 4. Excitation and emission spectra of the $Cs_3LuBr_6:Ce^{3+}$ crystal excited by UV.

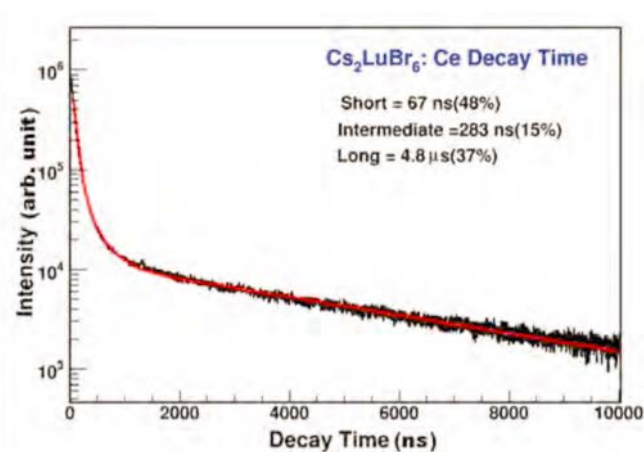## 2. Excitation and Emission Spectra excited by UV

The measurement of excitation and emission spectra of the $Cs_3LuBr_6:Ce^{3+}$ crystal was performed by using UV fluorescence spectrometer (LS 35, PerkinElmer) at room temperature. As shown in **Figure 4(a)**, the typical Ce^{3+} ion emission has shown the double band shape due to the 5d → 4f transitions [18]. The 4f ground state configuration yields two levels, via $^2F_{5/2}$ and $^2F_{7/2}$, due to spin-orbit coupling [19]. As shown in **Figure 4(b)**, the emission spectrum of the $Cs_3LuBr_6:Ce^{3+}$ crystal exhibits a double band shape between 300 nm and 480 nm, peaking at 375 nm and 400 nm which is due to 5d → 4f transition of the Ce^{3+}. The excitation spectrum of the crystal shows several peaks between 215 nm and 300 nm wavelength range, peaking at 234 nm. The Stoke's shift is about 141 nm.

3. Emission Spectrum excited by X-rays

As shown in **Figure 5**, the emission spectrum of the $Cs_3LuBr_6:Ce^{3+}$ crystal exhibits a double band shape between 360 nm and 480 nm, peaking at 396 nm and 422 nm which is due to 5d → 4f transition of the Ce^{3+}.

Under X-rays excitation, the emission spectrum of the $Cs_3LuBr_6:Ce^{3+}$ crystal is different from that under UV excitation. If the crystal is irradiated by high-energy X-ray, a large number of excitons are generated in the crystal compared with UV-irradiated. The excitons are trapped in the activator centers. So, the difference is produced in emission spectra between excited by X-ray and excited by UV [20].

4. Fluorescence Decay Time

Figure 6 shows the fluorescence decay time spectrum of the $Cs_3LuBr_6:Ce^{3+}$ crystal. Measurement of a decay time was performed by single photon counting technique [16]. The signals were created using 662 keV γ-rays from a ^{137}Cs radioactive source at room temperature. The fluorescence decay time is composed of three components. The fast component is 67 ns (48%), the slow component is 4.8 μs (37%), and the intermediate component is 283 ns (15%), respectively.

IV. Conclusion

We have grown $Cs_3LuBr_6:Ce^{3+}$ crystals as a new bromo-elpasolite structure scintillator by the Bridgman method. And we investigated the luminescence and scintillation properties of the $Cs_3LuBr_6:Ce^{3+}$ crystal for UV, X-rays, and γ-rays irradiation at room temperature. Under X-ray excitation, the emission spectrum of the $Cs_3LuBr_6:Ce^{3+}$ was observed in the range of 360~480 nm, peaking at 396 nm and 422 nm, which is due to the 4f → 5d transitions of the Ce^{3+}. Under UV (234 nm) excitation, the emission spectrum of the $Cs_3LuBr_6:Ce^{3+}$ was observed in the range of 300 ~ 480 nm, peaking at 375 nm and 400 nm, which is also due to the 4f → 5d transitions of the Ce^{3+}. The excitation spectrum of the $Cs_3LuBr_6:Ce^{3+}$ was observed in the range of 215 ~ 300 nm, peaking at 234 nm. We concluded that the fastest component decays of the $Cs_3LuBr_6:Ce^{3+}$ with 67 ns (48%) time constant, the intermediate component 283 ns (15%), while the slow component with 4.8 μs (37%), time constants.

Fig. 5. Emission spectrum of the $Cs_3LuBr_6:Ce^{3+}$ crystal excited by X-rays.

Fig. 6. Fluorescence decay time of the $Cs_3LuBr_6:Ce^{3+}$ crystal excited by γ-rays.

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