Optical properties of a Nd-doped SrBr₂ crystal grown by Bridgman technique

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Abstract

We have investigated the optical properties of 1mol% Nd-doped SrBr₂ crystal grown by Bridgman technique for an X-ray scintillator application. We succeeded in obtaining a transparent crystal, whose X-ray diffraction was measured under dry condition because of its hygroscopic nature. Roughly, we estimated that 90% of this crystal dissolved within 300 min. under 25 °C and 65-70% humidity. Under excitation by 270- and 400 nm photons several emission peaks originating from ⁴F_{3/2} or ⁴G₁₁→⁴I₁₂ (i1=5/2, 7/2, i2=13/2, 11/2, 9/2) transitions of Nd³⁺ were observed. 1mol% Nd:SrBr₂ had a maximum quantum yield of approximately 45%. Additional emission peaks were observed under X-ray excitation.

Keywords: Phosphor; Scintillator; Nd:SrBr₂

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1. Introduction

Scintillators are used in various fields such as medical imaging, oil well logging and astronomy [1, 2]. Although bromide scintillators generally have a hygroscopic nature, some of them such as Eu: BaBr₂, CeBr₃, Ce:GdBr₃ and Ce:LaBr₃, have high light outputs up to approximately 70,000 photons/MeV [3-8]. Especially, CeBr₃ and Ce:LaBr₃ are used for Gamma ray spectrometers due to their excellent energy resolution. We have searched for other bromide crystals which might be used as scintillators or phosphors.

0.5-mol% Eu-doped SrBr₂ has a light output of 20,000 ph/MeV, and an energy resolution of 7% at 662 keV [9]. The theoretical Light output (L_{th}) for this crystal is 100,000 ph/MeV when calculated from the following equation: $L_{th} = 10^6 / \beta E_g$, where E_g is the band gap of the host crystal and β is assumed to be 2.5 [10]. Additionally, this crystal has a band gap of 4.0 eV [9]. The difference between the theoretical and real light outputs may be because of the too small energy gap between the 5d excited state of Eu²⁺ and the bottom of the conduction band. There has been no report on SrBr₂ doped with other dopants, especially those with excited states placed at sufficiently lower energies compared to that of Eu, which would lead to higher separation of the excited state from the bottom of the conduction band and therefore higher light yield.

Nd-doped crystals show several emission lines originating from the f-f transitions, and some of them are used as laser levels with an emission wavelength of around 1.06 μ m. A Nd-doped scintillator is expected to have a near infra-red emission and some lines in the visible range above 500 nm. Some photodetectors such as a photomultiplier have low sensitivity for the wavelengths longer than 500 nm, while some silicon-avalanche photodiodes (Si-APD) have a quantum efficiency of more than 80% in the 500 to 800 nm region.

The SrBr₂ crystal has a low effective atomic number of 36.1 and low density of 4.216 g/cm³ compared with other conventional scintillators, and it is not very suitable for a gamma-ray detector. However, it has high enough atomic number and density to detect X rays. Thus, Nd:SrBr₂ might be used as a high-light-output X-ray scintillator (phosphor) for some X-ray detectors such as X-ray Computed Tomography using a Si-APD.

Since SrBr₂ has hygroscopic nature, we need to control the atmosphere during the crystal growth. Previously, our group prepared a hygroscopic crystal grown by the vertical Bridgman technique [11], and we also tried to grow a SrBr₂ crystal in the same way. Additionally, we have developed a photoluminescence setup for hygroscopic crystals using an integrating sphere in order to measure absolute quantum yield. In this paper, we report the optical properties of Nd:SrBr₂ grown by the Bridgman technique measured using our photoluminescence setup.

2. Materials and Experimental Methods

2.1 Crystal growth and characterization

1-mol% Nd-doped SrBr_2 was grown by the vertical Bridgman technique [11]. The starting powders (SrBr_2 and NdBr_3) of 99.99% purity were sealed within a quartz-glass ampoule in a low vacuum of a few Pa to be protected against absorption of water. The crystal growth ampoule had a diameter changing from approximately 2 to 7 mm and length of 25 mm as shown in Fig. 1. It was surrounded by a carbon (inner) and alumina (outer) insulators and heated with a radio frequency (RF) generator. Then it was heated up to the SrBr_2 melting temperature ($\sim 650^\circ\text{C}$), and subsequently pulled down from the hot zone with a pulling rate of ~ 0.03 mm/min while maintained at this temperature for 20 hours. After pulling, the ampoule was gradually cooled down to room temperature.

The single crystal was cut and polished under dry conditions before its optical properties were measured. The degree of hygroscopicity of this sample was roughly evaluated by eye using a fragment at a temperature of 25°C and humidity of 65-70%. In addition, part of the grown crystal was crushed into powder. Powder X-ray diffraction (XRD) analysis was carried out in the 2θ range of 20 - 80° using a diffractometer (RINT 2000, RIGAKU). The X-ray source was Cu-K α (accelerating voltage: 40 kV, beam current: 40 mA).

2.2 Optical properties

Emission and absorption spectra of this sample were measured with the setup depicted in the figure 2). Nd: SrBr_2 was excited by monochromatic UV photons using a Xenon lamp (150 W) and a monochromator (SP2150i, Princeton Instruments) controlled by a computer. The sample was placed within the integrating sphere, opposite to the fiber with UV excitation light. Emission light was collected by another optical fiber. Since Nd-doped phosphor has several emission lines from the visible to the infra-red region, the emitted photons were detected using two spectrophotometers (PMA-12, Hamamatsu KK), consisting of Si-APD (avalanche photodetectors). The shorter and longer wavelength spectrophotometers detected the photons emitted within a range of 200-950 and 350-1100 nm, respectively (hereafter described as short and long modes). Additionally, the sample was excited with different excitation wavelengths between 250-550 and 400-900 nm with an interval of 10 nm for the short and long modes, respectively. Using the above setup, intensity of the excitation light, reflected, and emitted photons were detected. This allowed us to evaluate the absorption spectrum of Nd: SrBr_2 .

The spectra were corrected by a correction curve. Although a Si-APD has a quantum efficiency of approximately 60-70% at 890 nm, photo-sensitivity is over 40 A/W for a near infra-red-high-sensitivity type APD. We usually use a short-wavelength type of Si-APD for the read out ultra-violet or blue scintillation light, which has a maximum photo-sensitivity of 20 A/W at approximately 600 nm [15].

The radioluminescence spectrum was obtained under X-ray irradiation. The X-rays were generated by a Cu target under 40 kV and 40 mA, and the emission spectrum was measured using a CCD camera (DU-420-OE, Andor). In order to protect it from moisture, the Nd: SrBr_2 sample was irradiated in a sample-holder sealed and filled with dry argon gas at 1 atm.

3. Results and discussion

3.1 Crystal growth and its evaluation

We succeeded in the growth of a Nd:SrBr₂ crystal using the vertical Bridgman technique as shown in Fig. 3. The studied sample was 1 mm thick. When a Nd:SrBr₂ crystal with a diameter of roughly 1-2 mm and length of 3 mm was exposed to the ordinary ambient conditions (25°C , 65-70% humidity), (i) liquid appeared after 10 min. of exposure, (ii) moisture made the crystal surface milky after 30 min, (iii) over 90% of the volume of the crystal was dissolved after 300 min.

The XRD pattern of the Nd:SrBr₂ is shown in Fig. 4. Although the observed peaks correspond to previously reported data for undoped SrBr₂, some peaks (e.g. around $2\theta = 42$ deg.) did not match with the previous data [12, 13]. Since the change of XRD pattern was due to presence of hydrates in case of SrI₂ [14], these un-known peaks may be ascribed also to hydrates such as SrBr₂·H₂O.

3.2 Optical properties

Emission spectra were measured with two spectrometers, under excitation with 270 and 400-nm photons for each detector (Fig. 5). The observed peaks originated from the $^4F_{3/2}$ or $^4G_{11} \rightarrow ^4I_{12}$ ($i_1=5/2, 7/2, i_2=13/2, 11/2, 9/2$) transitions of Nd³⁺, and the highest intensity peak was at around 880 nm due to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition. (The information about correction was placed within the Experimental section) The excitation-emission map is shown in Fig. 6. The most intense excitation bands between 300 and 550 nm for the 880nm emission of Nd³⁺ were located at around 360 nm and the excitation band in the 400 – 900 nm range for 1060 nm emission was detected around 880 nm. Absorption spectra show the highest peak around 590 nm originating from $^4I_{9/2} \rightarrow ^4G_1$ (Fig. 7). Here, the quantum yield is defined as $N_{\lambda_{em}}/N_{\lambda_{ex}}$, where $N_{\lambda_{em}}$ and $N_{\lambda_{ex}}$ are numbers of the photons emitted from the sample at a wavelength of λ_{em} and number of the absorbed excitation photons of wavelength λ_{ex} . Using the above data, the quantum yield of 1 mol% Nd:SrBr₂ was estimated to be approximately 35 and 25% for $(\lambda_{ex}, \lambda_{em}) = (360, 880 \text{ nm})$ and $(880, 1060 \text{ nm})$, respectively. These values are smaller than those for conventional scintillators or phosphors by 20-30%, because Nd³⁺ also has other emission peaks at wavelengths longer than 1100 nm, which were not measured in this experiment.

The Radioluminescence spectrum of this crystal under X-ray excitation is shown in Fig. 8. Compared with photoluminescence, some additional peaks were observed in the spectrum, most probably because of the different way of excitation of the Nd³⁺ ions. Although only wavelengths up to 820nm could be detected in our radioluminescence setup, the crystal is expected to show 890 nm and longer emission peaks in radioluminescence.

4. Conclusions

A 1 mol% Nd-doped SrBr₂ crystal was grown by the vertical Bridgman technique. Although this crystal has hygroscopic nature, we succeeded in obtaining photoluminescence spectra. This sample showed several emission peaks originating from $^4F_{3/2}$ or $^4G_{11} \rightarrow ^4I_{12}$ ($i_1=5/2, 7/2, i_2=13/2, 11/2, 9/2$) in Nd³⁺ in a wide wavelength region (visible and infra-red region). The maximum quantum yield of 1mol% Nd:SrBr₂ was estimated to be approximately 35%. The radioluminescence spectrum was also observed, and Nd:SrBr₂ can be used as X ray scintillator or phosphor.

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Figure captions

Figure1. Schematic view of a quartz-glass ampoule including Nd:SrBr₂ powder.

Figure2. Schematic view of the setup for the photoluminescence.

Figure3. Photograph of a Nd:SrBr₂ crystal grown by vertical Bridgman technique.

Figure4. Powder X-ray diffraction patterns of the Nd:SrBr₂ crystal.

Figure5. Emission spectra of the Nd:SrBr₂ crystal excited with 270-nm (a) and 400-nm (b) photons for short and long mode, respectively.

Figure6. Emission spectra as a function of excitation spectra for short (a) and long (b) mode.

Figure7. Absorption spectrum of the Nd:SrBr₂ crystal using long mode data.

Figure8. Radioluminescence spectrum of the Nd:SrBr₂ crystal irradiated with X rays.

Fig1

Fig2

Fig3

Fig4

Fig5

Fig6

Fig7

Fig8