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Sm-doped CsBr crystal as a new radio-photoluminescence (RPL) material

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Abstract: Radio-photoluminescence (RPL) is a phenomenon seen in luminescent materials in which the appearance of new photoluminescence (PL) emission is induced by an incident ionizing radiation such as X-rays; and the signal is stable even after the irradiation and during the PL measurement. Since the induced PL intensity is proportional to the irradiation dose, the RPL can be used in radiation measurements. The distinct advantage of RPL over the conventional thermally- or photo-stimulated luminescence (abbreviated as TSL or PSL) dosimeters is the stability of response signal. With an RPL detector, it allows us to readout the signal multiple time without signal fading. In this work, we discovered that CsBr:Sm showed an RPL phenomenon by X-ray irradiation, and we characterized this new material as an RPL detector. While the sample showed PL emissions mainly in the visible range, after an X-ray irradiation additional emissions could be observed in the red to near-infrared range around 650–850 nm and 900–1000 nm and longer. The RPL response was fairly stable overall, but very interestingly the 650–850 nm signal slightly increased while the 900–1000 nm decreased during PL readout. The dynamic range was confirmed over 1–10^4 mGy with linear response.

Keywords: radio-photoluminescence; RPL; CsBr; Sm; dosimeter; X-rays; rare earths

Rare-earth doped inorganic solids are a common choice of phosphor materials for ionizing-radiation measurements. They show various radiation-induced effects such as scintillation[1], thermally-stimulated luminescence (TSL)[2], photo-stimulated luminescence (PSL)[3], and radio-photoluminescence (RPL)[4], and in these materials rare earth ions typically play a major role to act as luminescent centres and/or charge trapping centres. Among these radiation-induced phenomena, the RPL is a relatively newly-recognized phenomenon in which the photoluminescence (PL) intensity typically increases with the radiation dose irradiated prior to the PL measurement. Since the extent of PL intensity is stably kept and does not fade out even after the readout process (unlike TSL or PSL), such RPL materials can be used for the measurement of radiation dose integrated over time, and it allows the readout of the signal multiple time[5,6]. Although there are not many RPL materials recognized today, some selected materials are LiF[7], Ag-doped phosphate glasses[8], Al_2O_3:C,Mg[9], and Sm-doped crystals, glasses, and glass-ceramics[4,10–15].

CsBr is of particular interest as it has shown exceptional properties for ionizing radiation detection. Particularly, CsBr:Eu shows effective PSL properties; therefore, it has been commercially used as an imaging plate material especially for X-ray radiography[16]. As an imaging plate, CsBr crystals can be used simply in the micro-grain powder form uniformly distributed in a polymer film whereas it can also be fabricated in the columnar structure[17]. The latter type of imaging plate has a distinct advantage that the PSL emission signals are locally confined along the columnar wells and propagate to the surface of imaging plate; therefore, cross-talk between the adjacent pixels are minimized and image resolution is effectively enhanced. Also, recently Winch et al.[18] have reported that CsBr:Eu^{2+} can be fabricated in a form of transparent ceramic and showed the capabilities as an imaging plate using PSL.

In this work, we synthesized and characterized Sm-doped CsBr single crystal, and we newly discovered that the CsBr:Sm showed RPL properties. In this paper, our preliminary experimental results of RPL in CsBr:Sm were presented and discussed.

1 Experimental

Sm-doped CsBr crystals were synthesized in a vacuum quartz ampule by the Bridgeman-Stockbarger method as

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follows: The starting materials for Sm-doped CsBr crystals were CsBr (99.999% purity) and $SmCl_3 \cdot 6H_2O$ (99.99% purity) powders. The powders were mixed in a stoichiometric ratio. The concentration of the Sm dopants was 0.2 mol.% for the luminescence center. The mixed powder was loaded into a quartz ampoule and heated at approximately 550 K in vacuum for 1 d in order to evaporate the water from the content. The crystals were grown at a rate of 1.0–2.0 mm/h in the furnace. After the synthesis process, an as-grown crystal was cut and polished into the dimensions of approximately 10 mm×3 mm×1 mm.

The crystal structure of synthesized samples was verified by a powder X-ray diffraction technique using an X-ray diffractometer (Ultima IV, Rigaku). The optical transmittance was measured using a spectrophotometer (V-670, JASCO). The photoluminescence emission spectrum was measured using our lab-constructed setup. As an excitation source, an xenon lamp (LAX-C100, Asahi Spectra) was used with a combination of bandpass filter to obtain a 340 nm excitation light, which was delivered to the sample. Upon excitation, the photoluminescence (PL) emission light was collected by a fibre-coupled lens and guided to a CCD-based spectrometer (QEPro, Ocean Optics) to digitize the PL spectrum. The excitation spectrum was measured using a spectrofluorometer (FP8600, JASCO). The PL lifetime was measured using a Hamamatsu Quantaurus-Tau (C11367-04). As a radiation source, an X-ray generator (XRBOP&N200X4550, Spellman) was used in this study. The X-ray generator is equipped with a conventional X-ray tube with a W anode and Be window. The applied voltage and current to the X-ray tube were fixed at 40 kVp and 1.2 mA, respectively. The reported dose measurements below are dose in air at the entrance of the sample.

2 Results and discussion

Fig. 1 illustrates a photograph of synthesized CsBr:Sm crystal sample. The XRD measurement (data shown in Fig. 2) has confirmed that the synthesized CsBr:Sm has the cubic structure. The as-prepared sample is reasonably

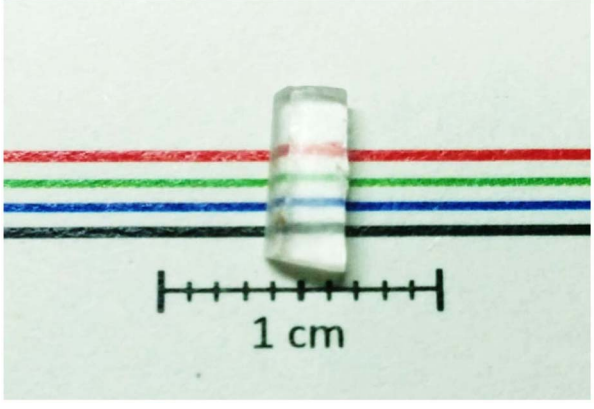

Fig. 1 A synthesized CsBr:Sm crystal sample

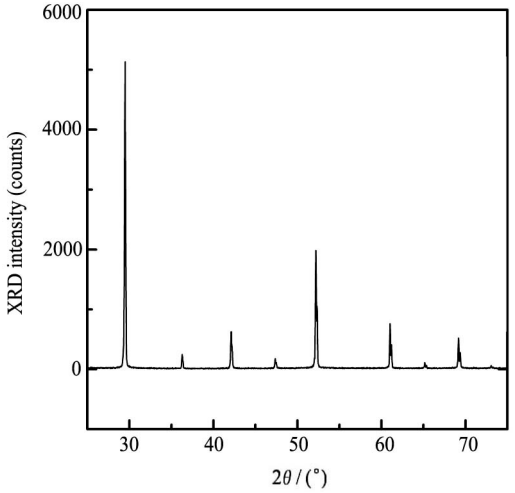

Fig. 2 XRD pattern of synthesized CsBr:Sm crystal

transparent without any noticeable colouration even with the inclusion of Sm ions. However, after X-ray irradiation, the sample is tanned light green colour. Fig. 3 shows the X-ray induced absorption spectra of CsBr:Sm with different X-ray doses. The absorption band around 690 nm is typical for CsBr and is due to F-centres formed by Br vacancies[17]. Furthermore, we found an additional induced absorption in the UV range. Although the absorption band cannot be clearly detected at lower doses below 1 Gy, it seems to increase with increasing irradiation dose. Moreover, the color change in green observed after irradiation is due to the appearance of these two absorption bands in the UV-blue and red ranges.

Fig. 4 shows PL emission spectra of CsBr:Sm before and after X-ray irradiation. The irradiation dose here is 10 Gy. The excitation wavelength is 340 nm. Before the X-ray irradiation, there are several different emissions observed: a predominant band emission in the blue range centering at 440 nm and sharp line emissions located around 620 and 700 nm. After the X-ray irradiation, additional emissions are observed in CsBr:Sm in the spectral range longer than 650 nm, hence RPL has been observed in the CsBr:Sm crystal. The emission bands due

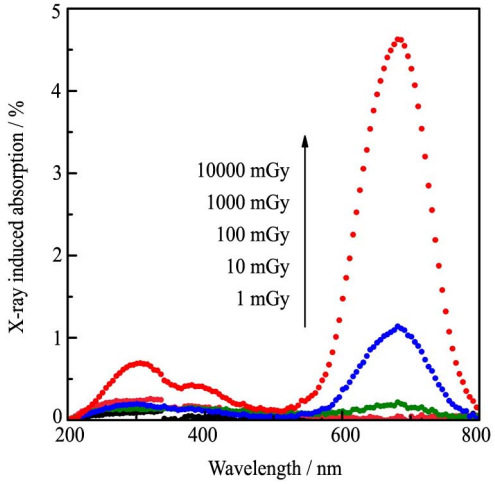

Fig. 3 X-ray-induced absorbance spectra as a function of X-ray dose delivered