Investigation on New Scintillators for Subnanosecond Time-Resolved X-Ray Measurements

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Abstract. We investigated new x-ray detectors for nuclear resonant scattering measurements with high energy x-rays. The organic-inorganic perovskite scintillator of phenethylamine lead halide (($\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3$)$_2\text{PbX}_4$) (X:Br, I) was used. These compounds have fast light emission due to an exciton. They include heavy atoms, which make the detector to have high efficiency to high energy x-rays. The merit of these scintillators is that we can make a thick crystal compared to a Si wafer which is used in an avalanche photo-diode detector. We successfully measured 67.41 keV x-ray signals, the energy of $^{63}$Ni nuclear resonant scattering, with high detection efficiency of 42.5% by the scintillator.

1. Introduction

In nuclear resonant scattering measurements, a large dynamic range is required, since large prompt electronic scattering signals must be masked to detect a single nuclear resonant quantum delayed by some nanoseconds. Silicon avalanche photo-diode (Si-APD) detectors were mainly used in these measurements since Si-APD detectors have good time resolution. However the nuclear resonant scattering measurements are spreading to high energy region and detectors are also required to have high efficiency to high energy x-ray signals. Si-APD detectors are made by very thin Si wafers up to 150 $\mu$m, and have low efficiency to high energy x-rays (lower than 15% to 20 keV x-rays). High efficiency detectors for these measurements are necessary for further development in this field.

Recently, organic-inorganic perovskite crystals are developed as scintillators[1]. These compounds have fast light emission caused by excitons[2]. Inorganic layers consist of metal halide (PbX$_4$, X:Br, I) are separated by organic layers includes alkyl chains. Inorganic layers are semiconductors and organic layers are insulators. Both layers make multiple quantum well structure, which keeps a strong photo-
luminescence in the material even at room temperature (RT). The merit of this material is heavy Pb atoms, since it shows the good absorption of x rays compared to Si-APD with light Si atoms. But thickness of 0.1mm was not enough to the detection of x rays with energy higher than 20 keV. To obtain larger crystal, alkyl chains are changed to phenetyl groups. A first one is an organic-inorganic perovskite scintillator of phenethylamine lead bromide ((C₆H₅C₂H₄NH₃)₂PbBr₄, abbreviated as PhE-PbBr₄). We have succeeded to measure ⁶⁷Ni nuclear resonant scattering (67.41 keV, lifetime: 7.6 ns)[3]. Second one is the same kind of scintillator of phenethylamine lead halide ((C₆H₅C₂H₄NH₃)₂PbBr₄₋zI₂, abbreviated as PhE-PbBr₄₋zI₂), in which bromide and iodide is mixed. The iodide sample showed faster scintillation decay in alkyl organic-inorganic crystals than scintillation decay of the bromide sample[2]. We have investigated optical properties of these crystals.

2. Experimental
The crystals we investigated here are PhE-PbBr₄, PhE-PbBr₄₋zI₂ (z:low), PhE-PbBr₄₋zI₂ (z:high). In fabrication of bromide and iodide mixture crystal, 20% of PbBr₂ was alternated with PbI₂ to make a crystal of PhE-PbBr₄₋zI₂ (z:low), and 40% to make a crystal of PhE-PbBr₄₋zI₂ (z:high). The structure and the fabrication of the first crystal is reported in ref. 4. The scintillation properties were investigated at beamline BL-14A of the Photon Factory, KEK, Tsukuba. The storage ring was operated in single bunch mode, which was suitable to investigate time domain properties of the scintillation. To obtain scintillation decay curve, crystal was set 38mm away from photo-multiplier tube (PMT, Hamamatsu R7400P) window in a vacuum chamber, to detect 1 photon or lesser in each x-ray pulse. The energy spectra are obtained by the crystals mounted on the window of PMT using optical grease and covered with Teflon tape.

3. Results and Discussion
The Scintillation decay curves from the samples are shown in Figure 1. The decay of iodide and bromide mixture crystals is faster than that of bromide crystals.

![Figure 1. Scintillation decay curves of samples.](image-url)
Table 1 shows the efficiency to 67.4 keV x-ray and the decay components of each scintillator. Decay components values are obtained by fitting experimental data by four exponential functions. The energy spectra and energy resolution are shown in Figure 2. The values of energy resolution are calculated from FWHM. Compared to bromide crystals, bromide and iodide mixture crystals showed lower light emission, and bad energy resolution. The PhE-PbBr₄ crystal is transparent, and the iodide mixture crystals are transparent with yellow color. The color may cause the self-absorption in the crystals. Since higher ratio of iodine retards the growth of the crystals, the thicknesses of iodide mixture samples are under 1 mm. Efficiency is mainly determined by the thicknesses of the crystals.

| Material               | Efficiency (%) | Decay components (ns (%))       |
|------------------------|----------------|---------------------------------|
| PhE-PbBr₄              | 42.5           | 5.3(10.3), 15(62.2), 54(20.8), 213(6.7) |
| PhE-PbBr₄-I₂ (z:low)   | 34.3           | 2.6(22.2), 8.1(58.0), 36(11.8), 168(7.9) |
| PhE-PbBr₄-I₂ (z:high)  | 18.4           | 1.3(12.4), 5.1(49.5), 15(23.9), 142(14.2) |

Figure 2. Energy spectra and energy resolution (FWHM) of scintillators for 67.4 keV x-rays.

4. Conclusion
In practical use in nuclear resonant scattering, bromide crystals showed best performance. Although bromide and iodide mixture crystals showed fast scintillation decay, the light emission and the energy resolution were not enough for practical application. It is supposed to be caused by self-absorption of the crystals.

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