

# Slow Scintillation Suppression in Yttrium Doped BaF<sub>2</sub> Crystals

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**Abstract**—Barium fluoride (BaF<sub>2</sub>) crystal has a fast scintillation light peaked at 195 nm and 220 nm with a sub-ns decay time. This ultra-fast scintillation promises a wide application in an area where extreme fast timing is important, such as future HEP experiments, gigahertz (GHz) hard X-ray imaging, and TOF-PET etc. BaF<sub>2</sub> crystal, however, has also a slow scintillation component peaked at 310 nm with a decay time of about 600 ns, which causes pile-up. Suppression of the slow scintillation component by selective doping, such as Ce, La, Tm and Y, was discussed twenty years ago. In this paper, we report suppression of the slow component in BaF<sub>2</sub> crystals by yttrium doping. Single crystals with 1 at% Y doping were grown by vacuum Bridgman technique at Shanghai Institute of Ceramics, Chinese Academy of Sciences. Their radioluminescence, optical transmittance, light output, fast/slow ratio, decay kinetics and light response uniformity were measured. The results show that 1 at% Y doping suppresses the slow scintillation component in BaF<sub>2</sub> crystals by a factor of 6, while the fast component remains unaffected.

**Index Terms**—Barium fluoride, Scintillation crystals, Slow component, Y<sup>3+</sup> doping.

## I. INTRODUCTION

Barium fluoride (BaF<sub>2</sub>) crystal is known as an ultrafast inorganic scintillator [1, 2]. Because of its fast cross-luminescence, peaks at 220 nm with a sub-nanosecond decay time BaF<sub>2</sub> crystal is considered promising for applications where very high count rates are expected. There is, however, a slow scintillation component with a decay time of about 600 ns and with a light yield of 5 time of the fast component, which would cause pile-up. It thus is important to reduce the amount of slow component for applications requiring clean fast scintillation light. Research along this line was recently discussed by V.N. Makhovin [3], and have been pursued for future high energy physics (HEP) experiments at the intensity frontier [4, 5], Gigahertz (GHz) hard X-ray imaging [6, 7] and time of flight positron emission tomography (TOF-PET) [8] etc.

The slow scintillation component in BaF<sub>2</sub> is believed due to relaxation of self-trapped excitons (STE) [9], which is sensitive to temperature. The light output ratio of the fast components to

the slow component has been determined to be about 1: 5 in room temperature [10]. Two approaches have been tried to suppress the slow component in BaF<sub>2</sub>: 1) by selective readout with either an band pass filter or solar-blind photodetector; and 2) slow component suppression by rare earth (RE) doping in BaF<sub>2</sub>, such as Ce, La, Tm and Y [5, 9, 11-19]. Our previous study shows that a 20 cm long La/Ce co-doped BaF<sub>2</sub> crystal grown in Beijing Glass Research Institute (BGRI) increases the F/S ratio from 1/5 to 1/1 [20], which is similar to what achieved twenty years ago.

RE<sup>3+</sup> doping in BaF<sub>2</sub> for suppression of the slow component was investigated extensively twenty years ago. While, most efforts were in La doping, Y<sup>3+</sup> doping was reported by B. P. Sobolev et al. in 1994 for BaF<sub>2</sub> powders, where the F/S ratio was reported to be increased by a factor of 30 with 10 at% Y<sup>3+</sup> doping [18]. This test with powders, however, has not been advanced to single crystals. The absolute scintillation efficiency of powdered samples was estimated by normalizing the luminosity of Ba<sub>0.9</sub>Y<sub>0.1</sub>F<sub>2.1</sub> powders to undoped BaF<sub>2</sub> powders. Internal absorption in the crystal bulk thus is not taken into account.

As a dopant, YF<sub>3</sub> has many advantages as compared with LaF<sub>3</sub>. Firstly, the melting point of YF<sub>3</sub>, 1387 °C, is very close to that of BaF<sub>2</sub>, 1368 °C, thus it's favorable for crystal growth. Secondly, YF<sub>3</sub> has a density of 4.01 g/cm<sup>3</sup>, compared with that of LaF<sub>3</sub>, 5.90 g/cm<sup>3</sup>, it's 47.1% lower leading to a potentially low cost for mass production of doped BaF<sub>2</sub> crystals with equal molar doping concentration. The last, but not the least, YF<sub>3</sub> has no intrinsic radioactive background, so may be used in applications requiring extreme low background.

In this paper, we present our first result on the suppression of the slow component in BaF<sub>2</sub> crystals doped with Y<sup>3+</sup>. BaF<sub>2</sub> crystals with 1 at% Y doping were grown at Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences (CAS). Their optical and scintillation properties, such as radioluminescence, optical transmittance, light output, fast/slow ratio, scintillation decay kinetics and light response uniformity were measured in Caltech HEP Crystal Laboratory. Section II describes the sample preparation and characterization. Sections III presents

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the results and discussions. A brief summary and conclusions are given in Section IV.

## II. SAMPLE PREPARATION AND MEASUREMENT

BaF<sub>2</sub> crystals with 1 at% Y doping were grown by vacuum Bridgman technique at SIC. Raw materials, BaF<sub>2</sub> (5N) and YF<sub>3</sub> (5N), are weighted in molar stoichiometric proportion of 0.99:0.01, homogeneously mixed, and then heated at 200°C in vacuum to remove moisture and other volatile components. A small portion of PbF<sub>2</sub> powder with 4N purity was added into the BaF<sub>2</sub>/YF<sub>3</sub> mixture as a scavenger to remove contaminations of O<sup>2-</sup> and hydroxyl. The single crystal ingots were then grown in a vacuum Bridgman furnace.

Table I lists the information of samples measured in this investigation. Samples (SIC-UA1, SIC-YA1) used for X-ray excited luminescence (XEL) measurements have a demission of 10×10×2 mm<sup>3</sup> with two 10×10 mm<sup>2</sup> faces polished. Samples of 30×30×20 mm<sup>3</sup> (SIC-U01, SIC-Y2A, SIC-Y3A, SIC-Y4A) used for longitudinal transmittance (LT), light output (LO), and decay kinetics measurements were cut from undoped and 1at% Y doped BaF<sub>2</sub> ingots respectively. A long Y doped BaF<sub>2</sub> sample (SIC-Y190) of 31<sup>2</sup> × 190 × 35<sup>2</sup> mm<sup>3</sup> was used for the longitudinal transmittance (LT) and light response uniformity (LRU) measurements.

TABLE I  
SAMPLES AND MEASUREMENTS

Sample ID	Sample Dimensions	Y <sup>3+</sup> Doping Concentration	Measurements
SIC-UA1	10 mm × 10 mm × 2 mm	0	XEL <sup>a</sup>
SIC-YA1	10 mm × 10 mm × 2 mm	1at%	XEL
SIC-U01	30 mm × 30 mm × 20 mm	0	LT <sup>b</sup> , LO <sup>c</sup>
SIC-Y2A	30 mm × 30 mm × 20 mm	1at%	LT, LO
SIC-Y3A	30 mm × 30 mm × 20 mm	1at%	LT, LO
SIC-Y4A	30 mm × 30 mm × 20 mm	1at%	LT, LO
SIC-Y190	31 <sup>2</sup> mm × 190 mm × 35 <sup>2</sup> mm	1at%	LT, LRU <sup>d</sup>

<sup>a</sup>XEL X-ray excited luminescence; <sup>b</sup>LT, longitudinal transmittance; <sup>c</sup>LO, light output; <sup>d</sup>LRU, light response uniformity.

X-ray excited luminescence (XEL) was measured by an Edinburgh Instrument FLS920 fluorescence spectrometer with an optional X-ray source from a 50 kV 20 mA tungsten target tube. The signals were detected by a Hamamatsu R928P PMT through a monochromator. Measured XEL spectra were corrected by using a calibrated light source. LT was measured by using a Perkin Elmer Lambda-950 spectrometer equipped with double-beam, double-monochromator and a general purpose optical bench with an optical path up to 40 cm. The systematic uncertainty of the LT measurement is about 0.2%.

Light output (LO) measurement is described in details in previous publications [12, 21]. A Hamamatsu R2059 PMT was coupled to the sample with a silicone grease (Dow Corning DC-200) and all uncoupled surfaces wrapped with two layers of Tyvek paper. The crystal was excited by a <sup>22</sup>Na source with a coincidence trigger. A MCA (LeCroy 3001 QVT) was used to digitize the pulse height. The LO as a function of the

integration time (decay kinetics) was measured by applying a series of eleven integration gates, from 50 to 3,000 ns, from a LeCroy 2323A programmable gate generator, from which the decay time of the slow component and the fast to slow ratio are extracted. The systematic uncertainty of the LO measurement is about 1%.

## III. RESULTS AND DISCUSSIONS

Fig. 1 shows a comparison of the XEL spectra for undoped (black, solid line) and 1 at% Y doped (blue, dashed line) BaF<sub>2</sub> crystals. Compared to the undoped BaF<sub>2</sub>, the 1 at% Y doped sample shows a reduced slow component around 300 nm by a factor of about 4, while the intensity of the fast component around 220 nm remains the same, similar to La doped BaF<sub>2</sub> crystals [12, 22].

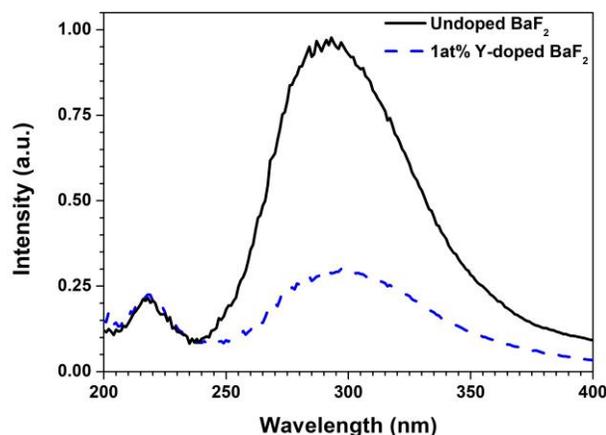


Fig. 1. X-ray excited luminescence spectra of undoped BaF<sub>2</sub> crystal (black, solid line) and 1at% Y doped BaF<sub>2</sub> crystal (blue, dashed line).

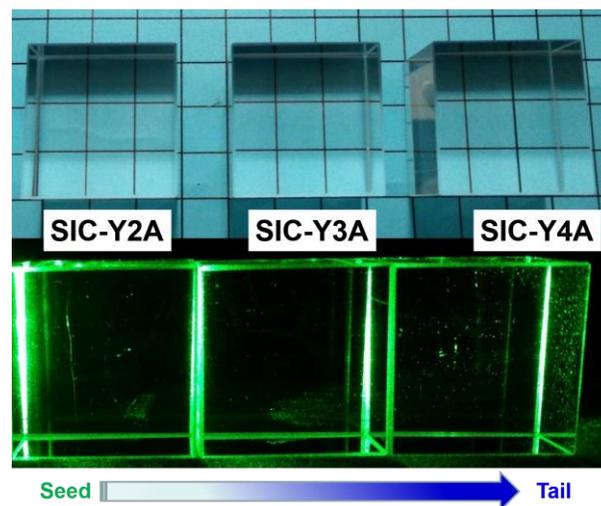


Fig. 2. Photographs show three 1at% Y doped BaF<sub>2</sub> crystal samples cut from one ingot. The top photograph was taken under natural light, while the bottom one was taken under illumination of a 523 nm green laser.

Fig. 2 shows a picture of three BaF<sub>2</sub> samples, SIC-Y2A, SIC-Y3A, and SIC-Y4A cut from a BaF<sub>2</sub> ingot with 1 at% Y doping. While SIC-Y2A is close to the seed end, SIC-Y4A is close to the tail end. The top photo was taken under natural light, showing no apparent scatters. The bottom photo was taken

under illumination of 523 nm green light, where only a small amount of scatters was visible near the surface close to the tail end, indicating a good optical quality.

Fig. 3 shows the optical transmittance from 200 to 800 nm for these three samples, and compared to the undoped sample SIC-U01 with the same dimensions. Also shown in the figure is the theoretical limit calculated by using the refractive index data of BaF<sub>2</sub> [23] and the emission weighted longitudinal transmittance (EWLT) for the fast and slow components, which is defined as [24]:

$$EWLT = \frac{\int LT(\lambda)Em(\lambda)d\lambda}{\int Em(\lambda)d\lambda} \quad (1)$$

where  $LT(\lambda)$  and  $Em(\lambda)$  are longitudinal transmittance and emission at wavelength ( $\lambda$ ).

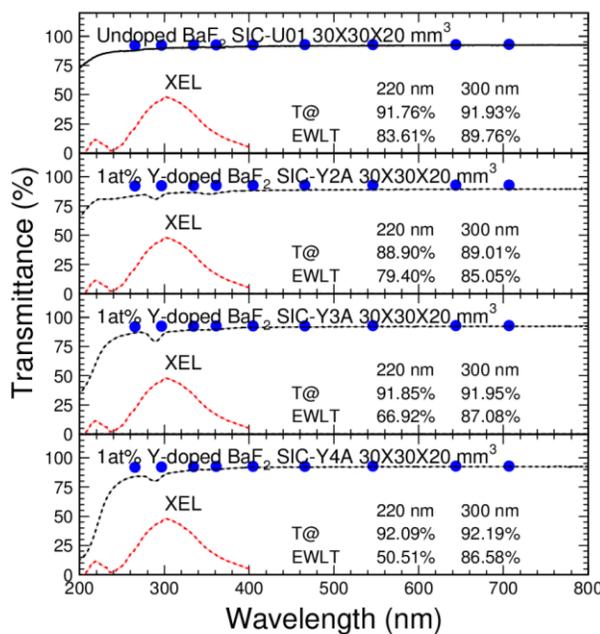


Fig. 3. Optical transmittance and EWLT of undoped and Y doped BaF<sub>2</sub> crystals.

The measured optical transmittance from 320 to 800 nm of all the 4 samples approaches the theoretical limit, indicating good optical quality in this region. The transmittance of SIC-Y2A is comparable with SIC-U01, indicating that current technology may grow Y doped BaF<sub>2</sub> crystals of high optical quality.

The EWLT values of the fast component for BaF<sub>2</sub> crystal sample is in the order as follows:  $EWLT_{SIC-U01} > EWLT_{SIC-Y2A} > EWLT_{SIC-Y3A} > EWLT_{SIC-Y4A}$ , indicating a poor transparency for the fast component in these BaF<sub>2</sub> samples developed at an early stage.

Fig. 4 shows the LO as a function of the integration time for these four BaF<sub>2</sub> samples, and the corresponding fit with an exponential decay constant  $\tau_s$  for the slow component:

$$LO(t) = F + S(1 - e^{-t/\tau_s}) \quad (2)$$

where  $F$  is the fast component and  $S$  is the slow component. The numerical values of the fit are presented in the figure and summarized in Table II together with the measured LO. Significant reduction of the slow component is observed in both the intensity and the decay time for the slow component. The corresponding  $F/S$  ratio is increased from 0.2 for undoped sample SIC-U01 to up to 1.3 for SIC-Y2A, while the LO of the fast component keeps the same. The decrease of fast component LO in SIC-Y3A and SIC-Y4A are consistent with the observation of absorption band in 200 - 250 nm in the LT. The strong absorption observed near the fast component is suspected to be caused by oxygen contamination.

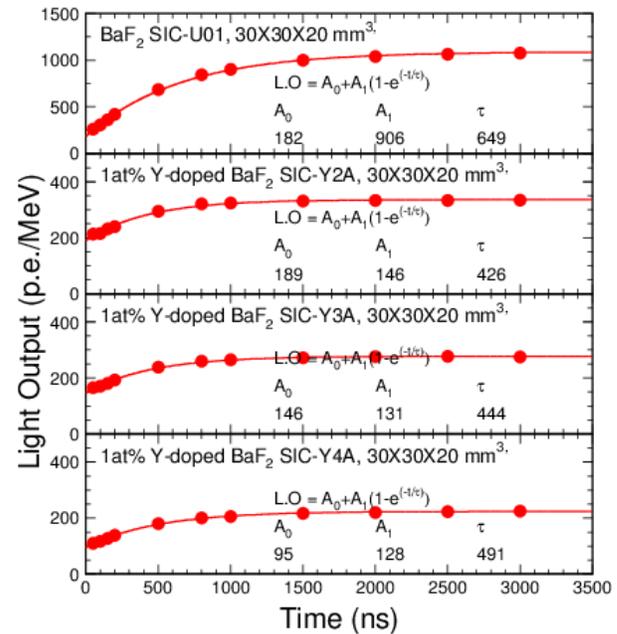


Fig. 4. Light output measured is shown as a function of integration time for undoped and three Y doped BaF<sub>2</sub> crystals.

TABLE II  
A SUMMARY OF LIGHT OUTPUT OF UNDOPED Y DOPED AND BaF<sub>2</sub> CRYSTALS

ID	LO of fast (p.e./MeV)	LO of slow (p.e./MeV)	F/S <sup>2</sup> ratio of LO	LO of 50 ns gate (p.e./MeV)	LO of 2500 ns gate (p.e./MeV)	50/2500 ns gate LO ratio (%)
SIC-U01	182	906	0.2	260	1062	24.5
SIC-Y2A	189	146	1.3	213	333	64.0
SIC-Y3A	146	131	1.1	165	302	54.6
SIC-Y4A	95	128	0.74	111	223	49.8

Fig. 5 shows a long BaF<sub>2</sub> crystal of 31<sup>2</sup>×190×35<sup>2</sup> mm<sup>3</sup> with 1 at% Y doping. Its longitudinal and transverse transmittance with a light path of 190 mm and 31-35 mm respectively are shown in Fig. 6. The small end with a 31<sup>2</sup> mm<sup>2</sup> cross-section is the seed end, while the large end with a 35<sup>2</sup> mm<sup>2</sup> cross-section is the tail end.



Fig. 5. A 190 mm long BaF<sub>2</sub> crystal with 1at% Y doping.

The LT of this sample is significantly lower than the theoretical limits (blue dots), indicating its poor optical quality. In addition, the transverse transmittance shows a significant variation along the 190 mm length. Although the transverse transmittance at 11 cm from the seed is close to the theoretical limit, the transverse transmittance at 17 cm from the seed is much lower than the theoretical limit. Compared with SIC-Y3A and SIC-Y4A, the overall transverse transmittance along SIC-Y190 in 200-250 nm range has been improved.

A strong absorption band around 290 nm, however, is observed in the LT spectrum as well as several other absorption bands. In our early study for a La/Ce co-doped crystal grown at BGRI, this absorption at 290 nm was attributed to the Ce dopant [20]. In this investigation, YF<sub>3</sub> with 99.999% purity is used as the dopant so the Ce<sup>3+</sup> concentration is very low, which is confirmed by no intrinsic Ce<sup>3+</sup> photo-luminescence observed from this sample. We plan to continue this investigation to clarify the nature of these absorption bands observed between 200 and 400 nm in our future publication.

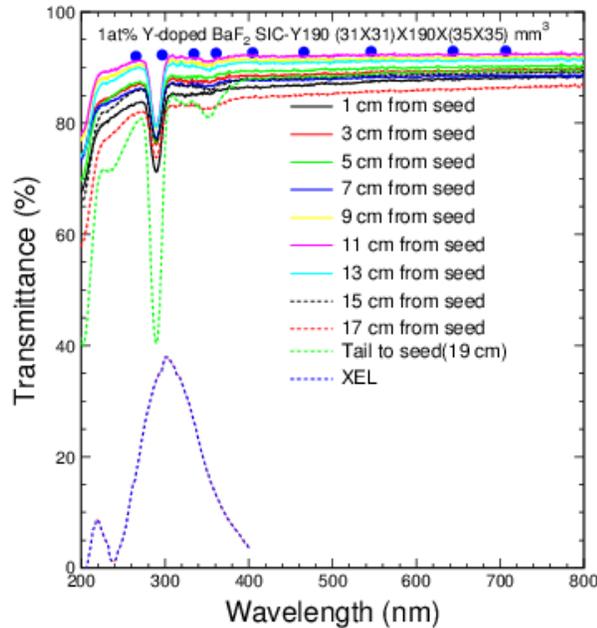


Fig. 6. Longitudinal and transverse transmittance of a 190 mm long Y doped BaF<sub>2</sub> crystal.

Fig. 7 shows the light output of 50 ns gate as a function of distance to PMT for this 190 mm long Y doped BaF<sub>2</sub> crystal with the seed (top) and tail (bottom) end coupled to the R2059 PMT. The light outputs were measured by injecting collimated  $\gamma$ -rays from a <sup>22</sup>Na source along the long crystal with a

coincidence trigger. The light response uniformity (LRU) is parameterized as  $\delta$  by a linear fit as follows:

$$\frac{LO}{LO_{mid}} = 1 + \delta \left( \frac{X}{X_{mid}} - 1 \right) \quad (3)$$

where  $LO_{mid}$  is the fitted value of the light output at the middle of the crystal ( $X_{mid}$ ). A small  $\delta$  of less than 5% is required for scintillation crystals to be used in HEP calorimeters. The large negative  $\delta$  values of -44.2% and -28.7% are caused by its poor optical quality shown in Fig. 6. In addition, a slightly tapered shape of the sample also leads to a focusing effect, which would increase the negative  $\delta$  value for the seed end coupling. R&D is underway to improve optical quality of long crystals so that the light response uniformity of Y doped BaF<sub>2</sub> crystal would be improved.

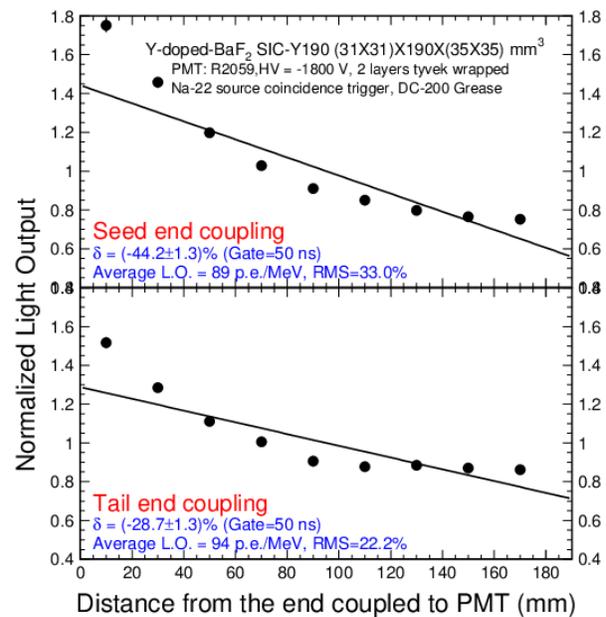


Fig. 7. Light response uniformity of 190mm-long Y doped BaF<sub>2</sub> crystal with 50 ns readout gate.

#### IV. CONCLUSIONS

BaF<sub>2</sub> crystals of small size without and with 1 at% yttrium doping were successfully grown in SIC, and show good optical quality. Characterization on their optical and scintillation properties show that 1 at% yttrium doping suppresses the slow component by about a factor of 6 while the intensity of the fast component is not affected. This indicates that yttrium's doping has a great potential in suppressing the slow component in BaF<sub>2</sub> crystal. A 190 mm long yttrium doped BaF<sub>2</sub> crystal was grown with poor optical quality. R&D is underway at SIC to further optimize crystal growth parameters and doping concentration, so that BaF<sub>2</sub> crystals of high quality will be developed for applications in future HEP experiments and GHz hard X-ray imaging.

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