Slow Scintillation Suppression in Yttrium Doped BaF_2 Crystals

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***Abstract*— Barium fluoride (BaF_2) crystal has a fast scintillation light peaked at 195 and 220 nm with a sub-ns decay time. This ultrafast scintillation promises a wide application in an area where extreme fast timing is important, such as future high-energy physics experiments, gigahertz hard X-ray imaging, and time-of-flight positron emission tomography. BaF_2 crystal, however, has also a slow scintillation component peaked at 310 nm with a decay time of about 600 ns, which causes pileup. Suppression of the slow scintillation component by selective doping, such as Ce, La, Tm, and Y, was discussed 20 years ago. In this paper, we report suppression of the slow component in BaF_2 crystals by yttrium doping. Single crystals with 1 at% Y doping were grown by vacuum Bridgman technique at the Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China. 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_2 crystals by a factor of 6, while the fast component remains unaffected.**

***Index Terms*— Barium fluoride, scintillation crystals, slow component, Y^{3+} doping.**

I. Introduction

BARIUM fluoride (BaF_2) 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_2 crystal are 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 five time of the fast component, which would cause pileup. 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 Makhov [3], and has 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 [8].

The slow scintillation component in BaF_2 is believed due to relaxation of self-trapped excitons [9], which is sensitive to temperature. The light output (LO) 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_2: 1) by selective readout with either an bandpass filter or solar-blind photodetector and 2) slow component suppression by rare-earth (RE) doping in BaF_2, such as Ce, La, Tm, and Y [5], [9], [11]–[19]. Our previous study [20] shows that a 20-cm-long La/Ce co-doped BaF_2 crystal grown in the Beijing Glass Research Institute (BGRI) increases the F/S ratio from 1/5 to 1/1, which is similar to what achieved 20 years ago.

RE^{3+} doping in BaF_2 for suppression of the slow component was investigated extensively 20 years ago. While, most efforts were in La doping, Y^{3+} doping was reported by Sobolev *et al.* [18] in 1994 for BaF_2 powders, where the F/S ratio was reported to be increased by a factor of 30 with 10 at% Y^{3+} doping. 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 $Ba_{0.9}Y_{0.1}F_{2.1}$ powders to undoped BaF_2 powders. Internal absorption in the crystal bulk thus is not taken into account.

As a dopant, YF_3 has many advantages as compared with LaF_3. First, the melting point of YF_3, 1387 °C, is very close to that of BaF_2, 1368 °C; thus, it is favorable for crystal growth. Second, YF_3 has a density of 4.01 g/cm^3, compared with that of LaF_3, 5.90 g/cm^3; it is 47.1% lower leading to a potentially low cost for mass production of doped BaF_2 crystals with equal molar doping concentration. The last, but not the least, YF_3 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_2 crystals doped with Y^{3+}. BaF_2 crystals with 1 at% Y doping were grown at the Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences, Shanghai, China. Their optical and scintillation properties, such as radioluminescence, optical transmittance, LO, fast/slow ratio, scintillation decay kinetics, and light response uniformity (LRU), were measured in the Caltech HEP Crystal Laboratory. Section II describes the sample preparation and characterization. Sections III presents the

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TABLE I
SAMPLES AND MEASUREMENTS

Sample ID	Sample Dimensions	Y^{3+} Doping Concentration	Measurements
SIC-UA1	10 mm × 10 mm × 2 mm	0	*XEL*[a]
SIC-YA1	10 mm × 10 mm × 2 mm	1at%	*XEL*
SIC-U01	30 mm × 30 mm × 20 mm	0	*LT*[b], *LO*[c]
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	31^2 mm × 190 mm × 35^2 mm	1at%	*LT, LRU*[d]

[a]*XEL X-ray excited luminescence;* [b]*LT, longitudinal transmittance;* [c]*LO, light output;* [d]*LRU, light response uniformity.*

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

II. Sample Preparation and Measurement

BaF_2 crystals with 1 at% Y doping were grown by vacuum Bridgman technique at SIC. Raw materials, BaF_2 (5N) and YF_3 (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_2 powder with 4N purity was added into the BaF_2/YF_3 mixture as a scavenger to remove contaminations of O^{2-} 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 $10 \times 10 \times 2$ mm^3 with two 10×10 mm^2 faces polished. Samples of $30 \times 30 \times 20$ mm^3 (SIC-U01, SIC-Y2A, SIC-Y3A, SIC-Y4A) used for longitudinal transmittance (LT), LO, and decay kinetics measurements were cut from undoped and 1at% Y doped BaF_2 ingots, respectively. A long Y doped BaF_2 sample (SIC-Y190) of $31^2 \times 190 \times 35^2$ mm^3 was used for the LT and LRU measurements.

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 photomultiplier (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%.

LO measurement is described in detail in [12] and [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 ^{22}Na source with a coincidence trigger. A multichannel analyzer (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 11 integration gates, from 50 to 3000 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%.

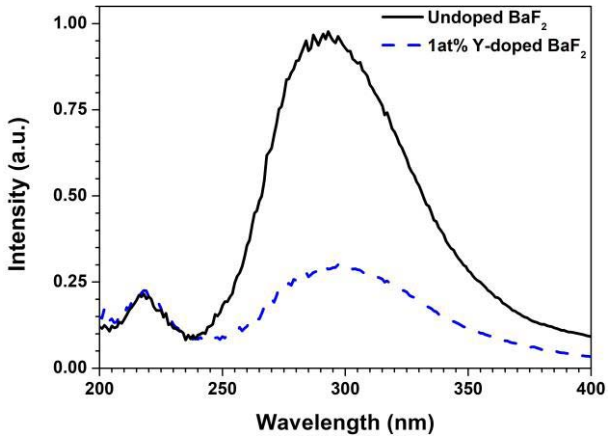

Fig. 1. XEL spectra of undoped BaF_2 crystal (black solid line) and 1 at% Y doped BaF_2 crystal (blue dashed line).

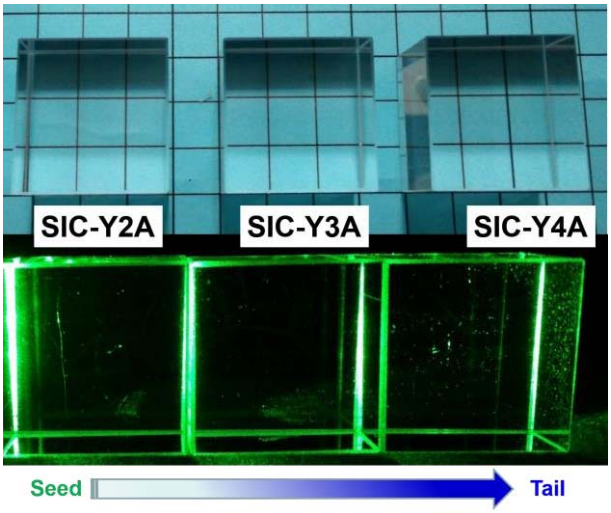

Fig. 2. Photographs show three 1 at% Y doped BaF_2 crystal samples cut from one ingot. The top photograph was taken under natural light, while the bottom one was taken under illumination of a 523-nm green laser.

III. Results and Discussion

Fig. 1 shows a comparison of the XEL spectra for undoped (black solid line) and 1 at% Y doped (blue dashed line) BaF_2 crystals. Compared to the undoped BaF_2, 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_2 crystals [12], [22].

Fig. 2 shows a photograph of three BaF_2 samples, SIC-Y2A, SIC-Y3A, and SIC-Y4A cut from a BaF_2 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 photograph was taken under natural light, showing no apparent scatters.

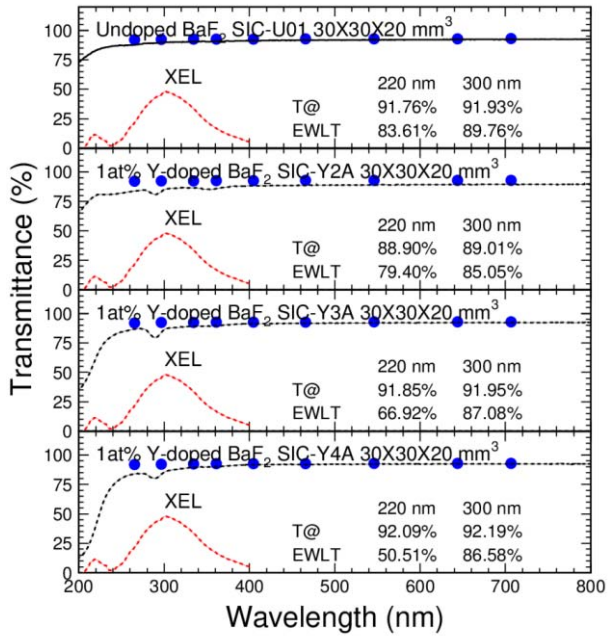

Fig. 3. Optical transmittance and EWLT of undoped and Y doped BaF_2 crystals.

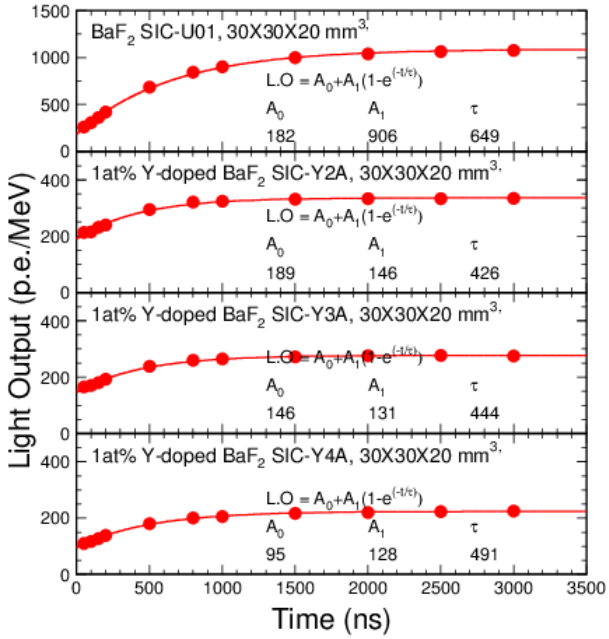

Fig. 4. Light output measured is shown as a function of integration time for undoped and three Y doped BaF_2 crystals.

The bottom photograph 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. Fig.3 also shows the theoretical limit calculated by using the refractive index data of BaF_2 [23] and the emission weighted LT (EWLT) for the fast and slow components, which is defined as [24]

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

where $\mathrm{LT}(\lambda)$ and $\mathrm{Em}(\lambda)$ are LT and emission at wavelength (λ).

The measured optical transmittance from 320 to 800 nm of all the four 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_2 crystals of high optical quality.

The EWLT values of the fast component for BaF_2 crystal sample is in the order as follows: $\mathrm{EWLT}_{\mathrm{SIC-U01}} > \mathrm{EWLT}_{\mathrm{SIC-Y2A}} > \mathrm{EWLT}_{\mathrm{SIC-Y3A}} > \mathrm{EWLT}_{\mathrm{SIC-Y4A}}$, indicating a poor transparency for the fast component in these BaF_2 samples developed at an early stage.

Fig. 4 shows the LO as a function of the integration time for these four BaF_2 samples, and the corresponding fit with an exponential decay constant τ_s for the slow component

$$\mathrm{LO}(t) = F + S\left(1 - e_s^{-t/\tau}\right) \tag{2}$$

where F is the fast component and S is the slow component. The numerical values of the fit are presented in Fig. 4 and summarized in Table II together with the measured LO. Significant reduction of the slow component is observed in both

TABLE II
SUMMARY OF LIGHT OUTPUT OF UNDOPED Y DOPED AND BaF_2 CRYSTALS

ID	*LO* of fast (p.e./MeV)	*LO* of slow (p.e./MeV)	F/S[a] 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

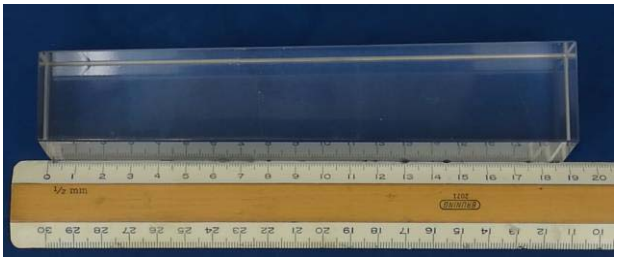

Fig. 5. 190-mm-long BaF_2 crystal with 1 at% Y doping.

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. 5 shows a long BaF_2 crystal of $31^2 \times 190 \times 35^2$ mm^3 with 1 at% Y doping. Its longitudinal and transverse transmittance with a light path of 190 and 31–35 mm, respectively, are shown in Fig. 6. The small end with a 31^2 mm^2 cross section

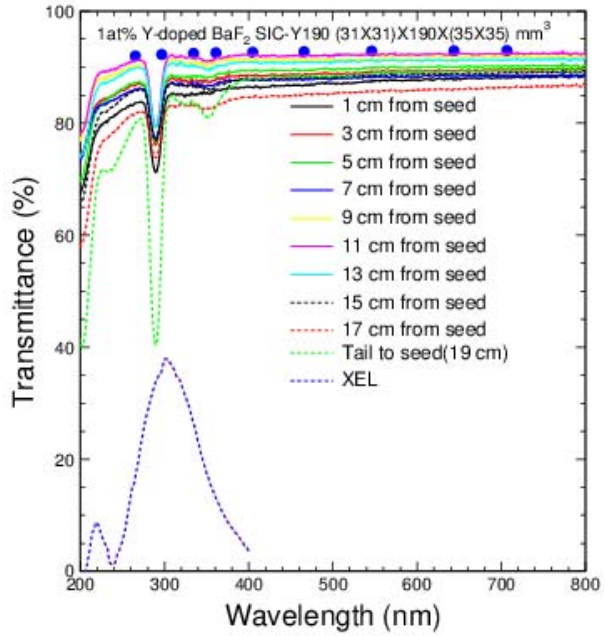

Fig. 6. Longitudinal and transverse transmittance of a 190-mm long Y doped BaF_2 crystal.

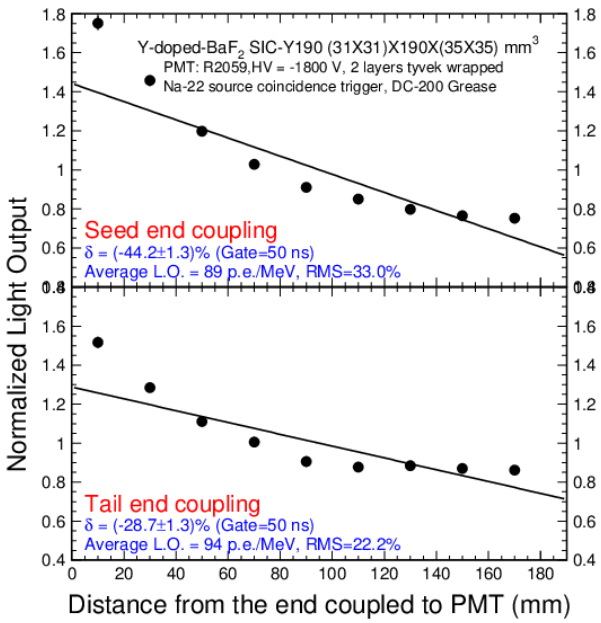

Fig. 7. Light response uniformity of 190-mm-long Y doped BaF_2 crystal with 50-ns readout gate.

is the seed end, while the large end with a 35^2 mm^2 cross section is the tail end.

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_3 with 99.999% purity is used as the dopant so the Ce^{3+} concentration is very low, which is confirmed by no intrinsic Ce^{3+} photoluminescence 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. 7 shows the LO of 50-ns gate as a function of distance to PMT for this 190-mm-long Y doped BaF_2 crystal with the seed (top) and tail (bottom) end coupled to the R2059 PMT. The LOs were measured by injecting collimated γ-rays from a ^{22}Na source along the long crystal with a coincidence trigger. The LRU is parameterized as δ by a linear fit as follows:

$$\frac{\mathrm{LO}}{\mathrm{LO}_{\mathrm{mid}}} = 1 + \delta\left(\frac{X}{X_{\mathrm{mid}}} - 1\right) \tag{3}$$

where $\mathrm{LO}_{\mathrm{mid}}$ is the fit value of the LO at the middle of the crystal (X_{mid}). A small δ of less than 5% is required for scintillation crystals to be used in HEP calorimeters. The large negative δ 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 δ value for the seed end coupling. Research and development is underway to improve optical quality of long crystals so that the LRU of Y doped BaF_2 crystal would be improved.

IV. Conclusion

BaF_2 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 shows 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_2 crystal. A 190-mm-long yttrium doped BaF_2 crystal was grown with poor optical quality. Research and development is underway at SIC to further optimize crystal growth parameters and doping concentration, so that BaF_2 crystals of high quality will be developed for applications in the future HEP experiments and GHz hard X-ray imaging.

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