

# Fluorescence Properties of $\text{Ce}^{3+}$ -Doped $\text{BaF}_2$

Xu Zizong, Gong Zhufang, Chang Jin, Shi Chaoshu, Shen Dingzhong,<sup>1</sup>  
Yuan Xianglong<sup>1</sup> and Yin Zhiwen<sup>1</sup>

(Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui, China)

<sup>1</sup>(Shanghai Institute of Ceramics, Shanghai, China)

The spectra and the decay times of a series of  $\text{Ce}^{3+}$ -doped  $\text{BaF}_2$  crystals have been measured. The results demonstrate that a  $\text{BaF}_2$  with a proper amount of  $\text{Ce}^{3+}$  doped have outstanding advantages: the emission spectra shift from UV band towards blue band, a near blue fluorescence with quite fast decay time (80 ns) replaces the slow component ( $\sim 600$  ns) and very fast one ( $\sim 0.8$  ns) of undoped  $\text{BaF}_2$ . The intensity of the new component is comparable with the sum of the odd ones.

---

## 1. INTRODUCTION

$\text{BaF}_2$  crystal, the fastest scintillator known today, is a new kind of the inorganic scintillator developed recently. Its fast emission component with decay time  $\tau \sim 0.8$  ns centers at around 195 nm and 220 nm, and the slow one with decay time  $\tau \sim 600$  ns has a wider band, peaking at around 310 nm [1]. The pulse formed by the fast component can be used for accurate time measurement to increase the measurement precision. Comparing to  $\text{NaI(Tl)}$   $\text{BaF}_2$  has many advantages, such as high density (4.83 g/cm<sup>3</sup>), high stopping capability (the radiation length  $x \sim 2.05$  cm) and non-deliquescence. The fluorescence transfer from  $\text{BaF}_2$  crystal to photocathode of PM is easier as compared with BGO because the refractive index of  $\text{BaF}_2$  is close to the one of glass. The disadvantages of  $\text{BaF}_2$  are: the stronger slow component (about 5 times the fast one) will cause the long dead time of the output system for high counting rate, the quite expensive UV photomultiplier must

---

Supported by the National Natural Science Foundation of China.

Received on November 19, 1991.

© 1993 by Allerton Press, Inc. Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by Allerton Press, Inc. for libraries and other users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of \$50.00 per copy is paid directly to CCC, 27 Congress St., Salem, MA 01970.

**Table 1**  
A series of BaF<sub>2</sub> crystals.

Crystal	B0	B1	B2	B3	B4	B5	B6	B7
Ce <sup>+3</sup> concentration (mol%)	0	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	0.1	1	5	10
Size ( $\phi \times h$ ) (mm $\times$ mm)	23 $\times$ 26	25 $\times$ 14	25 $\times$ 18	23 $\times$ 27	23 $\times$ 22	25 $\times$ 23	25 $\times$ 15	25 $\times$ 21

**Table 2**  
The time properties of the fluorescence of a series of BaF<sub>2</sub>.

Sample	B0	B1	B2	B3	B4	B5	B6	B7
$t_1$ (ps)	815	788	776	785	838	—	—	—
Error	$\pm 15$	$\pm 33$	$\pm 25$	$\pm 37$	$\pm 145$	—	—	—
$I_1$ (%)	7.5	9.8	8.1	2.3	0.6	—	—	—
$t_2$ (ns)	-	46	50	42	58	80	56	44
Error	-	$\pm 5$	$\pm 8$	$\pm 4$	$\pm 10$	$\pm 15$	$\pm 1$	$\pm 4$
$I_2$ (%)	-	4.5	7.2	10	34.1	100	100	100
$t_3$ (ns)	604	680	640	520	640	—	—	—
Error	$\pm 100$	$\pm 40$	$\pm 40$	$\pm 40$	$\pm 40$	—	—	—
$I_3$ (%)	92.5	85.7	84.7	87.7	65.3	—	—	—

be used to readout the far UV fast component. Its lower fluorescence yield will be compensated by the large amount deposited energy of high energy particles. In order to suppress the slow component and move the UV fluorescence to the long wavelength, we try to dope some kind of rare-earth elements in the pure BaF<sub>2</sub> crystals to improve its properties.

For this purpose, the fluorescence properties of a series of BaF<sub>2</sub> samples doped with cerium have been investigated.

## 2. Experimental Equipment

The samples of Ce-doped and undoped BaF<sub>2</sub> crystals grown in Shanghai Institute of Ceramics using the method of descending crucible are listed in Table 1. Both the top and the bottom surfaces of the cylindrical samples are polished optically. The optical transmission curves of the samples are measured by means of a UV-visible recording spectrophotometer UV-240. The emission spectra of the samples excited by the X-ray, which are produced with a 35 keV electron beam hitting a Cu-target, are obtained using the monochromator WDG05 (made in Suzhou). The decay time of the single crystal is determined with a time spectrometer shown in Fig. 1. The crystal coupled onto the photomultiplier PM1(XP2020Q) with the grease DC3076 which is transparent to UV. The PM2(XP2020Q) with a diaphragm of 8 mm diameter to limit the luminous flux is situated 10 cm from the top surface of crystal. The signals from both PM1 and PM2, amplified by an ORTEC-574 amplifiers and then passed through the constant fraction discriminators (CFD), act as the start signals and stop signals of the TAC respectively. The time distribution curve of the system is measured in such a way that the Cherenkov lights yielded by the  $\beta$ -particles from <sup>90</sup>Sr source passing through lucite slice were coupled to both PMs

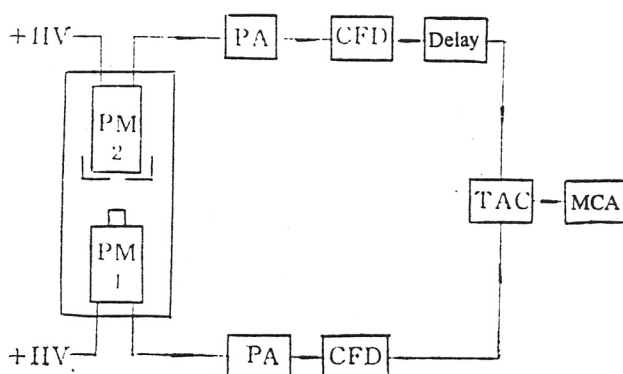


Fig. 1

The sketch of a time spectrometer.

simultaneously. The time resolution curve is shown in Fig. 2(a). Using  $^{137}\text{Cs}$  (662 keV)  $\gamma$ -ray irradiate on the samples, the pulse height spectra from PM1 and PM2 are shown in Fig. 2(b) and (c) respectively. Figure 2(c) also shows a noise spectrum with a tail produced by the single photon emitted by thermal electron of PM without  $^{137}\text{Cs}$  source on. With the source on, the counts of the single photon spectrum increase obviously. It demonstrates that PM2 is basically sensitive to the single photon. Figure 2(b), a typical  $^{137}\text{Cs}$  spectrum, indicates that the PM1 records most of fluorescence excited by  $^{137}\text{Cs}$   $\gamma$ -rays. It can be considered that the timer signal given by PM1 is determined by the weight center of the pulses caused by the fast fluorescence and using this signal as the reference time is appropriate. The time distribution curve measured with this system is the decay curve of the crystal fluorescence.

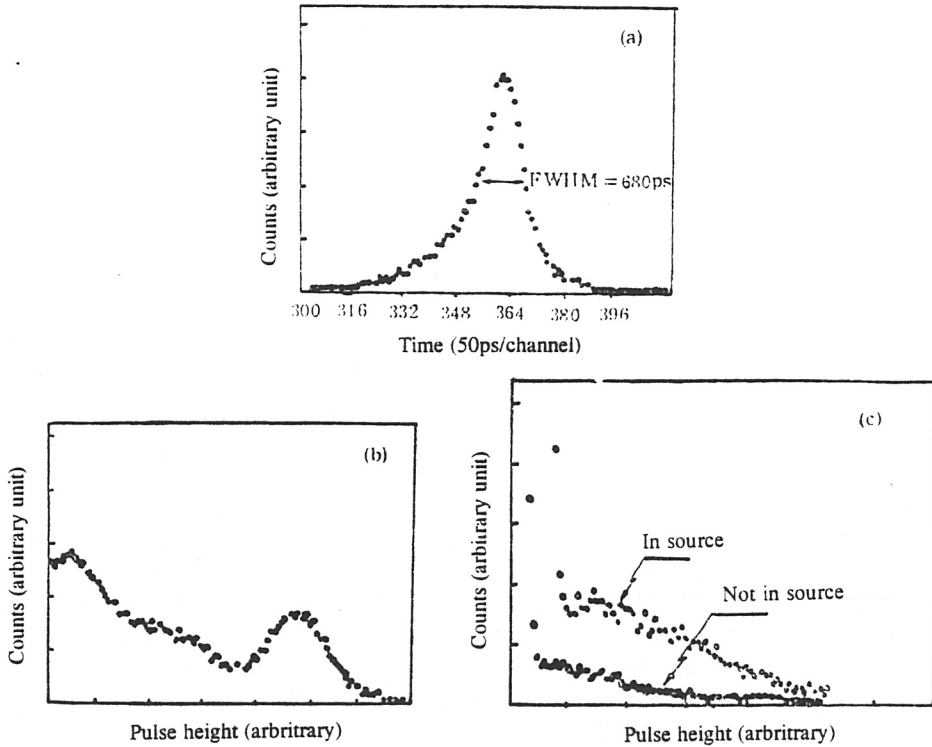
### 3. RESULTS AND DISCUSSION

#### 3.1 Transmission Curves

The transmission curves of samples with various amounts of doped  $\text{Ce}^{3+}$  are shown in Fig. 3. For the doped samples the absorption valley appears around 290 nm. With increase of  $\text{Ce}^{3+}$  concentration, the valley is deepened and expanded towards both shorter and longer wavelength sides. Only a weak component around 260 nm in the far-UV region survived when the  $\text{Ce}^{3+}$  concentration is up to 0.1 mol%. The UV component shorter than about 330 nm is completely absorbed for the samples with  $\text{Ce}^{3+}$  concentration not less than 1 mol%. According to the excitation spectra of these samples [2] the behavior of transmission curves described above could be explained by means of the absorption process between 4f-5d energy levels of  $\text{Ce}^{3+}$  ions [3].

#### 3.2 Emission Fluorescence Spectra Excited by X-Ray

The emission fluorescence spectra excited by X-rays for the samples with different  $\text{Ce}^{3+}$  concentration are shown in Fig. 4. For the undoped  $\text{BaF}_2$  crystal there are two emission band around 220 nm and 323 nm. With increase of the  $\text{Ce}^{3+}$  concentration, some new structures near the short wavelength side of 323 nm band appear. The 220 nm band seems to have no significant change up to 0.01 mol% doped  $\text{Ce}^{3+}$ . For the samples doped with more than 0.01 mol%  $\text{Ce}^{3+}$  concentration, the 220 nm band completely disappears and the structures near the short wavelength side of 330 nm band disappear gradually and the emission band moves to the longer wavelength side obviously. The



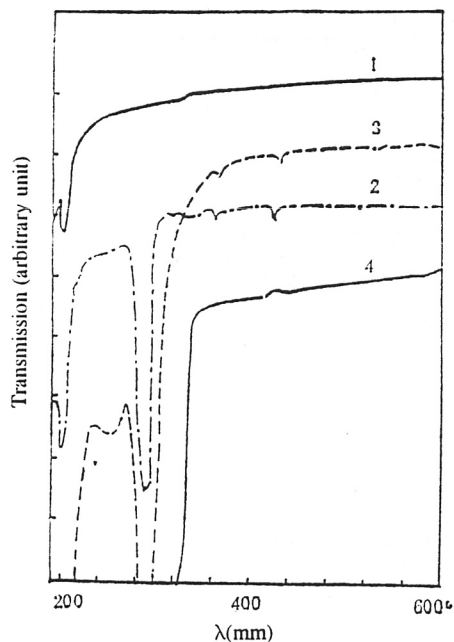
**Fig. 2**  
The characters of the time spectrometer.

(a) Time resolution curve; (b) The pulse height spectrum of PM1 receiving the fluorescence excited by  $^{137}\text{Cs}$   $\gamma$ -rays; (c) The pulse height spectrum of PM2 receiving the single photon spectra from emission of thermal electron and excited by  $^{137}\text{Cs}$ .

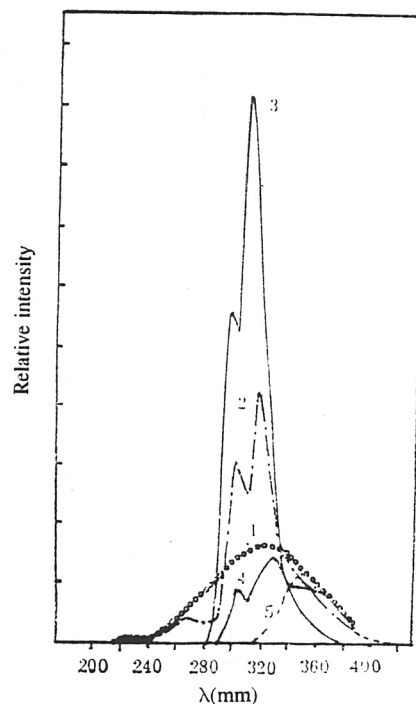
emission spectrum comes to a band centered at 353 nm when the  $\text{Ce}^{3+}$  concentration reaches 5 mol%. These changes of the structures of the emission spectra with  $\text{Ce}^{3+}$  concentration are caused by the absorption and emission of  $4f \leftrightarrow 5d$  energy levels of  $\text{Ce}^{3+}$  ions. The shift of the absorption and emission spectra to the longer wavelength could be explained by the following: when the  $\text{Ce}^{3+}$  concentration is higher their interactions cause the decrease of the energy of 5d state. The total fluorescence yields of the crystals doped with different amount  $\text{Ce}^{3+}$  concentration are expressed approximately by the areas under the spectra curves. Figure 5 indicates the change of the total fluorescence yield with the concentration of  $\text{Ce}^{3+}$  ions. The total fluorescence yield of  $\text{BaF}_2$  doped with 0.1 mol%  $\text{Ce}^{3+}$  concentration is about 2 times of the undoped one.

### 3.3 Decay Time of Fluorescence

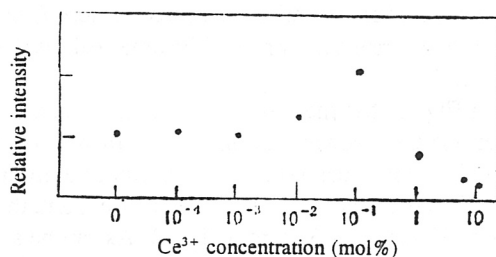
The time properties of the fluorescence pulse (read-out from the anode of the photomultiplier) produced by  $^{137}\text{Cs}$   $\gamma$ -rays irradiating the crystal are studied with a pulse digitized meter F903 [4] with sampling frequency of 100 MHz. It is clearly shown in Fig. 6 that undoped  $\text{BaF}_2$  has a fast component and a slower component, and a new moderate fast component is dominant for the  $\text{Ce}^{3+}$  doped crystal.

**Fig. 3**

The transmission curves of the samples. 1. Undoped crystal; 2. 0.001 mol%  $\text{Ce}^{3+}$ ; 3. 0.001 mol%  $\text{Ce}^{3+}$ ; 4. 1 mol%  $\text{Ce}^{3+}$ . The absolute values of the transmissions for different samples are relevant to the sizes and surface treatment of the crystals.

**Fig. 4**

The emission spectra of  $\text{BaF}_2$  excited by X rays. 1. Undoped crystal; 2. 0.01 mol%  $\text{Ce}^{3+}$ ; 3. 0.1 mol%  $\text{Ce}^{3+}$ ; 4. 1 mol%  $\text{Ce}^{3+}$ ; 5. 5 mol%  $\text{Ce}^{3+}$ .

**Fig. 5**

The total relative fluorescence yields of the different samples doped with  $\text{Ce}^{3+}$ .

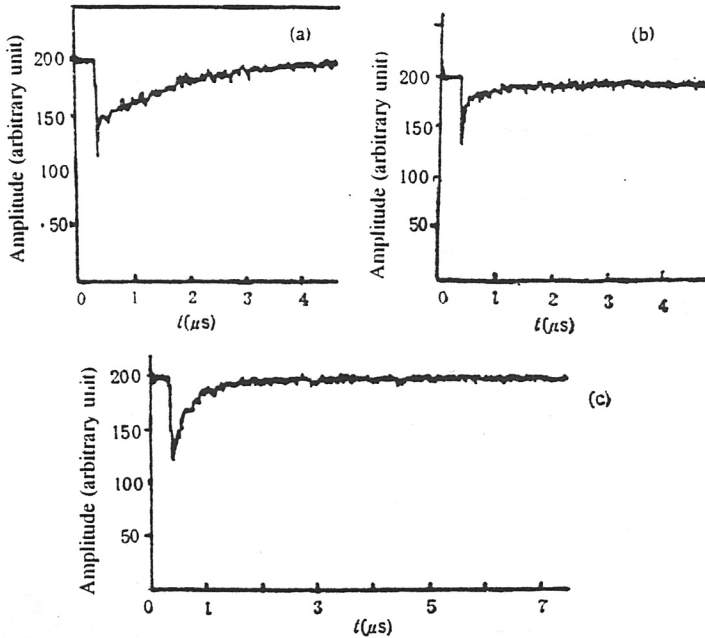


Fig. 6

The pulse shape of fluorescence output.

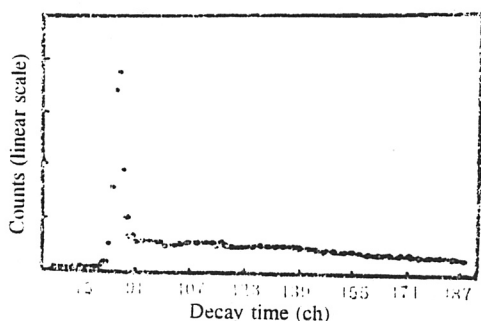
(a) Undoped  $\text{BaF}_2$ ; (b) 0.01 mol %  $\text{Ce}^{3+}$ ; (c) 1 mol %  $\text{Ce}^{3+}$ .

The quantitative results of the decay time are measured with the system shown in Fig. 1. The recorded time distribution of the fluorescence are shown in Figs. 7 and 8. The experimental curve of the time distribution is read point by point using the POSITRON·FIT program and then fitted by means of multiexponential function according to the resolution of the time spectrometer given in Fig. 2. The fitting formula is

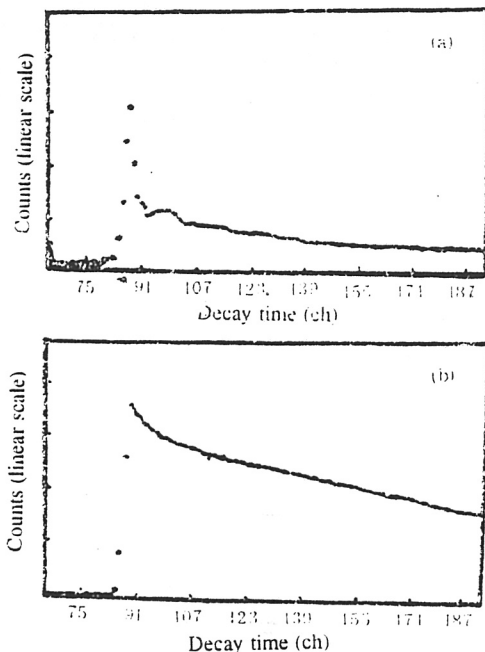
$$F(t) = \sum_{i=1}^n I_i e^{-t/t_i}$$

The fitting confidence level and the error of the parameters are in reasonable region through selecting the appropriate  $n$  (the number of exponential functions), where  $I_i$  and  $t_i$  are the relative intensity and the time constant of  $i$ -th fluorescence component. The obtained results of a series of samples are shown in Table 2 after for  $n = 2, 3$ .

It can be seen from Fig. 5 that the lower  $\text{Ce}^{3+}$  concentration has no significant effect on total fluorescence yield. When the  $\text{Ce}^{3+}$  concentration is more than 0.01 mol % the total fluorescence yield increase with increasing  $\text{Ce}^{3+}$  concentration. The total output of fluorescence of the sample with  $\text{Ce}^{3+}$  concentration 0.1 mol % (B4) is about twice the undoped one, and the spectral components centralize at two bands with peaks at 305 nm and 322 nm (Fig. 4). As can be seen in Table 2, in the total output of fluorescence of B4, the contribution from  $\text{Ce}^{3+}$  ions (305 nm, 322 nm,  $\tau \sim 58$  ns) take 34 % weight, and the one from the  $\text{BaF}_2$  intrinsic slow component (322 nm,  $\tau \sim 640$  ns) take 65 %, the intrinsic fast component almost disappears. The data in Table 2 also indicates, as the  $\text{Ce}^{3+}$  ions increase the contribution of its intrinsic component to the total output of fluorescence increase gradually. When the  $\text{Ce}^{3+}$  concentration is above 1.0 mol %, the intrinsic fast component of  $\text{BaF}_2$  fluorescence is absorbed



**Fig. 7**  
The time distribution of fluorescence of undoped  $\text{BaF}_2$  (1170 ps/channel).



**Fig. 8**  
The time distribution of fluorescence of  $\text{BaF}_2$  doped with  $\text{Ce}^{3+}$  (1170 ps/channel). (a) 0.01 mol%  $\text{Ce}^{3+}$ ; (b) 5 mol%  $\text{Ce}^{3+}$ .

or quenched, the slow component disappears completely, and the fluorescence of  $\text{Ce}^{3+}$  ions becomes dominant. As the  $\text{Ce}^{3+}$  concentration is higher than 0.1 mol% the total fluorescence yield starts to decrease with  $\text{Ce}^{3+}$  concentration increase.

#### 4. CONCLUSIONS

The  $\text{BaF}_2$  crystal doped with appropriate quantity  $\text{Ce}^{3+}$  (for example 1 mol%) is a new kind of scintillation crystal with improved quality. It keeps the advantages of high stop capability and non-deliqescence of the pure  $\text{BaF}_2$  crystal. The new moderate fast component ( $\tau \sim 40\text{--}80$  ns, 300–370 nm) of the new crystal replace the intrinsic components of pure  $\text{BaF}_2$ . The new crystal does not have the weaknesses of the long dead time caused by the slow component and does not need UV photomultiplier.

Compare to the  $\text{NaI(Tl)}$  and  $\text{BGO}$  the new crystal have better time property. It can be used widely in the time measurement with high counting rate.

#### ACKNOWLEDGEMENTS

We are much indebted to Prof. Song Zitai, Mr. Dong Yi and Mr. Tang Yewei for their help in data acquisition and analysis, and to Ms. Wang Congrong for drawing important figures.

## REFERENCES

- [1] P. Schotanus *et al.*, *Nucl. Instr. Meth.*, **A259** (1987), p. 581.
- [2] Dong Yi, Report on "WORKSHOP BaF<sub>2</sub> CALORIMETER", Shanghai, May 1991.
- [3] R. Visser *et al.*, *IEEE* **Ns38** (1991), p. 178.
- [4] Zhu Minghua and Wang Yanfang, *Appliance of High Speed Digitizer in High Energy Physics*, Lanzhou, August 1990.