Nuclear Instruments and Methods in Physics Research B61 (1991) 61–66
North-Holland

Light yield and surface treatment of barium fluoride crystals *

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Received 17 September 1990 and in revised form 15 February 1991

We report on a study of the light yield and surface treatment of barium fluoride (BaF_2) scintillation crystals. Using a bialkali photocathode the photoelectron (p.e.) yield of BaF_2 crystals was measured to be 130 p.e./MeV for the fast components and 700 p.e./MeV for the slow component. A somewhat hygroscopic nature for the BaF_2 is found. Teflon film was found to be the best wrapping material for the BaF_2 crystals. The radiation damage of the BaF_2 crystals can be fully annealed under 500 °C for 3 hours.

1. Introduction

Barium fluoride (BaF_2) is a unique high density inorganic scintillator with three emission spectra peaks at 195 nm, 220 nm and 310 nm, with decay time constants of 0.87, 0.88 and 600 ns respectively [1]. Because of the high speed of the fast component and the evidence of high radiation resistance [2], BaF_2 has gained widespread interest in recent years [3–5].

Previous measurements show that the total light output of BaF_2 is one fifth that of Na(Tl) [1]. The intensity ratio of the fast components to the slow component has been measured to be about 1 : 5 [1]. An improvement of the fast to slow ratio may be obtained by using lanthanum doping [6,7].

Fig. 1 shows the emission spectra of pure BaF_2 and BaF_2 doped with 1% lanthanum. The peak intensity of the slow component is reduced by a factor of about 5 with a little change in the fast components. It is also known that the intensity of the fast components have no temperature dependence, while the slow component increases with decreasing temperature, at a rate of $-2.4\%/°C$ [8].

Since the fast components and the slow component of BaF_2 are at different wavelengths, they are spectroscopically separable. Fig. 1 also shows the quantum efficiencies of two photomultipliers (PMTs): a special UV-sensitive, solar-blind PMT with a cesium telluride (Cs–Te) photocathode and a synthetic silica (quartz) window (Hamamatsu R3197), which has a quantum efficiency of 12% around 220 nm, and a PMT with a bialkali photocathode and a quartz window (Hamamatsu R2059), which has a quantum efficiency of about

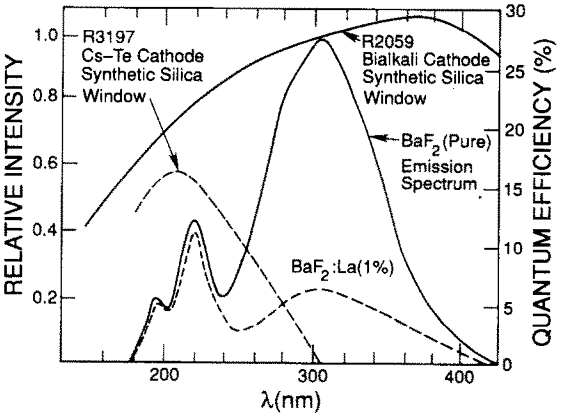

Fig. 1. BaF_2 scintillation spectra and PMT quantum efficiencies.

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* Work supported in part by US Department of Energy Contracts No. DE-AC03-81-ER40050.

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18% around 220 nm. By using the solar-blind photocathode (Cs ~ Te), one would be able to collect mainly the fast scintillation light.

In this report, we present results of a study on the light yield, and the influence of surface treatment, for BaF_2 crystals. BaF_2 samples were obtained from Harshaw (USA), OKEN (Ohyo-Koken in Japan), Merck (E. Merck Darmstadt in Germany), Harshaw (Holland), Beijing Glass Research Institute (BGRI) and Shanghai Institute of Ceramics (SIC). Section 2 of this report describes the sample preparation. The experiment and the result are reported in section 3. Section 4 gives a summary of the conclusions.

2. Sample preparation

Samples from Harshaw (USA), OKEN, Merck, Harshaw (Holland), BGRI and SIC are named after their manufacturer. The sample Merck (La) is a crystal doped with 1% lanthanum provided by the Merck company. All others are undoped crystals.

All samples, except those specified, have a standard shape, i.e. a cylinder of length 1 in. and diameter 1 in. The crystal SIC has a square cross section of 1.7 × 1.7 cm^2 and a length of 1.9 cm. The crystal Harshaw (Holland) has a square cross section of 2 × 2 cm^2 and a length of 5 cm. In addition, more samples with a standard shape were provided by SIC. They were called SH01, SH02 and SH03 respectively. All samples were polished before the measurements according to a procedure described in section 3.4.

3. Experimental results

3.1. Transmission spectrum measurement

A Hewlett Packard 8452A diode array spectrophotometer was used to measure the transmission spectrum of BaF_2 samples. This spectrophotometer has a wavelength coverage down to 190 nm. No corrections were made to the transmission spectra obtained. Since most samples are of standard length, i.e. 2.54 cm, the transmission spectra obtained are directly comparable.

Fig. 2 shows the measured transmittance curves for six BaF_2 crystals. Most crystals have very good transmittance down to 190 nm. The absorption peak at 205 nm in the Harshaw (USA) sample is attributed to Pb contamination [9].

3.2. Scintillation pulse

A Hewlett Packard 54111D digital scope was used to record the shape of the scintillation light pulse from BaF_2 crystals. Fig. 3 shows pictures of the scintillation light pulses from a pure BaF_2 crystal observed using a bialkali cathode (R2059), (a) and (d), and a Cs–Te cathode (R3197), (b) and (e). Also shown in the figure is the pulse from a BaF_2 crystal doped with 1% lanthanum observed by using a Cs–Te cathode, (c) and (f). The rise time of the scintillation light pulse in the picture was completely dominated by the 2.3 ns rise time of the PMTs. The full width at the half maximum (FWHM) of the fast scintillation light pulse is about 6 ns, which can be observed clearly in the figures with an expanded time scale, (a), (b) and (c).

The optical suppression factors for the slow component, defined as the photoelectron number of the fast components divided by the photoelectron number of

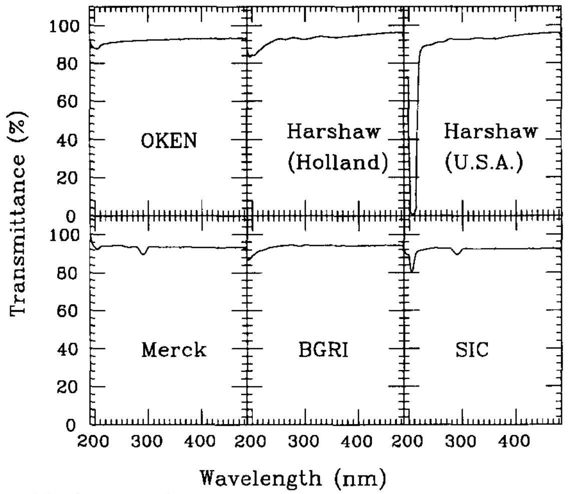

Fig. 2. Transmittance measurements for six BaF_2 crystals.

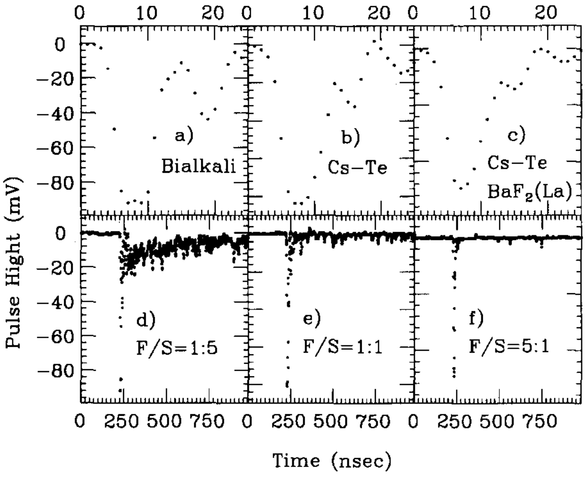

Fig. 3. Scintillation light pulse from a pure BaF_2 crystal observed using a bialkali cathode (a) and (d), a Cs–Te cathode (b) and (e), and from a La-doped BaF_2 crystal using a Cs–Te cathode (c) and (f).

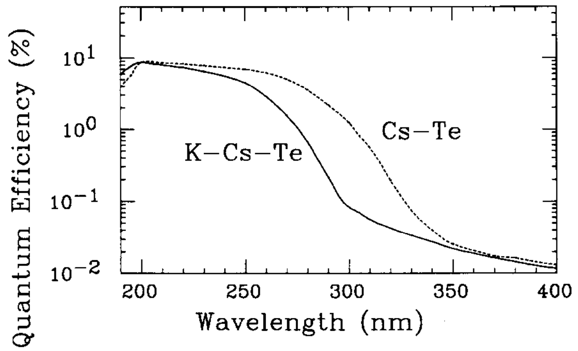

Fig. 4. Quantum efficiency of a Hamamatsu K–Cs–Te photocathode comparing with a conventional Cs–Te photocathode.

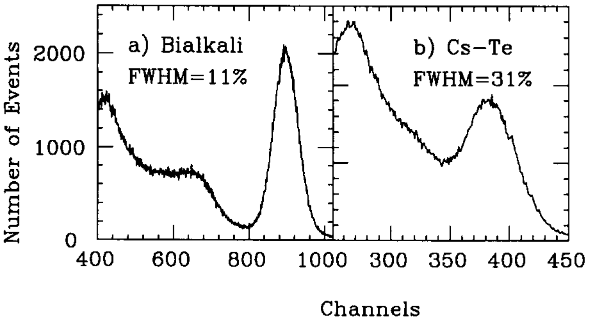

Fig. 5. A typical ^{137}Cs spectrum obtained from a BaF$_2$ crystal by using a bialkali photocathode (a) and a Cs–Te photocathode (b). The integration time is 2 μs.

the slow component (F/S), are also shown in the figure. (See section 3.3 for the definition of F and S.) With 1% lanthanum doping, a fast to slow ratio of 5 is obtained.

An additional optical suppression of the slow component can be achieved by using a new photocathode (K–Cs–Te) recently developed by the Hamamatsu corporation [11]. Fig. 4 shows a comparison of the quantum efficiency responses of this new solar-blind (K–Cs–Te) photocathode and a conventional solar-blind photocathode (Cs–Te). The K–Cs–Te photocathode has 10 times better suppression power in terms of QE(220 nm)/QE(310 nm), compared to the Cs–Te photocathode. It is thus expected that an $F/S = 10$ may be obtained by using this K–Cs–Te photocathode.

3.3. Light yield measurement

The scintillation light yield of BaF$_2$, in terms of photoelectron numbers per MeV of energy deposition, for a bialkali cathode (R2059) or a Cs–Te cathode (R3197) was measured by using a ^{137}Cs γ-ray source. While the bialkali cathode reads out both the fast and the slow components, the Cs–Te cathode reads mainly the fast components, as indicated in fig. 1. The BaF$_2$ crystals were wrapped with two layers of teflon tape as a UV reflector. The PMTs were coupled to the crystals with Dow Corning 200 fluid which has very good UV transmittance [5].

The scintillation light pulses collected by PMTs were integrated by a LeCroy 3001 QVT in the Q mode. A series of 10 integration gates, ranged from 55 to 2000 ns, was provided by a LeCroy 2323A programmable gate generator to measure the light yield as a function of integration time. Fig. 5 shows typical ^{137}Cs spectra obtained with R2059 and R3197 PMTs.

A Gaussian fit was carried out to determine the ADC channel numbers, corresponding to the ^{137}Cs peak, which was subsequently converted to photoelectron numbers by using a series of calibration functions for each integration gate. The calibration functions were obtained in a series of LED runs for each integration gate. In the LED run, the relative width of a Gaussian fit, σ/peak, was used to obtain the 1/(photoelectron number)$^{1/2}$. A slight nonlinearity was found in LED runs. The calibration function for each gate width thus has a form of

$$\text{photoelectron number} = a \times \text{ADC Channel} + b \times (\text{ADC Channel})^2$$

where b is of the order of 10^{-3} of a.

The photoelectron numbers measured can be converted to the photon yield of BaF$_2$ crystals, taking into account of quantum efficiency of the photocathode and the efficiency of light collection etc. To predict the performance of a precision electromagnetic calorimeter made by BaF$_2$ crystals, however, only the photoelectron statistics are important.

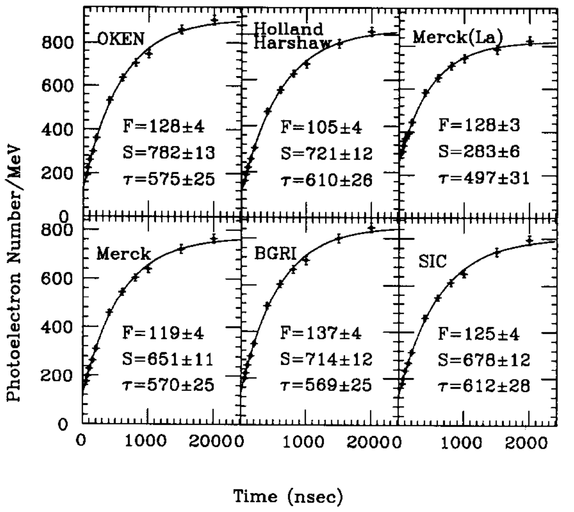

Fig. 6. Photoelectron yield for six BaF$_2$ crystals, measured with a bialkali photocathode (R2059 PMT), are shown as a function of the integration gate width.

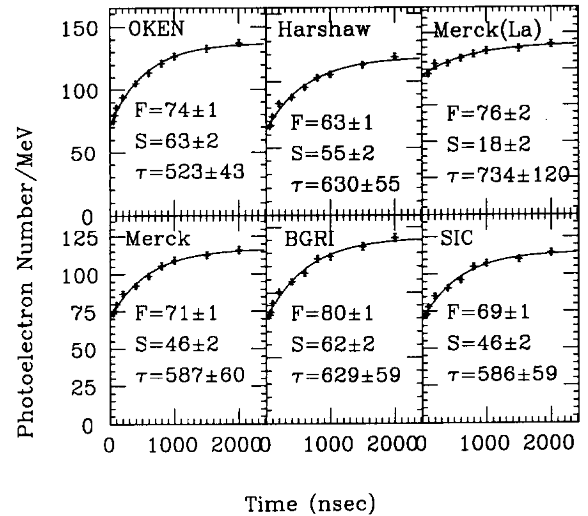

Fig. 7. Photoelectron yield for six BaF_2 crystals, measured with a Cs–Te photocathode (R3197 PMT), are shown as a function of the integration gate width.

3.3.1. Bialkali photocathode

Fig. 6 shows the measured photoelectron yield per MeV as a function of the integration time for six BaF_2 crystals measured with a bialkali photocathode (R2059 PMT). The data points in the figure were fitted to a sum of contributions from the fast components (F) and from the slow component (S) with an exponential decay constant τ:

$$y = F + S(1 - e^{-t/\tau}).$$

The numerical results of the fit are also shown in the figure. In summary, around 130 fast photoelectrons/MeV and 700 slow photoelectrons/MeV were observed. The fast component is about 16% of the total light observed.

3.3.2. Cs–Te photocathode

Fig. 7 shows a similar result for the same six BaF_2 samples measured using a solar blind Cs–Te photocathode (R3197 PMT). In summary, around 80 fast photoelectrons/MeV and $F/S \sim 1$ were observed for the Cs–Te cathode. The crystal doped with 1% of lanthanum has an $F/S \sim 5$ if a Cs–Te cathode is used. This photoelectron yield measurement with Cs–Te cathode is very promising in providing a very fast readout for a very high resolution electromagnetic calorimeter at the Superconducting Super Collider [5].

3.4. Surface treatment

The surface treatment and coating of the BaF_2 crystal are important to achieve high efficiency in the light collection. To obtain good light collection, a standard polishing technique was developed, which uses 0.3 μm alumina powder and alcohol to polish all surfaces of BaF_2 crystals. To test the hygroscopic nature of BaF_2 crystals a water treatment was carried out by immersing the sample in water for one day.

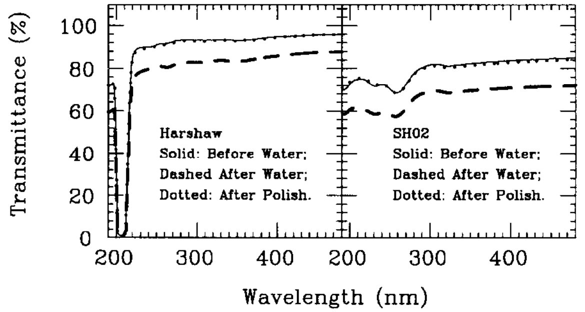

Fig. 8. Transmission spectra of BaF_2 crystals before and after surface treatment.

Fig. 8 shows the transmission spectra of samples Harshaw and SH02, measured before and after water treatment, and after final polishing. After water treatment, something blurred appeared on the surface of crystal, it could not be removed with acetone. After the polish process, however, the transmittance of crystal was recovered completely to the level before water treatment. This result indicates that the surface of a crystal will deteriorate when in contact with water or humid air, a consequence of the slightly hygroscopic nature of BaF_2. A similar observation was obtained by Anderson and Lamb [12].

Table 1 lists the light output of SIC samples SH01, SH02 and SH03 before and after surface treatment. The light output was expressed with photoelectron numbers per MeV for 55 ns and 2 μs gate width. The light output decreased after water treatment, and completely recovered after polishing. This result indicates that the light output depends on not only the transmission of bulk material, but also the surface quality of the crystal.

3.5. Wrapping

Four materials were selected as candidate coating materials for BaF_2 wrapping: white paper, aluminum

Table 1
BaF_2 light yield (p.e./MeV) before and after surface treatment

Crystal	Gate width	Before water	After water	After polishing
SH01	55 ns	76 ± 2	67 ± 2	78 ± 2
	2 μs	405 ± 8	368 ± 7	420 ± 9
SH02	55 ns	77 ± 2	74 ± 2	82 ± 3
	2 μs	398 ± 7	353 ± 7	405 ± 9
SH03	55 ns	87 ± 3	79 ± 3	92 ± 3
	2 μs	494 ± 10	390 ± 8	510 ± 10

Table 2
BaF$_2$ light yield (p.e./MeV) with different wrapping material

Crystal	Gate width	NE560	Paper	Al	Teflon
OKEN	55 ns		116± 3	137± 4	192± 6
	2 μs	170±3	513±10	608±12	904±18
Merck	55 ns		106± 3	137± 4	175± 5
	2 μs	157±3	432± 9	587±12	764±15

film, teflon film and the white paint NE560 from Nuclear Enterprise which has been used to paint the BGO crystals for the L3 experiment [10]. Table 2 lists the photoelectron yield obtained with these four wrapping materials. The NE560 white paint was found to be not suitable for BaF$_2$, presumably because of its absorption of the UV light. As seen from the table the best wrapping material is the teflon film. The teflon, however, is known to be sensitive to radiation. A further search will be carried out to look for good coating or wrapping materials for the BaF$_2$ to obtain a high light yield as well as good light uniformity of the crystal.

3.6. Annealing

BaF$_2$ is known to have very good radiation resistance [2]. Commercial available BaF$_2$ crystals, however, suffer radiation damage at different levels. Our research on radiation damage indicates that the BaF$_2$ radiation damage is not caused by an intrinsic color center in the bulk material of the crystal, such as O^{2-} vacancies in BGO, but rather by an externally introduced impurity [5]. By control the impurity level in BaF$_2$, one thus would be able to provide radiation hard crystal. The details of a radiation damage study of BaF$_2$ will be presented in a separate paper. We present here only the results for the thermal annealing which has been used to remove the radiation damage in BaF$_2$ crystals.

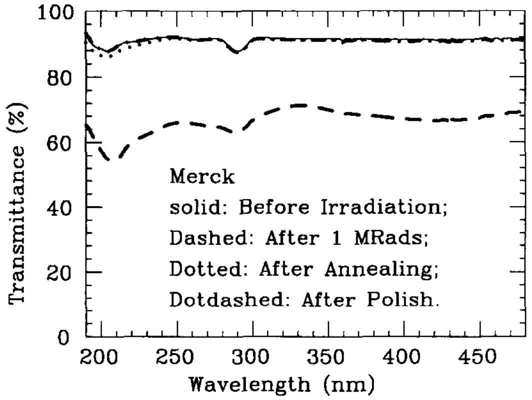

Fig. 9. Transmission spectra of a BaF$_2$ crystal before and after annealing.

To test the radiation resistance of BaF$_2$ crystals, an irradiation was performed with a ^{137}Cs γ-ray source. The dose was delivered at a rate of 50 krad/h. Annealing was carried out by placing a BaF$_2$ crystal in an oven filled with nitrogen gas at the temperature of 500 ° C for 3 h. If the annealing were carried out in air, oxidation of the crystal surface would occur, which then has to be removed by repolishing the crystal.

Fig. 9 shows the transmission spectra of sample Merck before and after irradiation, after annealing, and after repolishing. The damage caused by irradiation was almost fully recovered after annealing, and was completely recovered after polishing. The decrease in transmittance before polishing can be explained by the oxidation of the BaF$_2$ surface under the high annealing temperature.

4. Conclusion

We summarize our main observations in this report as follows:

- The scintillation photoelectron yield of a typical BaF$_2$ crystal observed with a bialkali photocathode (R2059 PMT) has been measured to be 130 p.e./MeV for the fast components (195 and 220 nm) and 700 p.e./MeV for the slow component (300 nm).
- A UV-sensitive solar blind photocathode, such as Cs–Te, may be used to readout mainly the fast components for BaF$_2$ crystals. A Fast/Slow ratio of 1 has been observed with a commercially available Cs ~ Te photocathode. A further factor of 10 improvement is expected by using a K–Cs–Te photocathode developed recently by Hamamatsu.
- The light output of BaF$_2$ crystals depends not only on the transmission of the bulk material, but also on the surface quality of the crystal. The surface of a BaF$_2$ crystal deteriorates when in contact with water or humid air, because of its slightly hygroscopic nature.
- The light yield of BaF$_2$ depends also on the wrapping material. Teflon film is found to be the best wrapping material. Further study is needed to find a better coating material which would provide high light yield and good light uniformity for a large size BaF$_2$ crystal.
- The radiation damage suffered by BaF$_2$ crystals was fully removed by annealing the crystal at 500 ° C for 3 hours in a nitrogen filled oven, and by a subsequent repolishing if the annealing was carried out in air. The necessity of repolishing is explained by the surface oxidation of the BaF$_2$ crystals.

Acknowledgements

We are grateful to Drs. F. Takasaki and D. Scigocki and to Merck, Inc. who provided BaF$_2$ crystal samples for this test. Many useful discussions with Drs. G. Charpak, H. Ma, T. Matsuda, D. Scigocki, S. Suzuki and C. Woody are greatly appreciated. The assistance of S. Sondergaard, J. Hanson, and many members of the Caltech technical staff is also acknowledged.

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