Atomic Energy, Vol. 90, No. 1, 2001

CHARACTERISTICS OF BaF_2 SCINTILLATION CRYSTALS

S. V. Vladimirov,[1] V. S. Kaftanov,[1]
A. F. Nilov,[1] Yu. A. Semenov,[1]
V. T. Smolyankin,[1] V. I. Ushakov,[1]
O. A. Goronkov,[2] E. N. Zvonarev,[2]
O. I. Kozlov,[2] V. P. Mashirev,[2]
V. V. Shatalov,[2] T. T. Basiev,[3]
V. A. Konyushkin,[3] V. V. Osiko,[3]
A. G. Papashvili,[3] and V. N. Skvortsov[3]

UDC 539.1.071.13

The characteristics of BaF_2 barium fluoride crystals, grown from the materials provided by manufacturers, were investigated. The parameters which are important for application of the crystals in low-energy physics, electromagnetic high-energy calorimeters for detecting γ rays and electrons, and measurement of energy in the maximum possible range from tens of MeV up to hundreds of GeV, as well as applications in medicine, instrument building, geology, and so on, were measured. 7 figures, 3 tables, 13 references.

Barium fluoride BaF_2 single crystals are widely used in science and technology. They are used to fabricate optical windows, prisms, and lenses transmitting radiation ranging from infrared to vacuum ultraviolet. BaF_2 single crystals are heavy scintillators with short emission times and are used in nuclear physics and elementary-particle physics for detecting γ radiation and electrons in electromagnetic calorimeters [1–10]. These crystals can also be used in applied problems, for example, positron tomography.

The radioluminescence spectrum of BaF_2 crystals contains two components – a fast component with wavelength in the deep ultraviolet range 175–250 nm and a extremely short emission time 0.6 nsec and a slow component in the wavelength range ~250–400 nm with emission time 620 nsec (Fig. 1). The existence of a fast component makes it possible to use such crystals in nuclear physics to measure the time of flight of elementary particles. Of course, the use of photomultipliers with quartz or MgF_2 windows for highly efficient detection of ultraviolet radiation makes it more expensive to use BaF_2 scintillation crystals. However, the simpler and cheaper technology for growing such crystals, as compared with other scintillation crystals, compensates this drawback. We also note that the difference in the particle-energy dependence of the light output of the radiation components of BaF_2 crystals can be used to identify α particles, protons, and γ rays in low-energy nuclear physics [11]. In high-energy particle physics research, the relatively short radiation length X_0 ~ 2 cm, the radiation resistance ~10 Mrad, the high light putput per unit absorbed energy (reaching 25% relative to the standard NaI(Tl) crystals), the absence

[1] State Science Center – Institute of Theoretical and Experimental Physics.
[2] All-Russia Scientific-Research Institute of Chemical Engineering.
3 Institute of General Physics, Russian Academy of Sciences.

Translated from Atomnaya Énergiya, Vol. 90, No. 1, pp. 49–55, January, 2001. Original article submitted October 13, 2000.

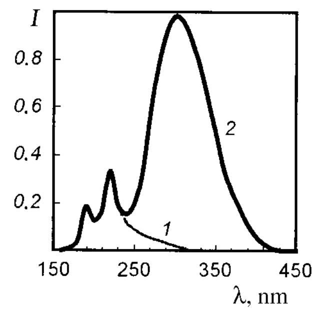

Fig. 1. Fast τ ~ 0.6 nsec (*1*) and slow τ ~ 600 nsec spectrum (*2*) of the radioluminescence of BaF_2 crystals.

TABLE 1. Properties of Some Inorganic Scintillators

Characteristics	Na(Tl)	Cs(Tl)	YAP	BGO	PWO	BaF_2	CeF_3
Chemical bond	NaI	CsI	$YalO_3$	$Bi_4Ge_3O_{12}$	$PbWO_4$	BaF_2	CeF_3
Activator	Tl	Tl	Ce	–	–	–	–
Z_{eff}	50	57	36	74	76	52	53
ρ, g/cm^3	3.67	4.53	5.55	7.13	8.28	4.8	6.16
X_0, cm/g/cm^2	2.6/9.5	1.9/8.4	2.9/1.6	1.1/7.9	0.9/7.3	2.06/9.9	1.68/10.4
Molière radius, cm	4.3	3.8	3.1	2.3	2.2	3.4	2.63
dE/dX_{min}, MeV/cm	4.1	5.1	6.6	8.1	9.3	6	–
Critical energy, MeV	12.5	10.2	~19	8.8	8.5	12.0	~13
Light output, % NaI	100	85	40	13	~1	25	7
Component fraction, %	100	–	97/3	9/91	60/40	20/80	21/79
Number of photons per MeV, 10^3	38.0	32	19.7/0.6	0.7/7.5	0.3/0.2	0.2/6.5	1.2/4.5
Absorption length (511 keV), cm	3.5	–	2.24	1.11	0.96	2.1	1.9
λ_{max}, nm	410	550	347	480	530	210–310	285–307
Refractive index at λ_{max}	1.85	1.8	1.94	2.15	2.16	1.56	1.68
Mohs hardness	2	2	8.5	5	4	3	4
Temperature coefficient, %°C	~0	–0.6	–	–1.6	–2	–2	0.14
Chemical activity	High	Low	Low	Low	Low	Low	Low
Hygroscopicity	Strong	Low	None	None	None	None	None

of hygroscopicity, and weak chemical activity make it possible to produce compact electromagnetic calorimeters with high energy and temporal resolution at energies ranging from several tens of MeV to hundreds of GeV (Table 1). Consequently, BaF_2 crystals could find wide application in high-energy particle physics, nuclear physics, and for the solution of other applied problems.

Methods for Growing Crystals and Measuring Their Characteristics. Four series of BaF_2 single crystals, grown by directed crystallization from melts of stock obtained from different manufacturers, were investigated. The crystals of the series I–IV were distinguished not only by their geometric dimensions, which were 7.1 × 7.7 × 10 mm, 7.1 × 7.7 × 78 mm, 5 × 5 × 4 mm and ∅ 33.5 × 44.7 mm, respectively, but also by the purity of the initial materials and the materials of the crucibles in which they were prepared. The crystal growing chamber, constructed for operation at inert and fluorinating gase pressures up to $1.5 \cdot 10^5$ Pa and temperatures up to 2000°C, made it possible to obtain a 10^{-3} Pa vacuum. Graphite crucibles and

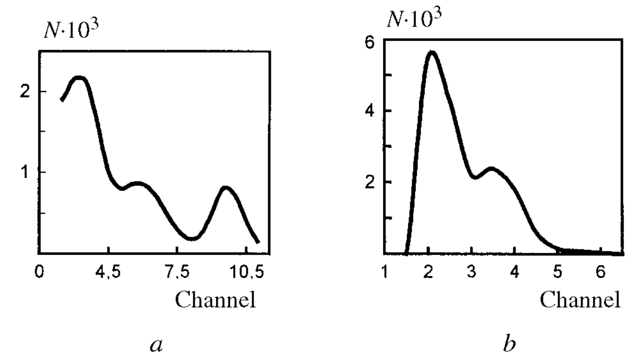

Fig. 2. Amplitude distribution of the light pulses with irradiation of BaF_2 crystals by ^{137}Cs γ rays.

heaters were used. The impurity concentration in the initial charge did not exceed 10^{-3} mass%. The initial raw material consisted of synthetic barium fluoride powders. Finely dispersed BaF_2 powders, prepared from pure grade $BaCO_3$ by fluorination, were used for growing single crystals. The crystals were grown in nickel crucibles for sample No. 3, platinum crucibles for sample No. 7; OSCH-7–5 grade $BaCO_3$ and nickel and platinum crucibles were used for samples Nos. 6 and 1, respectively. The temperature coefficient in the crystallization zone was ~100°C/cm, and the linear growth rate was 10–15 mm/h. The primary assessment of the optical qualities of all crystals was made visually using crossed polaroids and a neon-helium laser with 632.8 nm wavelength. Optically uniform crystals were obtained only if the technology for preparing the initial materials and the growth conditions gave a low impurity level. Specifically, it was established that light scattering in the crystals is due to precipitation of a finely dispersed phase of nonisomorphic barium oxide impurity in the grown crystal. Consequently, the growth process was conducted in a static fluorinating atmosphere in order to obtain optically uniform crystals.

The setup for measuring the characteristics of the crystals consisted of a light-tight box into which a photomultiplier, a Garantiya-3 amplifier, BaF_2 crystals, and a device for moving a collimator with radioactive ^{137}Cs and ^{60}Co sources were placed. Ultraviolet photons from the BaF_2 crystals up to wavelength ~170 nm were detected with a FÉU-39A photomultiplier with a quartz window and a 40 mm in diameter photocathode. The optical contacts between the crystals and the photomultiplier window were illuminated using a pure-grade (CH) vaseline oil, thin silicone rubber, BI-630 gel from the BIKRON Company or pure transparent rubber gel. Teflon ribbon and aluminized lavsan were used for packing the crystals. Radiation from ^{137}Cs and ^{60}Co was passed through a 40 mm long steel collimator with an 8 mm in diameter opening. The collimator axis was perpendicular to the long axis of the crystals. The collimated source could move over a fixed distance along the crystal in order to change the irradiation zones when measuring the dependence of the energy resolution and amplitude on the distance between the irradiation zone and the photocathode. The CAMAC standard was used for the measurement electronics. Information was accumulated and output using a PC/AT-386 personal computer with MES software. The anode pulses from the FÉU-39A photomultiplier were fed into a 12-channel analog-to-digital converter ADC 2249A Le Croy with 60 μsec time resolution and 0.2–256 pK range. When necessary, the pulses were preamplified with a low-noise Garantiya-3 integrated amplifier. The pulse duration of the gates for the analog-to-digital converter was regulated from 40 to 1000 nsec. To eliminate the high-frequency noise, the high- and low-voltage constants of the voltage source were fed through filters placed in a box containing the photomultiplier and right next to the Garantiya-3 amplifier. A CC217.10 module was used as the CAMAC crate controller. The assembly work was monitored by detecting the ^{137}Cs (E_γ = 662 keV) and ^{60}Co ($E_{\gamma1}$ = 1.173 and $E_{\gamma2}$ = 1.332 MeV) radiation with a ∅ 40 × 40 mm NaI(Tl) crystal. All reference spectra obtained using this crystal possessed well-expressed photopeaks and Compton and backscattering peaks.

Measurement Results. The BaF_2 crystals from the first series, with dimensions 7.1 × 7.7 × 9.8 mm (Fig. 2*a*) and 7.1 × 7.7 × 10 mm (Fig. 2*b*), were packed, after being carefully polishing, into a container using a teflon ribbon which reflected ultraviolet light well. Vaseline oil was used to produce an optical contact between the output faces of the crystals and the

TABLE 2. Comparative Characteristics of BaF_2 Crystals (U = 1 kV)

Organization	Crystal size, mm	Amplitude E, arb. units	Amplitude resolution $\sigma(E)$, arb. units	$\sigma(E)/E$, %
Institute of General Phyiscs, Russian Academy of Sciences	7.1 × 7.7 × 9.8	3.57 ± 0.013	0.49 ± 0.02	13.7
All-Russia Scientific-Research Institute of Chemical Engineering	7.1 × 7.7 × 10	9.66 ± 0.007	0.68 ± 0.007	7.0

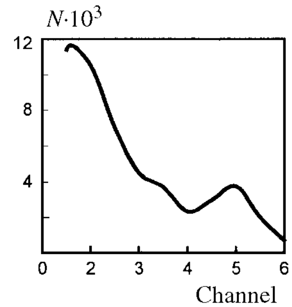

Fig. 3. Amplitude distribution with irradiation of 7.1 × 7.7 × 78 mm BaF_2 crystals by ^{137}Cs γ rays.

input window of the photomultiplier. The spectrum and energy resolution of the crystals were measured using ^{137}Cs (E_γ = 0.662 MeV) γ rays. A well-resolved photopeak, corresponding to 662 keV, is observed in the spectrum against the background of the continuous Compton distribution (see Fig. 2*a*); the photopeak in the spectrum is much less distinct (see Fig. 2*b*). The results of the descriptions of both spectra by a superposition of normal distributions made it possible to estimate the position of the lines and the energy resolution of the crystals with 662 keV γ rays.

It follows from the data in Table 2 that the scintillation light output of the crystals in the first series, which were grown from material obtained from the Institute of General Physics of the Russian Academy of Sciences, is more than twice the light output of crystals grown from the material obtained from the All-Russia Scientific-Research Institute of Chemical Engineering. In accordance with the high light output, the relative energy resolution of the crystals in detection and measurement of the energy of 662 keV γ rays is almost two times better. The low light output is most likely due to an inadequate degree of purity of the initial BaF_2 powders used for growing the single crystals at the All-Russian Scientific-Research Institute of Chemical Engineering.

BaF_2 crystals from the second series were distinguished by their large length 7.1 × 7.7 × 78 mm. Initial measurements of their spectrometric characteristics were performed without packing in two geometric positions relative to the photocathode of the photomultiplier: horizontal and vertical. Optical contact between the faces of the crystals and the entrance window of the photomultiplier was obtained using a thin layer of vaseline oil. Figure 3 shows a typical amplitude distribution obtained by irradiating one of the four crystals with ^{137}Cs γ rays (E_γ = 662 keV). The average relative resolution obtained for the four crystals in a horizontal position fitting Gaussian distributions to the experimental spectra was $\sigma(E)/E \cong 15\%$. Since for a vertical arrangement of the crystals no photopeak was observed, and the characteristics of all four crystals in the horizontal position turned out to be close, measurements were performed with an assembly of all four crystals placed in a single light-reflecting teflon vessel. A photopeak was obtained and an energy resolution $\sigma(E)/E \sim 30\%$ was obtained with γ-ray energy 662 keV. The use of an additional Garantiya-3 amplifier, placed directly near the photomultiplier anode, improved the energy resolution; $\sigma(E)/E$ in this case was ~20%. It was noted that vaseline oil and VI-630 gel from the BIKRON Company, which were used to obtain an optical contact between the crystal and the photomultiplier, gave approx-

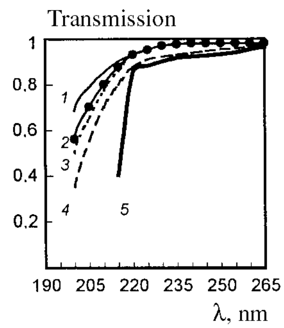

Fig. 4. Light transmission coefficient of BaF_2 crystals versus wavelength for samples which are grown from a charge prepared in platinum (*1*, *3*) and nickel (*2*, *4*) crucibles, OSCH-7–5 and CH grade $BaCO_3$, respectively; *5*) industrial sample.

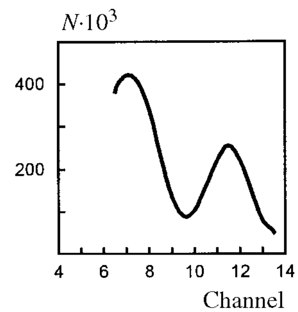

Fig. 5. Typical amplitude distribution obtained by irradiating a $5 \times 5 \times 4$ mm BaF_2 crystal, grown from a charge prepared in a platinum crucible from OSCH-7–5 $BaCO_3$.

imately the same amplitude resolution. The latter observation could indicate high absorption of photons from the deep-UV component of the 175–250 nm radiation in the structural components of the reflector and in the crystals themselves.

In working with the third series, the scintillation characteristics of the crystals grown from BaF_2 powders synthesized using $BaCO_3$ compounds with different purity in nickel and platinum crucibles were compaired. The initial materials consisted of the following grades of $BaCO_3$: pure grade (CH) and ultrapure grade (OSCH-7–5). The scintillation characteristics were compared with the analogous crystals obtained under industrial conditions.

The dimensions of all samples after processing and polishing were $5 \times 5 \times 4$ mm. The transmission coefficients in the wavelength range 0.2–18 μm were measured for all crystals. In measuring the transmission, the thickness of the experimental samples was identical (5 mm). Figure 4 shows the transmission spectra in the UV range. All experimental samples of barium fluoride crystals possessed higher transmission than the industrial sample in the UV region of the spectra. In the UV region, the crystals grown from BaF_2 powder prepared from OSCH-7–5 $BaCO_3$ possessed higher optical transparency. In addition, it can be concluded that the crystals grown from BaF_2 powder obtained in platinum crucibles had, on the average, higher optical transparency in the UV region 200–250 nm. In the infrared range, all crystals were identically transparent up to wavelength ~12 μm. A sharp reduction of transmission to 5–10% was observed only in the range 11–14 μm.

The scintillation characteristics were measured for unpacked crystals and for crystals packed in teflon ribbon and placed inside a teflon vessel of the reflector (Fig. 5). All measurements were performed by irradiating crystals with ^{137}Cs γ rays. The spectra corresponding to crystals of this series and different types of packings did not differ much with respect to

TABLE 3. Comparative Characteristics of 5 × 5 × 4 mm Crystals, Grown from BaF_2 Powders, Synthesized from $BaCO_3$ of Different Purity, in Nickel and Tantalum Crucibles

Crucible, material	Amplitude E, arb. units	Amplitude resolution $\sigma(E)$, arb. units	$\sigma(E)/E$ with E_γ = 662 keV, %
Platinum, pure grade	11.35 ± 0.02	0.883 ± 0.022	7.80
Platinum, ultrapure grade	11.50 ± 0.02	1.036 ± 0.018	9.01
Nickel, pure grade	11.88 ± 0.02	0.900 ± 0.017	7.58
Nickel, ultrapure grade	12.98 ± 0.03	1.292 ± 0.035	9.95

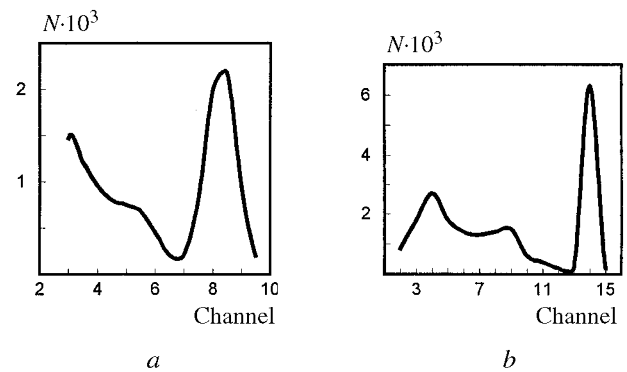

Fig. 6. Amplitude distribution with irradiation of a ∅ 33.5 × 44.7 mm BaF_2 crystal (*a*) and a standard ∅ 40 × 40 mm NaI(Tl) crystal (*b*) by ^{137}Cs γ rays with energy E_γ = 0.662 MeV.

the position of the centers of the photopeaks (total absorption peaks) and the relative energy resolution. Table 3 gives the measured characteristics of four crystals packed in a teflon vessel-reflector. Analysis shows the following:

– comparing the UV transmission coefficients of the samples (see Fig. 4) is not an adequate criterion for selecting scintillation crystals;

– for crystals grown from BaF_2 powders, prepared in platinum crucibles, from CH and OSCH-7–5 grade $BaCO_3$, no substantial difference is observed in the intensity of scintillation bursts; the difference in energy resolution does not exceed 13%;

– crystals grown from BaF_2 powder prepared from OSCH-7–5 $BaCO_3$ in a nickel crucible give an appreciably higher scintillation intensity, but they also have an almost 25% larger line width.

It is also important to note that, even though the light transmission by the thin layer of vaseline oil is good up to the deep ultraviolet range, using this oil for producing an optical contact between crystals packed in teflon ribbon and the input window of the photomultiplier can be strongly problematic, since the strong capillary effect can cause the vaseline oil to be drawn into the packing between the layers of the teflon ribbon, changing the reflection coefficient in a less favorable direction and destroying the optical contact.

Experience in growing BaF_2 scintillation crystals in the first three series made it possible to grow large single crystals in the fourth series.

Figure 6*a* shows the energy spectrum of ^{137}Cs γ rays (E_γ = 0.662 MeV), which was obtained by irradiating a ∅ 33.5 × 44.7 mm BaF_2 crystal packed in a reflective teflon-ribbon container. To obtain an optical contact between the input window of the photomultiplier and the crystal, vaseline oil was used because a thin layer of this oil has the best transmission in the radiation range of the BaF_2 crystal up to its deep ultraviolet range. Sharp separation of the total-absorption peak demon-

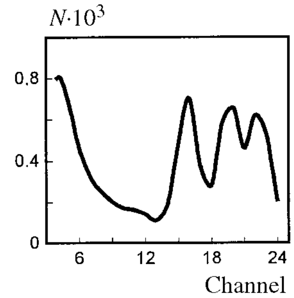

Fig. 7. Background energy distribution for a
∅ 33.5 × 44.7 mm BaF_2 crystal.

strated the the quality of the crystal was good and made it possible to estimate the energy resolution at E_γ = 0.662 MeV as $\sigma(E)/E$ ~ 6.4%. The energy resolution obtained under the same conditions for the NaI(Tl) standard crystal was $\sigma(E)/E$ ~ 3.6% (see Fig. 6*b*). Comparing the energy resolution confirmed that BaF_2 crystals with a large diameter ~30 mm, grown by directed crystallization technology, possess a high light output and long crystals (15–20 radiation lengths) can be good elements for producing electromagnetic calorimeters in high-energy particle physics.

Background measurements in the laboratory room gave an energy spectrum recorded with BaF_2 crystal without irradiation with any radioactive source. The spectrum showed three sharply separated lines, one of which could be compared with the ^{40}K line with γ-ray energy 1.486 MeV (Fig. 7). This line is, as a rule, manifested with different intensity in low-background measurements in any rooms. However, preliminary estimates of the energies of the lines did not make it possible to identify any such line as a ^{40}K line. To understand the origin of the sources of the ionizing radiation, control measurements were performed of the background of the setup and of the room using a ∅ 40 × 40 mm NaI(Tl) reference crystal and a ∅ 33.5 × 44.7 mm BaF_2 crystal. In addition, an attempt was made to detect radiation possibly emanating from the BaF_2 crystal itself using the NaI(Tl) standard crystal. After the measurements and careful calibration of the energy scale of ^{137}Cs, ^{60}Co, and ^{23}Na were performed, it was determined that the BaF_2 crystal contains sources of short-range radiation, which does not travel beyond the boundaries of the crystal and its teflon packing. Repeated measurements performed every 4.5 months confirmed the previously obtained results. The final measurements of the energy of these three lines are as follows: 1.58–1.66, 2.12, and 2.2 MeV. The ^{60}Co lines (1.173 and 1.332 MeV) were used as references to determine the energy of the lines. The closest energies to those of the lines obtained in the experiment were the energies of the lines of a ^{226}Ra source with the tabulated values 1.66, 2.12, and 2.29 MeV [2, 13]. Such a radioactive source with a 3-yr half-life inside the crystal can be used for periodic calibration during operation of a device (detector). We note that these measurements all required careful monitoring of the stability of the spectrometer scale and reducing to a minimum the amplitude drift of the scintillation counter in time.

Conclusions. The results of the measurements of the scintillation characteristics of BaF_2 crystals grown from the initial materials obtained different manufacturers showed that they are suitable for use in electromagnetic calorimeters and for measuring the energies of high- and low-energy electrons and γ rays. The technology developed for obtaining inexpensive, pure polycrystalline BaF_2 raw material makes possible mass production of large crystals (~20X_0) with stable characteristics for use in science and technology.

REFERENCES

1. R. Zhu, G. Gratta, and H. Newman, "Crystal calorimeters for particle physics," *Nucl. Phys. B (Proc. Suppl.)*, **44**, 88 (1995).
2. R. Novotny, "Performance of the BaF_2-calorimeter TAPSP," *Nucl. Phys. B*, **61**, 137–142 (1998).
3. R. Zhu, "On quality requirements to barium fluoride crystals," *Nucl. Instrum. Meth. A*, **340**, 442 (1994).

4. R. Novotny, R. Beck, W. Doering, et al. “Electromagnetic-calorimetry with $PbWO_4$ in the energy regime below 1 GeV,” in: *The 5th International Conference on Inorganic Scintillators and Their Applications,* Scint-99, Moscow, Russia (1999), *Book of Abstracts*, p. 4.
5. R. Novotny, “The BaF_2 photon spectrometer tapes,” *IEEE Trans. Nucl. Sci.*, **NS-38**, 379 (1991).
6. A. Gabler, W. Doering, M. Fuchs, et al., “Response of TAPS to monochromatic photons with energies between 45 and 790 MeV,” *NIM A*, **346**, 164–176 (1994).
7. R. Novotny, W. Doering, V. Hejny, et al., “A plastic – BaF_2 phoswich telescope for charged-neutral particle and photon detection,” *IEEE Tran. Nucl. Sci.*, **NS-43**, 1260 (1996).
8. I. E. Gurskii, V. S. Kaftanov, A. F. Nilov, et al., “Investigation of the properties of CeF_3 scintillation crystals,” *Prib. Tekh. Éksp.*, No. 1, 36 (2000).
9. P. Schotanns, C. Van Eijk, R. Hollander, et al., “Temperature dependence of BaF_2 scintillation light yield,” *Nucl. Instrum. Meth. A*, **238**, 564 (1985).
10. M. Kobayashi, A. Konaka, K. Miyake, et al., “Test of BaF_2 scintillators coupled to a photomultiplier with a CsTe photocathode,” *Nucl. Instrum. Meth. A*, **270**, 106 (1988).
11. O. Ryaboukhin, V. Ivanov, and A. Kruzhalov, “Investigation of core-valence luminescence under proton excitation,” in: *5th International Conference on Inorganic Scintillators and Their Applications*, Scint-99, Moscow, Russia (1999), *Book of Abstracts*, p. 82.
12. W. Bowman and K. MacMurdo, “Radioactive-decay gammas ordered by energy and nuclide,” *Atomic Data and Nuclear Data Tables*, **13**, Nos. 2–3, 1–202 (1974).
13. M. Martin and P. Blichert-Toft, “Radioactive atom, Auger-electron, α, β, γ, and *X*-ray data,” *Nuclear Data Tables*, **8**, No. 1–2, 1–198 (1970).