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THE APPLICATION OF BARIUM FLUORIDE LUMINESCENCE: CHALLENGES AND PROSPECTS

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The problem of obtaining BaF₂ crystals with a predominant sub-nanosecond luminescence component has been considered. A detailed analysis of methods for suppressing the slow component of the crystal luminescence was carried out. It was shown that the introduction of a number of dopants led to the suppression of the slow component, but, as a rule, the intensity of the sub-nanosecond component decreased, and the transparency and radiation hardness of the crystal also deteriorated. The results of spectral and kinetic measurements of BaF₂:Tm and BaF₂:Sc luminescence were presented. It was shown that the solution of the problem can be achieved by using an undoped BaF₂ crystal in combination with a filter suppressing the slow luminescence component.

Keywords: barium fluoride, core-valence luminescence, ultrafast scintillators, optical filters

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ПРОБЛЕМЫ И ПЕРСПЕКТИВЫ ПРИМЕНЕНИЯ ЛЮМИНЕСЦЕНЦИИ ФТОРИДА БАРИЯ

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Рассмотрена проблема получения кристаллов BaF₂ с преобладающим субнаносекундным компонентом рентгенолюминесценции. Проведен подробный анализ методов подавления медленного компонента указанной люминесценции данного соединения. Показано, что введение ряда примесей приводит к подавлению медленного компонента, однако, как правило, интенсивность субнаносекундного компонента также снижается, при этом ухудшаются прозрачность и радиационная стойкость кристалла. Приведены результаты измерения спектрально-кинетических характеристик кристаллов BaF₂:Tm и BaF₂:Sc. Показано, что проблему можно решить путем использования нелегированного кристалла BaF₂ в сочетании с фильтром, подавляющим медленный компонент люминесценции.

Ключевые слова: фторид бария, остовно-валентная люминесценция, сверхбыстрый сцинтиллятор, оптический фильтр

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Introduction

Barium fluoride (BaF_2) has been the focus of extensive research spanning several decades, ever since subnanosecond (0.7–0.8 ns) luminescence in the range between ultraviolet (UV) and vacuum ultraviolet (VUV) spectral regions [1, 2] has been discovered in this compound in the early 1980s. Radiative electronic transitions between the top core ($5p$, Ba) and valence ($2p$, F) levels of the crystal were later confirmed to be responsible for this luminescence [3]. The phenomenon was termed core-valence luminescence (CVL) [4], or cross-luminescence [5]. BaF_2 has a short decay time, making it a promising option for use in medical diagnostic systems, experimental nuclear physics and astrophysics as a fast scintillator. A wide luminescence band with a maximum of 310 nm (in addition to CVL) is another known problem with barium fluoride. Self-trapped excitons (STE) are responsible for this luminescence, which has a decay time $\tau = 630$ ns. Numerous studies have been dedicated to suppression of this long (and often undesirable) component of luminescence [6–9]; this problem is also considered in our study.

Another issue is related to the spectral position of CVL bands: two emission peaks are located at wavelengths of 220 and 196 nm (UV and VUV ranges). Very few types of photodetectors can effectively operate in this spectral region; solar-blind photomultipliers with CsTe photocathodes making it possible to reduce the output signal from the slow component by 9 times have long been used for this purpose; however, the signal from the fast component also decreased by 1.84 times [7].

Solar-blind photodetectors with a response time of 15 ps and a quantum efficiency of about 12% have been developed [10]; a quantum efficiency of 17% at 220 nm was recently obtained for an avalanche photodiode (APD) [11].

Moreover, interest in the characteristics of barium fluoride has been renewed because this compound is considered as a working material for a new calorimeter, aimed at observing muon-to-electron conversion (the Mu2e experiment at Fermilab [11, 12]). Effort is currently underway to improve the luminescent characteristics of barium fluoride by introducing impurities, changing the conditions of growth and annealing of crystals, using such materials as nanoparticles, composites and ceramics.

In our study, we have carried out generalization and analysis of the most important results on improving the luminescence and

scintillation characteristics of barium fluoride, giving the experimental data for $\text{BaF}_2:\text{Tm}$ and $\text{BaF}_2:\text{Sc}$ crystals.

$\text{BaF}_2:\text{Tm}$ samples have been chosen because thulium (Tm) is one of the best dopants among rare-earth ions for suppressing the slow luminescence component [5, 6]. As for the second dopant, scandium (Sc) is the least studied “suppressive” dopant among the ions with a filled outer shell.

Suppression of slow component of luminescence in barium fluoride by introducing dopants

Ions with a filled outer shell. Numerous studies considered “suppression” of the slow luminescence component (310 nm band), which is undesirable for fast scintillators. Ions with a filled outer electron shell, such as La^{3+} , Y^{3+} , Lu^{3+} , Sc^{3+} and Cd^{2+} are the best dopants for this purpose since they do not generate additional emission bands. The first experiments showed that substantial suppression of slow luminescence is always accompanied by a slight decrease in CVL [5, 6]. For example, the slow component in $\text{BaF}_2:\text{La}(0.2\%)$ decreases by 1.72 times, while the fast one decreases by 1.09 times [13]; the slow and the fast components in $\text{BaF}_2:\text{La}(0.5\%)$ decrease, respectively, by 3.6 and 1.6 times. According to [8], suppression of the slow component in crystalline $\text{BaF}_2:\text{La}$ starts when the lanthanum content exceeds 1% (Fig. 1). The concentration dependence of slow X-ray luminescence (XRL) in $\text{BaF}_2:\text{Y}$ is similar to that for $\text{BaF}_2:\text{La}$ (Fig. 1). A $\text{BaF}_2:\text{Y}(1 \text{ at.}\%)$ crystal whose slow component was suppressed by 6 times, and the CVL intensity was the same as in pure BaF_2 was synthesized recently [14].

Introducing cadmium considerably suppresses the slow XRL component of $\text{BaF}_2:\text{Cd}$ (curve 3 in Fig. 1). With the cadmium content of 0.35 mol.%, the intensity of this component is less than 10% compared to that for an undoped crystal, while the intensity of the fast component practically does not change. Unfortunately, Cd^+ ions form in a $\text{BaF}_2:\text{Cd}$ crystal irradiated with X-rays, generating absorption bands in the visible and UV spectral regions [8].

Lutetium (Lu) reduces the intensity of the slow component in BaF_2 by 4 times, but the fast component also decreases considerably [15]. Aside from that, introducing lutetium resulted in deteriorated radiation hardness of such a crystal. According to [6], the CVL decay time for $\text{BaF}_2:\text{Lu}(1.0 \text{ mol.}\%)$ is 0.4 ns;

this means that a small loss in CVL intensity is compensated by a nearly twofold decrease in the luminescence decay constant.

The spectral and kinetic characteristics of BaF_2 crystals with scandium contents of 0.5, 1.0, and 2.0 mol.% were studied in [16], where the intensity of the slow component for the $\text{BaF}_2:\text{Sc}(1.0\%)$ decreased by 2.4 times.

Since the RbF crystal has CVL [4], it was proposed to increase the intensity of the fast component by introducing rubidium fluoride into barium fluoride. The experiment with a $\text{BaF}_2:\text{Rb}$ crystal revealed no CVL and a slight decrease in the slow XRL component [17].

Rare-earth ions. A large number of studies have been dedicated to suppression of the slow luminescence component (310 nm band), which is undesirable for fast scintillators. Trivalent rare-earth (RE^{3+}) ions were introduced into barium fluoride crystals as dopants for this purpose. It was established that any rare-earth dopant reduces the intensity of the slow scintillation component [5, 6]. The presence of interstitial fluorine ions F^- serving as charge compensators for trivalent dopants was traditionally believed to be the reason for suppression of the slow component of scintillation by RE^{3+} ions. It was assumed that because these interstitial

ions generate energy levels near the top of the crystal's valence band (in the bandgap), they can trap holes from the valence band [8]. This trapping is a competing process between formation of V_k centers and self-trapped excitons, or $(V_k e^-)^*$ -centers, resulting in decreased STE luminescence intensity. While this model is certainly attractive, it does not explain suppression of the slow component in BaF_2 crystals doped with divalent Cd^{2+} , Mg^{2+} and Sr^{2+} ions [18]. Comparing the dependences of XRL intensity in $\text{BaF}_2:\text{La}$ and $\text{BaF}_2:\text{K}$ crystals, the authors of [8] concluded that interstitial F^- ions are only partially responsible for the suppression effect. It was also established that diffusion of excitons to the centers of their nonradiative annihilation makes the main contribution to this effect [8].

Suppression of slow luminescence component of barium fluoride by thermal quenching

CVL intensity is characterized by high thermal stability (tested up to 500°C [18]); this property can be used to eliminate the slow component. The intensity and decay time of the slow XRL component considerably decrease at higher temperatures ranging from room temperature. For example, if the oper-

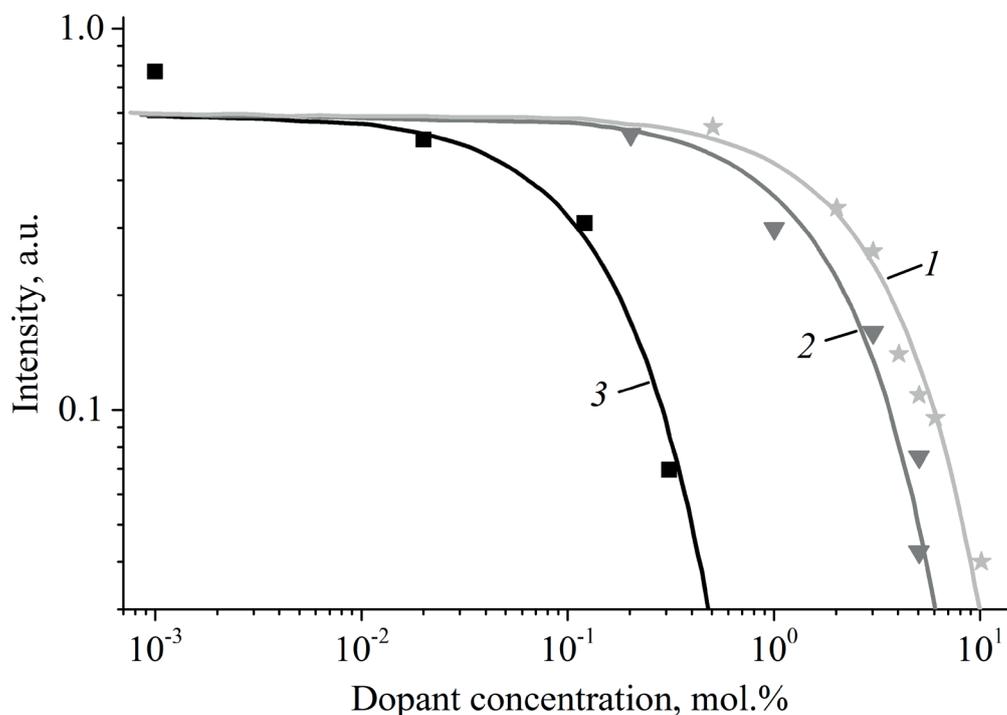


Fig. 1. Concentration dependences of slow XRL luminescence intensity for $\text{BaF}_2:\text{La}$ (1), $\text{BaF}_2:\text{Y}$ (2) and $\text{BaF}_2:\text{Cd}$ (3) crystals (based on data given in [8])

ating temperature of the device is chosen to be 120°C, the intensity of the slow component is lower than that of the fast component, and the decay time of STE luminescence is approximately 40 ns. This mode of operation of the scintillator can be established in an individual physical experiment, but it is hardly suitable for technical devices. It was found in [19] that the slow XRL component of barium fluoride is completely suppressed at 220°C, and the light yield of the subnanosecond component is 1000 photons/MeV.

Conversion of exciton emission to faster activator luminescence

The main idea of these experiments is to transform emission of self-trapped excitons into faster activator luminescence rather than suppress it. The elements at the beginning of the lanthanide series (Ce, Pr, Nd) are known to possess the most effective allowed (i.e., fast) $5d \rightarrow 4f$ transitions. The heavier rare-earth elements tend to have slow UV luminescence governed by high-spin (HS) $5d \rightarrow 4f$ transitions, forbidden by the spin selection rule. Additionally, a large number of $4f$ levels in some ions (Nd, Eu, Tb, Dy) leads to slow (undesirable) luminescence due to forbidden $4f \rightarrow 4f$ transitions. Therefore, light rare-earth ions Ce^{3+} , Pr^{3+} , Nd^{3+} , as well as ions with a relatively small number of $4f$ levels (Gd^{3+} and Tm^{3+}) are the best candidates for barium fluoride activators.

BaF₂:Ce compound. Cerium serves as an activator in many modern phosphors and scintillators; for this reason, introducing Ce^{3+} ions into barium fluoride was expected to increase the light yield of the crystal and obtain scintillation decay times of several tens of nanoseconds. Early experiments revealed that the light yield of BaF₂:Ce at the optimal concentration (about 0.2 mol.%) of Ce^{3+} ions (the optimal concentration is the one with the maximum luminescence intensity) was slightly lower compared to pure BaF₂ [20, 21]. It was suggested that either Ce aggregates or ($Ce^{3+}-O^{2-}$) centers form in the crystal if the content of Ce^{3+} ions exceeds 0.2 mol.% [21]. A later study [22] reported on a slight increase in the light yield for a BaF₂:Ce crystal, finding that self-trapped holes in the form of V_k and H centers participate in the recombination process.

Subsequent studies managed to increase the light yield of BaF₂:Ce by 2.5 times compared with pure barium fluoride, but the kinetic characteristics of XRL could not be significantly

improved [23]. The BaF₂:Ce crystal exhibits some unusual properties: the XRL spectrum corresponds to emission of Ce^{3+} ions (308 and 322 nm bands), and the kinetics to emission of self-trapped excitons (the main decay constant is equal to 250 ns). A luminescence decay constant of 31 ns is detected in the BaF₂ crystal upon direct UV excitation of Ce^{3+} ions [22]. This behavior of BaF₂:Ce is due to superposition of the absorption band of Ce^{3+} ions on the emission band of self-trapped excitons in the region of 280–300 nm, resulting in energy transfer from excitons to Ce ions (STE \rightarrow Ce^{3+}).

Introducing a lutetium dopant into BaF₂:Ce leads to a decrease in the intensity of the two main Ce^{3+} emission bands and to a new wide XRL band appearing, with a peak at 355 nm [15]. The XLR band at 355 nm in BaF₂:Ce, Lu is believed to be associated with interstitial fluorine ions.

BaF₂:Pr compound. Trivalent praseodymium has a shorter decay time ($5d \rightarrow 4f$ transitions) and a slightly lower XLR intensity in different crystals, compared with those parameters for the Ce^{3+} dopant. The BaF₂:Pr³⁺ crystal has the main decay constant of 28 ns, and a faster component with a duration of 7–8 ns appears as the Pr³⁺ content exceeds 1%. However, the $5d \rightarrow 4f$ emission band overlaps with the core-valence luminescence band; as a result, energy transfer from CVL transitions to Pr³⁺ ions occurs (CVL is not detected). Another drawback of the crystals containing Pr³⁺ is the presence of $f \rightarrow f$ transitions with slow emission.

BaF₂:Nd compound. The first experiments showed a very weak (below the CVL level) ($5d \rightarrow 4f$) luminescence of Nd³⁺ in BaF₂ (slightly higher than the XLR intensity in BaY₂F₈:Nd) [25]. It was subsequently proved for crystals with a higher quality that BaF₂:Nd(1%) samples emit in the UV spectral region (175–200 nm), with the main decay constant of 12 ns [26]. The light yield of the crystal was only 7% lower than that of BaF₂. Adding lanthanum improves the characteristics: the (La_{0.9},Ba_{0.1})F_{2.9}:Nd crystal has a narrow (12 nm) luminescence band with a maximum at 175 nm and a short decay time, $\tau = 6.1$ ns [27].

BaF₂:Tm compound. Interconfiguration $5d \rightarrow 4f$ transitions of Tm³⁺ ions in BaF₂ are manifested as a luminescence band with a maximum at 178 nm and a decay time of 5–6 ns [28]. The intensity of this luminescence is lower than the CVL intensity. As the Tm³⁺ concentration increases from 0.1 to 10%, the intensity of the STE band decreases substantially (the same as

for other rare-earth ions), but the yield of the subnanosecond component also decreases with a thulium concentration $C_{\text{Tm}} > 0.1\%$.

Ref. [29] investigated the ($5d \rightarrow 4f$) luminescence of Nd^{3+} , Sm^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} ions in barium fluoride and other alkaline earth fluorides. It was established that the exciton mechanism of energy transfer to $5d$ states of these ions is inefficient in fluorides.

Suppression of slow luminescence component in barium fluoride by double doping

$\text{BaF}_2:\text{Gd,Ce}$ compound. It was proposed in [30] to introduce 10% of Gd^{3+} into barium fluoride with the addition of the Ce^{3+} co-activator not only as a means of suppressing the slow emission component but also to improve other characteristics of the material. The synthesized $\text{Ba}_{0.9}\text{Gd}_{0.1}\text{F}_{2.1}$ crystal had a high density equal to 5.11 g/cm^3 (4.89 g/cm^3 for undoped BaF_2), and a higher mechanical strength of 240 kg/mm^2 (80 kg/mm^2 for BaF_2). As Ce^{3+} ions were introduced into the compound, the peak of the luminescence band of self-trapped excitons shifted to the long-wavelength region to a value of 350 nm. The $\text{Gd}_{0.1}\text{Ba}_{0.9}\text{F}_{2.1}:\text{Ce}(0.1 \text{ mol.}\%)$ crystal had a 46% light yield compared to pure barium fluoride and a luminescence decay constant of 30–40 ns. Notably, the decay constant characteristic for the Ce^{3+} ion is manifested in the spectrum due to a shift of the luminescence band to the long-wavelength region. The slow XRL component the crystal was almost completely suppressed. The optimal (before the quenching started) concentration of Ce^{3+} ions in a $\text{Ba}_{0.9}\text{Gd}_{0.1}\text{F}_{2.1}$ is 0.2–0.3 mol.% [30]. Unfortunately, the radiation hardness of a $\text{Ba}_{0.9}\text{Gd}_{0.1}\text{F}_{2.1}:\text{Ce}(0.1 \text{ mol.}\%)$ crystal is lower than that for pure barium fluoride.

$\text{BaF}_2:\text{La,Er}$ compound. As noted above, the ions of the second half of the lanthanide series have slow ($5d \rightarrow 4f$) luminescence from the HS $5d$ state. In particular, slow emission of $5d(\text{HS}) \rightarrow 4f$ transitions is prevalent in the $\text{BaF}_2:\text{Er}^{3+}$ crystal, which has a high intensity due to presence of a ${}^2F_{5/2}$ energy level between LS (low-spin) states and HS (high-spin) $5d$ states. This level promotes nonradiative energy transfer to the $5d(\text{HS}) \rightarrow 4f$ luminescence component, prohibited by the spin selection rule. A red shift of $5d$ excitation bands of Er^{3+} was obtained by introducing 30% of LaF_3 into barium fluoride ($\text{BaLaF}_2:\text{Er}^{3+}$ crystal), and the ${}^2F_{5/2}$ level was located higher than the $5d(\text{LS})$ and $5d(\text{HS})$ levels [31]. As a result, $5d(\text{LS}) \rightarrow 4f$ transitions,

allowed by the selection rules and generating two emission bands in the 140–150 and 152–160 nm regions with a luminescence decay time of 35 ns, were prevalent in the crystal obtained by the authors [31].

$\text{BaF}_2:\text{La,Ce}$ compound. Since lanthanum usually serves as a “suppressor” of the slow XRL component, and cerium is the best activator, it was of interest to introduce these ions in barium fluoride together. The experiment in [32] established that the decay constant in the $\text{BaF}_2:\text{La,Ce}$ compound is 76 ns, the slower component is substantially suppressed, and the light yield is lower than in pure barium fluoride.

Radiation hardness of doped BaF_2 crystals

Crystals intended for collider experiments should have a high radiation hardness [5], and high-purity barium fluoride crystals [33, 34] fully satisfy this requirement. F centers induced by radiation are formed in the crystal, generating a broad optical absorption band with a peak at 570 nm. This absorption does not affect the position and intensity of the core-valence luminescence bands. Introducing dopants (RE^{3+} , Me^{2+} , etc.) typically reduces the radiation hardness of barium fluoride [34]. The crystals doped with La^{3+} acquire a red color upon irradiation with X-rays, which is due to interstitial fluorine ions forming. A monovalent metal is introduced into the $\text{BaF}_2:\text{La}$ crystal in the same concentration as the concentration of lanthanum ions in order to increase radiation hardness (reducing the number of interstitial fluorine ions). For example, it was demonstrated that a $\text{BaF}_2:\text{La}(0.3\%)\text{K}(0.3\%)$ crystal has a higher radiation hardness but a lower suppressive effect than a potassium-free crystal, $\text{BaF}_2:\text{La}(0.3\%)$ [8]. Alkali-containing crystals acquire a blue color upon irradiation with X-rays, which is associated with F -aggregates forming due to the presence of fluorine vacancies [8].

The optical absorption level near 500 nm is higher in the irradiated $\text{BaF}_2:\text{La}$ crystal than in pure barium fluoride, but the absorption intensity becomes comparable for these crystals in the UV region of the spectrum [13]. Radiation resistance of the BaF_2 crystal (absorption bands in the range of 200–800 nm) deteriorates upon doping with Tm, Nd, Gd, Eu. Notably, lead is the most dangerous residual dopant that suppresses CVL, with the maximum of the absorption band located at 205 nm [13].

Other methods for reducing the intensity of slow luminescence component

Using nanoparticles. Nanoparticles are known for their high surface/volume ratios and therefore have different properties than the corresponding single crystals [35, 36]. Luminescence intensity can be increased and luminescence decay time can be decreased by decreasing the size of nanoparticles. These effects are well studied for excitons in semiconductor nanoparticles. Studies into high-band-gap dielectric materials with small-radius excitons are currently in their initial stages. Another advantage of nanoparticles over ordinary particles is that higher activator concentrations can be introduced for them to increase luminescence intensity.

The behavior of luminescence in barium fluoride nanoparticles ranging in size from 20 to 100 nm was studied in [35]. The intensity of the CVL band with decreasing size of nanoparticles from 80 to 30 nm practically does not differ from the CVL intensity for a single-crystal sample of BaF_2 , and it is only for samples with the size of 20 nm that it does decrease by 1.5 times. The luminescence intensity of self-trapped excitons decreases by an order of magnitude when nanoparticles 20 nm in size are used instead of a single crystal. The sizes of the given nanoparticles (20–100 nm) substantially exceed the diffusion length of the core hole (about 1.5 nm), which explains the relative stability of CVL intensity. The luminescence intensity of STE decreases starting from a nanoparticle size of 80 nm. The critical size of barium fluoride nanoparticles, for which the luminescence intensity of STE decreases sharply, is about 50 nm. This size is comparable with the thermalization length of photoelectrons (30–100 nm) in fluorides [35].

BaF_2 :Ce nanoparticles were obtained and studied in a number of works [37, 38]. The BaF_2 :Ce nanoparticles obtained in [37] with a size of 18 ± 3 nm had a cerium luminescence band with a maximum at 370 nm; in this case, the core-valence and exciton luminescence bands were absent. The luminescent characteristics of BaF_2 :Ce nanoparticles ranging in size from 1 to 30 nm were considered in [38]. The samples had a wide luminescence band with a maximum at 355 nm. The maximum luminescence intensity was achieved for cerium content of about 15%. The optimal concentration of Ce^{3+} ions in the nanopowders was higher compared to single crystals, which the authors attributed to the decrease in the number of

defects (traps) with decreasing nanoparticle size of nanoparticles.

Using composites. Nanoparticles with good scintillation properties are difficult to use as radiation detectors. Composites consisting of heavy inorganic micro- and nanoparticles and ultrafast organic phosphors are used to synthesize bulk scintillators. The inorganic (“heavy”) particles in a composite scintillator efficiently absorb ionizing radiation, while part of the absorbed energy is transferred to organic molecules in contact with the particles, with nanosecond scintillation pulses then induced in the molecules. A polymer based on polystyrene activated with PPO (2,5-diphenyloxazole) and POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene) scintillators is usually chosen as an organic binder, since it has fast (less than 2 ns) scintillations.

Barium fluoride has a low refractive index $n = 1.478$ at a wavelength of 500 nm, which is convenient for combining it with a polymer matrix. BaF_2 :Ce nanocomposites were prepared in [38] using epoxy resins. The light yield of the BaF_2 :15%Ce composite was approximately 5 times higher than that of the BaF_2 :2%Ce crystal.

Zinc oxide is known as an effective scintillator with a subnanosecond luminescence time (like BaF_2). Bound excitons are responsible for its luminescence [39]. Zinc oxide (ZnO) nanoparticles 7.5–30 nm in size were successfully embedded into a barium fluoride film in [40]. Radiofrequency magnetron sputtering with subsequent thermal annealing of the samples was used for this purpose. Barium fluoride has a low refractive index compared with zinc oxide (whose refractive index is $n \approx 2.4$), contributing, it is believed, to formation of optical waveguides in the crystal. It was established that the intensity of the subnanosecond ZnO luminescence component in BaF_2 increases significantly with annealing temperature increasing from 400 to 800°C [40].

Synthesizing ceramics. Attempts have been made in the recent years to improve kinetic and other characteristics of barium fluoride by creating ceramics, including nanoceramics [23, 41]. Notably, ceramics have a number of advantages over single crystals, in particular, high mechanical and thermal strength.

Optical ceramics of barium fluoride was prepared by hot-pressing and thermoforming using the K-2718 system (INKROM CJSC) [23, 41]. Maximum transparency of ceramics in a wide optical range was achieved by varying

two main parameters: temperature and degree of deformation. To increase the intensity of the fast component and reduce the decay constant of the slower component, the ceramics was annealed in gaseous carbon tetrafluoride CF_4 for 24 hours at a temperature of about 1180°C . As a result, the transparency of the ceramics obtained was comparable to the transparency of the corresponding single crystal in the visible spectral region and slightly lower than that in the short-wave region ($\lambda < 250 \text{ nm}$).

Using filters and other devices. Subnanosecond luminescence of barium fluoride can be induced with a suitable UV filter, however, as a rule, the filter reduces the luminescence intensity. A special short-wave filter has been developed recently, suppressing the slow luminescence component of barium fluoride to 1% [42].

The so-called shifters, i.e., organic substances that shift the UV luminescence to a longer wavelength region are used to make the “fast” UV luminescence of barium fluoride more acceptable for photomultipliers that are sensitive in the visible region of the spectrum. Defenyl-anthracene, perylene, and other shifters were tested in [43]; using them helped increase the time constant to 2.5–7 ns, and decrease the light yield.

Since the decay times of the fast and slow components differ by almost 3 decimal orders, these components can be separated at the output of the photodetector using electronic devices. A schematic for such a device was proposed in [44].

Experimental procedure

The given crystals were grown by the Stepanov–Stockbarger method at INKROM. The obtained samples were classified as VUV crystals, i.e., as materials with high transparency in the short-wave region of the spectrum. Polished samples of single crystals prepared in the form of parallelepipeds $5 \times 10 \times 15 \text{ mm}$ in size were used for spectral measurements. The optical transmission spectra of the samples were recorded from the longitudinal size of the sample (15 mm) using a VMR-2 spectrophotometer. The luminescence spectra were captured with continuous X-ray excitation (40 kV, 14 mA). The detecting part of the setup contained an MDR-2 monochromator and a Hamamatsu H8259-01 photon counting system. Thermally stimulated luminescence (TSL) curves were measured in samples 1 mm thick. Before the

measurements, the samples were irradiated with an X-ray beam at a temperature of 80 K, and then heated at a rate of 0.3 K/min.

An X-ray source with the following parameters was used to measure the luminescence kinetics: 30 kV, 500 mA, pulse duration of 1 ns, and pulse repetition rate of 12 kHz [45]. The detecting part of the device was assembled by the standard start/stop scheme; the time resolution of the system was no worse than 50 ps. The luminescence spectra and kinetics were measured in reflection geometry: the angle between the direction of X-ray radiation and the photodetector was 90° . The measurements were taken at room temperature.

Experimental results and discussion

X-ray luminescence (XRL) spectra of BaF_2 and $\text{BaF}_2:\text{Tm}$ crystals are shown in Fig. 2. The spectra exhibit an intense exciton band with a peak at 310 nm and a core-valent luminescence (CVL) band with peaks at 196 and 220 nm; the spectra were not corrected for sensitivity of the setup, which means that the intensity of the CVL bands is actually higher. The low-intensity bands with peaks at 347, 360, and 450 nm (curves 2 and 3, Fig. 2) are responsible for the $f \rightarrow f$ electronic transitions in the thulium ion Tm^{3+} [28]. Evidently, the intensity of the exciton band decreases by 6 times when the thulium content is 0.5%, but the CVL intensity also slightly decreases. Introducing 2.0% of thulium leads to a decrease in the exciton band by 7 times, and CVL decreases by 1.6 times. Thus, the necessary (by more than 10 times) suppression of the exciton band cannot be achieved without a significant decrease in CVL for the $\text{BaF}_2:\text{Tm}$ crystal.

Inset to Fig. 2 shows the XRL decay curves recorded in BaF_2 and $\text{BaF}_2:\text{Tm}(0.5\%)$ crystals. It can be seen that the intensity of the slow XRL component of the doped compound is slightly lower than that of pure barium fluoride. The decay time constant of the slow component for thulium-doped sample is noticeably lower and is about 400 ns (while for pure barium fluoride it is 630 ns). As follows from the XRL spectra and kinetics, the effect of suppression of the slow component in $\text{BaF}_2:\text{Tm}$ begins with a thulium content of 0.5%.

The total optical transmission spectra of the crystals are shown in Fig. 3. The $\text{BaF}_2:\text{Tm}(0.5\%)$ spectrum contains a minimum at 260 nm, for which the ${}^3H_6 \rightarrow {}^5P_2$ electronic transition in the Tm^{3+} ion is responsible, as well as

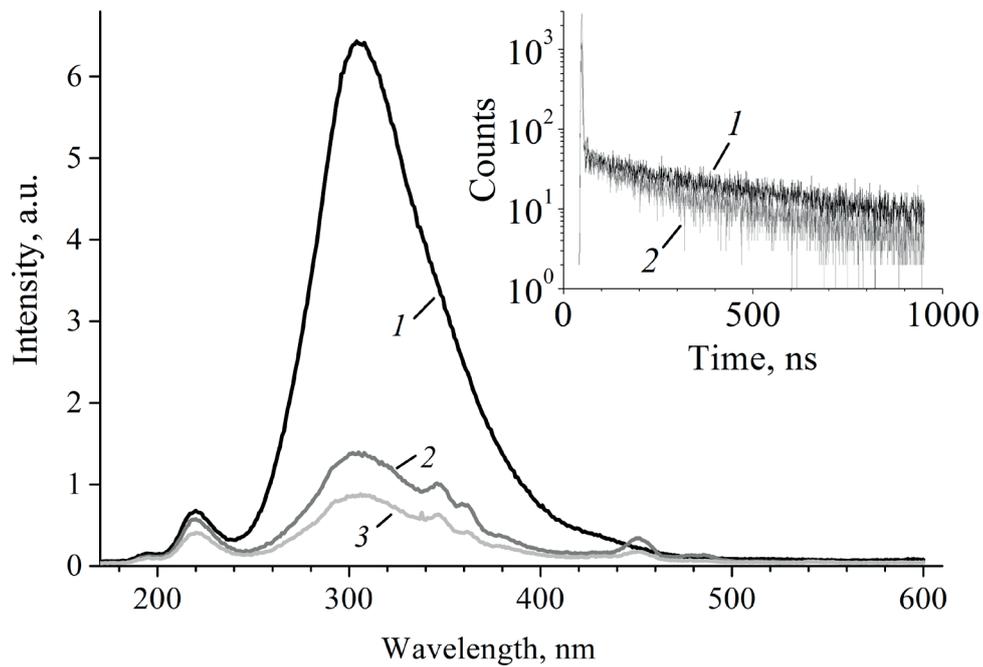


Fig. 2. X-ray luminescence spectra and kinetics of BaF₂ (1), BaF₂:Tm(0.5%) (2) and BaF₂:Tm (2.0%) (3) crystals

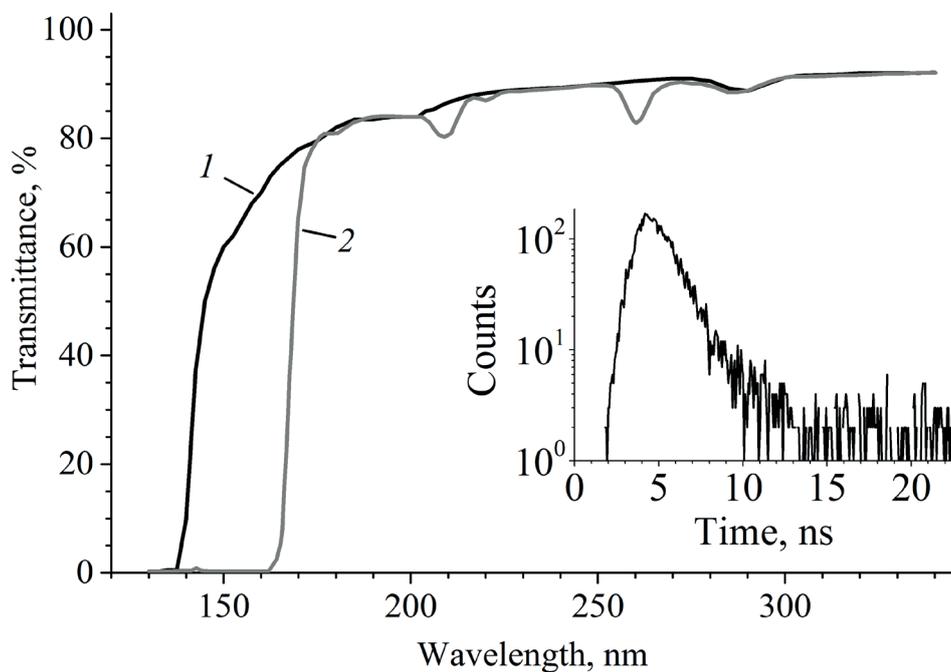


Fig. 3. Optical transmittance spectra for BaF₂ (1) and BaF₂:Tm(0.5%) (2) crystals; samples were 5 mm thick. Inset shows XRL kinetics of the BaF₂:Tm(0.5%) crystal, measured in a short time interval

a minimum of unknown origin at 208 nm. The $\text{BaF}_2:\text{Tm}(0.5\%)$ crystal 5 mm thick has rather high (more than 80%) transparency in the CVL region (175–260 nm), however it is lower than in pure barium fluoride (see Fig. 1). Therefore, introducing Tm^{3+} ions into BaF_2 worsens the conditions for fast luminescence (CVL) from the crystal, which is particularly important for large samples. Inset to Fig. 3 shows, as an example, the XRL kinetics curve of a $\text{BaF}_2:\text{Tm}(0.5\%)$ crystal, measured in a short time interval. The decay time of the fast component of the compound was 0.8 ± 0.1 ns.

It is known that radiation hardness of a material can be assessed by the intensity of thermally stimulated luminescence (TSL) peaks. Fig. 4 shows the TSL curves for BaF_2 and $\text{BaF}_2:\text{Tm}(1.0\%)$ crystals, measured after the crystals were irradiated with X-rays (40 kV) for 2 minutes. It can be seen that the non-activated crystal has an intense thermal peak with a maximum at 114 K. Such low-temperature peaks are characteristic for crystals of the fluorite group, reflecting the delocalization of V_k -centers. The low-temperature peak in the $\text{BaF}_2:\text{Tm}(1.0\%)$ crystal is located at 138 K, and thermal peaks are recorded in the region from 200 to 300 K, for which V_{kA} centers and aggregates of Tm^{2+} ions and interstitial fluorine

ions are responsible [46]. Additionally, a high-temperature peak is recorded at 453 K in $\text{BaF}_2:\text{Tm}(1.0\%)$, induced by deep traps. These traps may be involved in afterglow luminescence, impairing the scintillation properties of the crystal. The data obtained indicate that doping barium fluoride with Tm_{3+} ions worsens the radiation hardness of the crystal; the same conclusion was reached in [5].

Introducing Sc^{3+} ions into a BaF_2 crystal leads to significant suppression of the slow component; the corresponding XRL spectra have the form similar to that shown in Fig. 2. Fig. 5 shows the total transmittance spectra of the BaF_2 and $\text{BaF}_2:\text{Sc}(1.0\%)$ crystals. $\text{BaF}_2:\text{Sc}(1.0\%)$ exhibits a characteristic reduction in the transmission near 290 nm. We also recorded an absorption band at 290 nm in a $\text{BaF}_2:\text{Cd}$ crystal (not shown). Interestingly, this band is also observed when La^{3+} [5] and Y^{3+} ions are introduced into BaF_2 [14]. The nature of this band remains unknown; it can be argued only that substituting barium with an ion with a filled outer shell leads to a defect appearing in BaF_2 , producing absorption at 290 nm.

Inset to Fig. 5 shows the X-ray decay curves of BaF_2 and $\text{BaF}_2:\text{Sc}(1.0\%)$ crystals. A noticeable decrease in the integral intensity of the slow XRL component was registered in a

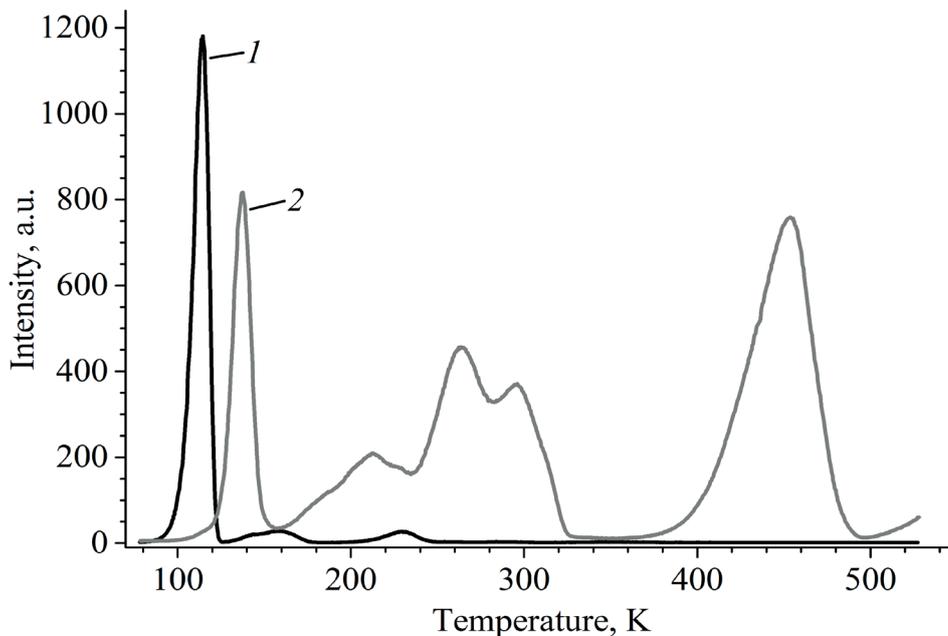


Fig. 4. Thermally stimulated luminescence curves for BaF_2 (1) and $\text{BaF}_2:\text{Tm}$ (2.0%) (2) crystals. Sample heating rate was 0.3 K/min

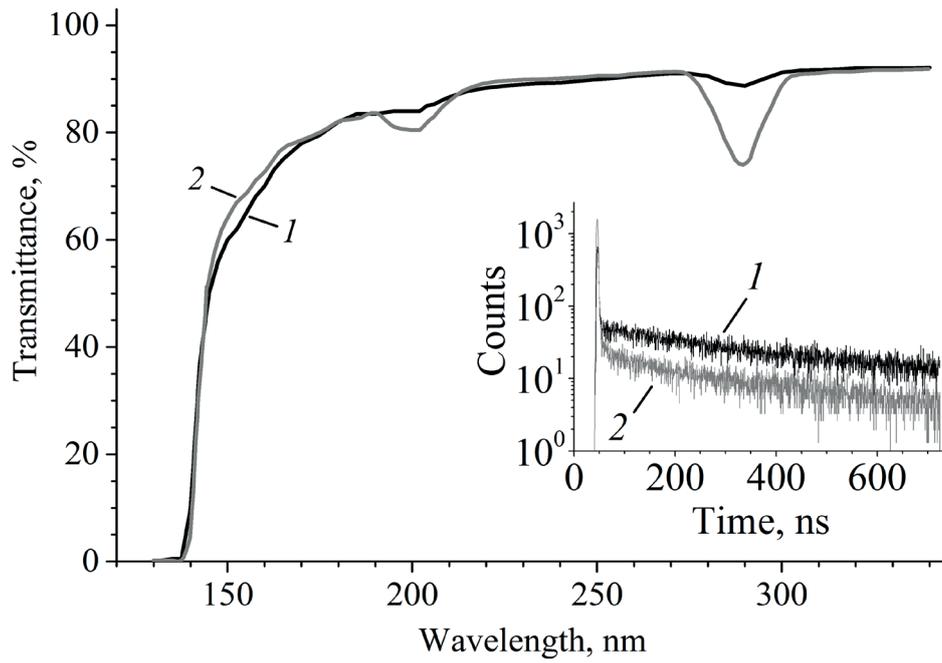


Fig. 5. Optical transmittance spectra and XRL kinetics (inset) of BaF₂(1) and BaF₂:Sc(1.0%) (2) crystals; spectra were collected for 5 mm thick samples

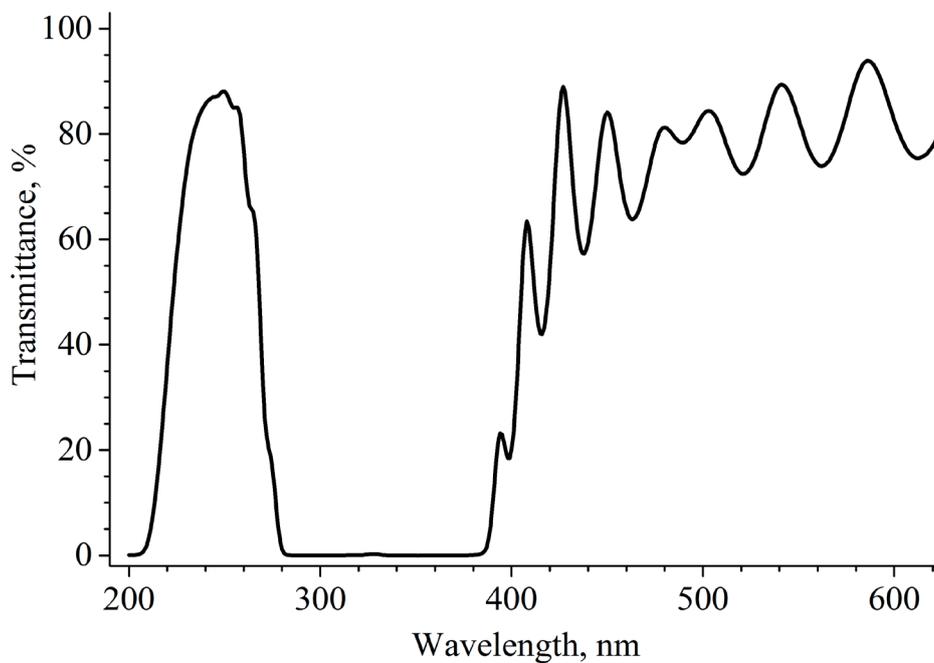


Fig. 6. Optical transmittance spectrum of multilayer filter sprayed on quartz glass



BaF₂:Sc(1.0%) crystal, as compared with pure barium fluoride. The time decay constant of the slow component of the sample doped with scandium is less than that of pure BaF₂ and is about 240 ns.

Another way to suppress the slow luminescence component is to use a filter that is transparent in the spectral region of CVL and opaque in the region of exciton radiation of BaF₂. Fig. 6 shows the transmission spectrum for a filter of this type, obtained by layer-by-layer sputtering of rare-earth oxides on a quartz substrate. Apparently, the transparency of the filter in the region of the main OVL peak (220 nm) is 50%, and is close to zero near the exciton luminescence peak (310 nm).

Conclusion

We have conducted a series of experiments and analyzed the data given in literature, concluding that suppressing the slow component of X-ray luminescence in barium fluoride by introducing a dopant seems insufficiently effective. Introducing trivalent ions leads to defects forming, in particular in interstitial fluorine ions. The crystal structure of divalent ions is typically distorted. Suppressing the slow com-

ponent of luminescence by introducing dopants into BaF₂ has the following disadvantages:

required decrease in the intensity of the slow component (by more than 10 times) is accompanied by a substantial decrease in CVL;

doped crystal is generally less transparent than a pure one;

radiation hardness of barium fluoride typically deteriorates as dopants are introduced;

it is fairly difficult to uniformly distribute dopants in large crystals (the required length of BaF₂ samples for the new collider is more than 20 cm).

Studies of nanoparticles, nanoparticle-based composites and ceramics aimed at obtaining the optimal ratio of intensities of the fast and slow luminescence components of BaF₂ have not yielded satisfactory results either.

We have found that using a filter that is transparent in the spectral region of CVL and opaque in the region of exciton luminescence of BaF₂ is the most effective method to suppress the slow component of luminescence. Such a filter can be sprayed directly onto the surface of the output window of the BaF₂ sample.

We plan to assemble and test a system that includes a BaF₂ scintillator with a filter and a solid-state photodetector.

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