Physics of the Solid State, 2025, Vol. 67, No. 8

09,10,16

Spectral characteristics of crystals and nanoceramic based on BaF_2:Ce^{3+}

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Received May 27, 2025
Revised July 7, 2025
Accepted July 15, 2025

Gamma-luminescence (GL) of the BaF_2:Ce^{3+} single crystals and nanoceramic based thereon is comparatively studied. During γ-irradiation of the crystals and the ceramic samples within the spectral range 300−350 nm we observed an intense doublet GL band with the maximums at 308 and 322 nm, which is typical for $f-d$-transitions of the Ce^{3+} ions. As a result of γ-irradiation we obtained an effective cerium luminophore based on the optical fluoride ceramic.

Keywords: fluoride crystals, nanoceramic, gamma-luminescence, photoluminescence, excitation spectra.

DOI: 10.61011/PSS.2025.08.62277.146-25

1. Introduction

The barium fluoride crystals (BaF_2) have a number of unique physical properties such as a high density (4.89 g/sm^3), a high melting point (1386 °C), non-hygroscopicity, high thermal conductivity (11.72 W/m · K at 286 K), relative simplicity of processing and polishing as well as low cost of raw materials. These characteristics make BaF_2 one of the most promising and high-speed scintillation materials [1–3].

During excitation by ionizing radiation, the BaF_2undoped crystals exhibit core-valence luminescence within the region of 220 nm due to recombination of a core hole with a valence band electron and intrinsic radiation within the spectral range 250−320 nm, which is attributed to an autolocalized exciton [4]. Presence of a super-fast glowing component with the disintegration time of 0.6 ns and an emission component at 220 nm in the BaF_2 crystal makes it possible to create ionizing radiation detectors with high time resolution (up to 110 ps) [2,5]. But integral intensity (it is light yield (LY) for scintillators) of this fast component is not large in barium fluoride. Besides, the radiation spectrum of BaF_2 exhibits an exciton band ($\lambda \approx 300$ nm) with undesirably long decay time (600−800 ns) [6,7]. Two main approaches were proposed for solving the said problems:

1. Doping BaF_2 with dopants, in particular, La^{3+} ions that suppress a long component of the autolocalized excitons [8], wherein their action mechanism is not yet fully understood.

2. Introduction of an activator that transforms exciton radiation into faster activator glowing. The most natural choice was Ce^{3+} that is widely applied in the scintillation crystals, since luminescence of trivalent cerium that occurs instead of ALE radiation is characterized by a relatively short decay time (20−70 ns) due to $d-f$-transitions [5,9].

The absorption spectra of the unirradiated BaF_2:Ce^{3+} crystals exhibit intensive absorption bands with maximums at 205 and 285 nm, which are caused by $f-d$-transitions of the Ce^{3+} ion. During excitation within the band of 285 nm, bands with the maximums 305 and 320 nm are recorded in the photoluminescence (PL) spectrum of the unirradiated BaF_2:Ce^{3+} crystal. No other bands of absorption and photoluminescence are detected within the spectral range 200−800 nm for the unirradiated BaF_2:Ce^{3+} sample [10,11].

The concentration dependence of intensity of X-ray luminescence (XL) of trivalent cerium in the BaF_2:Ce^{3+} crystals exhibits a maximum with the Ce^{3+} content of 0.1 mol.%. With further increase of the cerium concentration, the intensity of X-ray luminescence is reduced [4].

A significant problem that prevents wide application of the alkaline earth fluorides as scintillators is their low light yield [12].

Researchers have recently increased their interest to optical ceramic materials, including materials based on alkali-earth fluorides, as active media for lasers and scintillators [13,14]. Substantial improvement of the mechanical characteristics has been demonstrated for the fluoride optical ceramic: microhardness increased by 15 % and fracture resistance K_{1c} increased in 4−6 times [15]. A significant increase in UV luminescence light yield and radiation resistance was recorded for the known BaF_2:Ce^{3+} scintillator [10,16] when transitioning from single crystals to a ceramic [10,17,18]. These results stimulate searching and designing effective optical materials for lasers and scintillators. Moreover, it is shown that conversion of BaF_2 from a single-crystal form into a ceramic form (for example, by hot uniaxial deformation) can result in suppression of the slow exciton component (~ 310 nm) without variation of intensity of the fast component (~ 220 nm), thereby additionally applicability of these materials in the high-speed detectors [19].

Luminescent materials based on barium fluoride that is activated by cerium ions attract increased attention due to their promising characteristics for use in radiation detection, scintillation systems and photonics. Some studies were undertaken to investigate in detail luminescent properties both of the single crystals and the ceramic based on BaF_2:Ce^{3+}, including the influence of dopant additives on spectral parameters and kinetics of luminescence [12,16,18]. The obtained data made it possible to identify main laws of formation of a luminescent response in a dependence on a composition and a structure of the material.

However, despite an accumulated scope of information a behavior of the said materials under effect of high doses of ionizing radiation is still understudied. This is especially true for radiation-induced changes of the luminescent characteristics, which play a key role when operating the materials under conditions of a hard radiation environment.

In this regard, the present study is aimed at comparatively analyzing spectral and radiation-optical properties of the BaF_2:Ce^{3+} single crystals and the respective optical nanoceramic after irradiation by γ-quanta of the ^{60}Co isotope. This approach makes it possible to identify particular features of radiation stability and mechanisms of degradation of luminescence in a dependence on a material morphology.

2. Research samples and methodology

The BaF_2 crystals dope with 0.12 mol.% CeF_3 were grown by vertical directional solidification [20]. Lead fluoride was used as a fluorinating agent. The ceramic was produced by hot pressing [21] from a powdered precursor prepared according to the method described in the papers [22,23]. The base of the precursor is barium hydrofluoride BaF_2HF, which releases a fluorinating agent HP during heat treatment. Cerium fluoride dissolves in the matrix during the sintering process [24]. The surfaces of the samples were optically treated before the measurements (Figure 1). They were irradiated by γ-quanta of the ^{60}Co source with the average energy $E_\gamma \approx 1.25$ MeV and power of 125 rad/s in a gamma installation belonging to Institute of Nuclear Physics AS RUz.

Gamma-luminescence (GL) of the samples was studied at the temperature of 300 K in a modified installation described in the study [25]. Gamma-luminescence was excited by gamma radiation from the ^{60}Co source. The GL spectra were not corrected taking into account spectral sensitivity of a recording system.

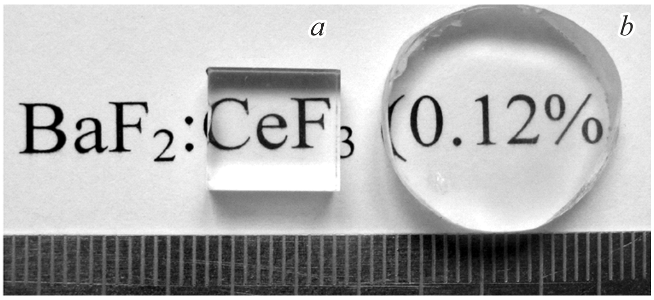

Figure 1. Appearance of the studied samples of the single crystal of and (*a*) and the ceramic of (*b*) BaF_2:Ce^{3+}.

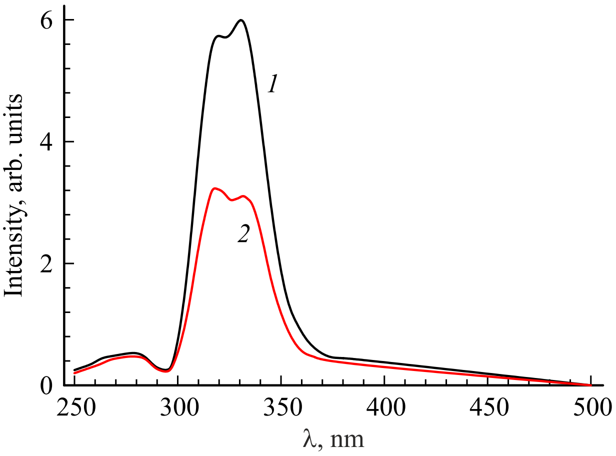

Figure 2. Spectra of gamma-luminescence of the BaF_2-CeF_3 sample at the room temperature: *1* — the unirradiated sample, *2* — the sample irradiated by gamma quanta of the dose of 10^7 rad.

3. Experimental results and discussion thereof

When being excited by γ-radiation, both the crystalline as well as the ceramic samples exhibit gamma-luminescence (GL). In the single crystals, within the spectral interval 300−350 nm we recorded the intense doublet GL band with the maximums around 308 and 322 nm that are typical for $f-d$-transitions of the Ce^{3+} ions (Figure 2, the curve *1*). The intensity of both the bands are almost the same. Besides, an exciton radiation component is detected in the spectrum and it is a band with a maximum at 270 nm.

The ceramic samples exhibit the same GL bands as in the single crystals. At the same time, the intensity of the band at 332 nm in the ceramic is approximately in two times higher than in the single crystal. In the BaF_2-CeF_3 ceramic samples, the band at 308 nm is manifested as a shoulder of the band of 322 nm (Figure 3, the curve *1*). Generally, the shape of the GL spectra of the crystals and the respective ceramic samples is quite similar.

The study [18] provides spectra of X-ray luminescence (XL) of the crystal and the ceramic based on BaF_2:Ce^{3+}. It is found that the shape of the XL spectra of these materials is almost identical, but XL light yield of the BaF_2:Ce^{3+} ceramic is approximately in 1.5 times higher than that of the respective single crystal.

The absorption spectra (AS) of the BaF_2:CeF_3 crystals exhibit intensive absorption bands (AB) with maximums at 205, 285 nm, which are caused by $f-d$-transitions of the Ce^{3+} ions. In addition to these bands, the absorption spectra of the ceramic samples also exhibit additional bands within the region 250 and 282 nm [10,11].

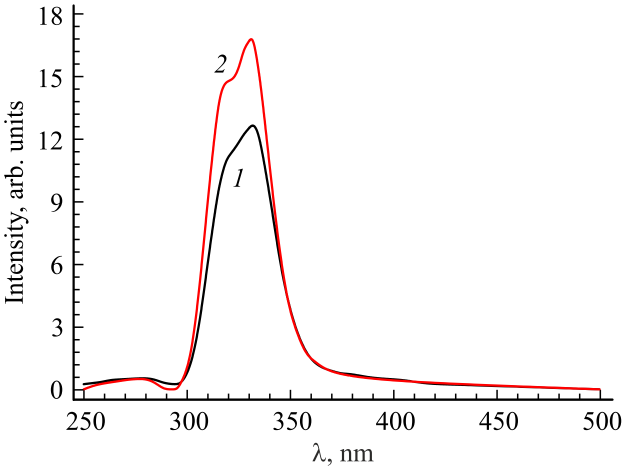

Figure 3. Spectra of gamma-luminescence of the BaF_2-CeF_3 ceramic at the room temperature: *1* — the unirradiated sample, *2* — the sample irradiated by gamma quanta of the dose of 10^7 rad.

The study [11] investigates photoluminescence of the BaF_2:Ce^{3+} single crystals as compared to the nanoceramic based thereon. In the single-crystal samples, during excitation within the band $\lambda_{ex} = 285$ nm only a PL doublet band with the maximums at 305 and 320 nm, which corresponds to the Ce1 centers, is detected. Unlike this, in addition to the said doublet, additional luminescence bands that correspond to various types of cerium centers were recorded in the optical nanoceramic: the Ce2 centers ($\lambda_{ex} = 310$ nm, $\lambda_{rad} = 370$ nm), the Ce3 centers ($\lambda_{ex} = 250$ nm, $\lambda_{rad} = 425$ nm) and the Ce4 centers ($\lambda_{ex} = 345$ nm, $\lambda_{rad} = 550$ nm). The Ce1 centers are identified as isolated trigonal C_{3V}-centers, the Ce2-centers — as paired cerium centers, the Ce3- and Ce4-centers — as cerium centers localized at grain boundaries and boundaries between nanolayers in the nanoceramic.

Complication of the spectra of absorption and photoluminescence in the ceramic samples as compared to the single crystals is related by the authors of the studies [11,26] to presence of the cerium ions in defective positions, in particular, at grain boundaries or in a region of dislocations.

As shown in the study [10], the single-crystal samples begin to be dyed under effect of γ-radiation even at the doses $\sim 10^5$ rad, whereas the ceramic samples demonstrate higher radiation resistance: no variation of their optical properties is observed up to the doses 10^8 rad. With gamma radiation by the dose of 10^7 rad, there is reverse dynamics of variation of intensity of gamma-luminescence: it is reduced in the single crystals (Figure 2, the curve *2*), while in the nanoceramic it increases, on the contrary (Figure 3, the curve *2*). The similar result was previously found in the study [27], too, but a cause of this phenomenon was not identified. It is found in the present study that under effect of irradiation the ceramic samples not only get dyed, but their luminescent properties are even significantly improved.

As shown in some studies [28–33], metastable Frenkel pairs of defects, which occur under irradiation of various solid-state materials (metals, alloys, semiconductor and dielectrics), significantly affect their properties. During irradiation, these unstable pairs of defects are formed with a frequency that is by 1–2 orders higher than that of stable defects and, therefore, they manage to significantly affect processes of radiation-induced migration of point defects, phase transformations and general evolution of radiation damages.

One of the typical manifestations of effect of such unstable defects is a phenomenon of „radiation shaking“ of the crystal. In terms of its consequences, it is similar to effects caused by a temperature increase, but it is pronounced much more strongly [29,30,33]. It was shown on the example of the ion crystals of KBr and LiF that under irradiation by pulsed electron beams at high temperatures (more than 700 K) a diffusion constant increased in 10-10^3 times as compared to its value at purely thermal diffusion [33]. A mechanism of this phenomenon is as follows: when the Frenkel pairs of radiation defects are created and annihilated, local changes of the volume occur in the crystal, and they result in origination of elastic stress waves. These waves interact with existing point defects and cause activationless migration of interstitial atoms and their annihilation with the vacancies. As a result, the defects are not accumulated. On the contrary, their number is reduced and the material structure approaches a more balanced state as compared to the initial one [29,30,33]. The proposed mechanism was confirmed both in some numerical modelings [34,35] and real physical experiments [36–42]. It is found that a so-called effect of small doses exists ($D = 10^3 - 10^7$ rad), at which there is rebuilding and ordering of the crystal structure, unlike an effect of large doses. It is due to release of the crystal-accumulated energy as a result of chain reactions of defect annihilation, which are initiated by ionization. A transition of the unbalanced, more disordered material into the equilibrium state is accompanied by improvement of some of its physical properties: by variation of a trap concentration, improvement of conductivity [39,42], an increase of lifetime of minority charge carriers [40], etc.

The performed studies identified fundamental differences in the radiation-induced behavior of the single-crystal and ceramic samples of BaF_2:Ce^{3+}. In particular, after γ-irradiation the single crystals exhibit significant reduction of intensity of luminescence. It is due to effective formation of radiation defects that originate from nonradiative decay of the electron-excited states, thereby resulting in degradation of the luminescent centers and reduction of total light yield.

In contrast, the ceramic samples exhibit an increase of intensity of gamma luminescence after γ-irradiation. It is assumed that this effect is caused by a nanostructured morphology of the ceramic, which is characterized by a high initial degree of disordering in a region of intergranular and twin boundaries. Under effect of gamma radiation, the so-called „radiation shaking“ of the crystal lattice occurs and it is accompanied by generation of elastic stresses and activation of the defect annihilation processes. It results in structural ordering, reduction of a concentration of non-radiation recombination centers and an increase of efficiency of energy transfer to the activator Ce^{3+} centers. Thus, in case of the nanoceramic radiation effect does not result in degradation, but on the contrary, it contributes to improvement of its luminescent characteristics, thereby making this material promising for application in extreme radiation conditions.

4. Conclusion

The optical nanoceramic based on BaF_2:Ce^{3+} features not only higher radiation resistance, but demonstrates the increase of intensity of gamma luminescence after γ-irradiation. This effect is explained by structural rebuilding of the ceramic under effect of the so-called „radiation shaking“, which results in ordering of the defect structure and, consequently, amplification of the luminescent properties of the material. The detected additional luminescent centers localized at the grain boundaries emphasize an important role of the nanostructured morphology in formation of the spectral characteristics of the material. The obtained results make it possible to regard the γ-irradiated BaF_2:Ce^{3+} ceramic as a promising radiation-stable luminophore for application in the ionizing radiation detectors as well as in the optoelectronic devices that operate in the extreme conditions.

Funding

This study is financed from state budge funds of the Republic of Uzbekistan.

Acknowledgments

The authors would like to thank P.P. Fedorov for kind provision of the crystalline and ceramic samples.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by M.Shevelev