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Gamma-Luminescence of BaF_2:Ce^{3+} Optical Nanoceramics in Comparison with Single Crystals

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Abstract. Comparative studies have been carried out on the gamma-luminescence of BaF_2:Ce^{3+} single crystals and the corresponding nanoceramics. Under γ-irradiation, both crystalline and ceramic samples exhibit an intense doublet GL band in the 300–350 nm spectral range, with maxima at 308 nm and 322 nm, which are characteristic of the f–d electronic transitions of Ce^{3+} ions. The results demonstrate that γ-ray irradiation enables the formation of an efficient cerium-activated phosphor based on optical fluoride ceramics.

Key words: fluoride crystals, nanoceramics, gamma-luminescence, photoluminescence, gamma irradiation.

I. INTRODUCTION

BaF_2 crystals, combining high density, thermal stability, non-hygroscopicity, good thermal conductivity, ease of processing, and low raw material cost, are regarded as one of the most promising and rapidly developing scintillation materials[1,2].

When undoped BaF_2 crystals are excited by ionizing radiation, luminescence appears near 220 nm, originating from core–valence electronic transitions within the valence band. In the 250–320 nm spectral range, intrinsic emission is also observed, which is associated with self-trapped excitons [3].

The presence in BaF_2 of the ultrafast luminescence component with a decay time of 0.6 ns and an emission component of 220 nm makes it possible to design ionizing radiation detectors with a high (110 ps) time resolution [2,4]. However, in barium fluoride, the integral intensity (in the case of scintillators, this is the light yield (LY)) of this fast component is low. Moreover, the emission spectrum of BaF_2 contains an exciton band ($\lambda_m \approx 300$ nm) with undesirably long decay time (600–800 ns). The indicated problem has been solved by the two main methods:

1) The incorporation of an impuritie into BaF_2, in particular La^{3+}, which suppresses the long-term component of self-trapped excitons [5], the mechanism of which has not yet been reliably established;

2) The introduction of an activator transforms the exciton emission into a faster activator luminescence. The Ce^{3+} impurity, which has been widely used in scintillation crystals, became a natural choice of an activator, since the luminescence of trivalent cerium, which appears instead of the self-trapped exciton (STE) emission, has a fairly short (20–70 ns) decay time (d–f transitions) compared to the STE luminescence [4,6].

The absorption spectra of unirradiated BaF_2:Ce^{3+} crystals contain intense absorption bands at 205 and 285 nm, which are responsible for the f–d transitions of Ce^{3+} ion. Under excitation in the 285 nm band of non-irradiated BaF_2:Ce^{3+} crystal, the photoluminescence (PL) spectrum shows bands with maxima at 305 and 320 nm. In the spectral range 200–800 nm of an unirradiated BaF_2:Ce^{3+} crystal, no other absorption and PL bands were detected [7,8].

The concentration dependence of the X-ray luminescence (XL) of cerium in BaF_2:Ce^{3+} crystals has an intensity maximum at 0.1 mol.%, and a further increase in the cerium concentration causes the XL intensity decrease [3].

A significant problem that hinders the widespread use of alkaline earth fluorides as scintillators is their low light yield [9].

Recently, the interest of researchers in optical ceramic materials (including those based on alkaline earth fluoride crystals) as active laser and scintillation materials has increased [10]. On fluoride optical ceramics, the possibility of drastically improving the mechanical characteristics was demonstrated: increasing microhardness by 15%, fracture toughness K_{1c} by 4-6 times [11]. For the well-known BaF_2:Ce^{3+} scintillator [7,12] was reported a significant increase in the UV luminescence light yield and radiation resistance in going from single crystals to ceramics [7,13,14]. All this stimulates the search and development of effective optical ceramic materials for lasers and scintillators.

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In this work, were carried out to reveal the specific features of the spectral and radiation-optical characteristics of BaF_2:Ce^{3+} single crystals and optical nanoceramics based on it, comparative studies of their luminescence characteristics under irradiation with gamma rays isotope ^{60}Co.

II. SAMPLES FOR RESEARCH AND RESEARCH METHODOLOGY

BaF_2 crystals doped with 0.12 mol.%. CeF_3 were grown by vertical directional crystallization [15]. As a fluorination agent used lead fluoride. Ceramics were produced by hot-pressing [16] precursor powder prepared as described elsewhere [17,18]. The key component of the precursor was barium hydrofluoride, BaF_2·HF, which releases HF as a fluorination agent during heat treatment. Cerium fluoride dissolved in the host fluoride in the course of sintering [19]. The samples were irradiated with gamma rays in a ^{60}Co source at the gamma-installation of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan at radiation doses of 10^5–10^8 rad.

The study of gamma-luminescence (GL) of the samples was carried out at a temperature of 300 K on a modified setup described in [20]. The GL was excited by gamma rays from a ^{60}Co source. GL spectra were measured using the MDR-12 monochromator, the luminescence was recorded using an FEU-106 photomultiplier tube in the range of 200–800 nm.

III. RESULTS AND DISCUSSION

Under the gamma irradiation, both crystal and ceramic samples emit GL. In single crystals in the spectral range of 300–350 nm, an intense doublet GL band is observed with a maximum at 308 and 322 nm, which are characteristic of the f–d transitions of Ce^{3+} ions (Fig. 1, curve 2). The intensity of these bands is almost the same. A part of the exciton emission manifests itself in the form of the band with a maximum at 270 nm.

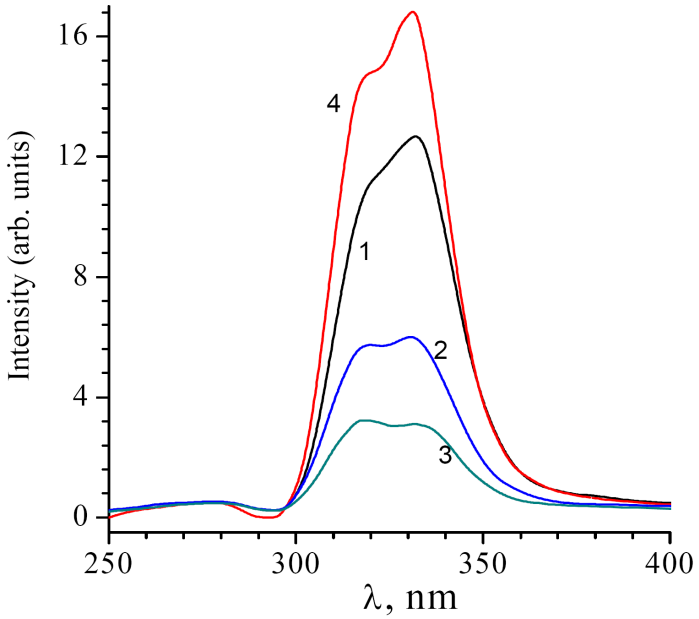


FIG. 1. Gamma-luminescence of the BaF_2:Ce (0.12 mol. %) crystal and ceramic at room temperature: 1,2- unirradiated, 3,4 - gamma-irradiated (10^8 rad).

In ceramic samples, the same GL bands are observed, while the intensity of the 332 nm band in ceramics is approximately 2 times higher than in a single crystal. In the BaF_2-CeF_3 ceramic samples, the 308 nm band is observed as a shoulder of the 322 nm band (Fig.1, curve 1). The shape of the GL spectra of crystals and corresponding ceramics is very similar. Similar results were also shown in [14]. The broad exciton band with a maximum near 270 nm is more intense in the crystal.

The absorption spectrum of BaF_2:CeF_3 crystals contains intense absorption bands with maxima at 205 and 285 nm, which are responsible for the f–d transitions of the Ce^{3+} ion. In the absorption spectra of ceramic samples, besides these bands, additional bands were found at 250 and 282 nm [7,8].

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In [8], the photoluminescence of BaF_2:Ce^{3+} single crystals and nanoceramics based on them have been comparative investigated. In single-crystal samples, upon excitation in the excitation band λ_{ex}=285 nm, only a doublet PL band with maxima at 305 and 320 nm (Ce1 centers) was found. In contrast, in optical nanoceramics, in addition to the above doublet, additional luminescence bands of the Ce2 (λ_{ex}=310 nm, λ_{rad}=370 nm), Ce3 (λ_{ex}=250 nm, λ_{rad}=425 nm) and Ce4 (λ_{ex}=345 nm, λ_{rad}=550 nm). Ce1 centers were identified as isolated trigonal C_{3V} centers, Ce2 centers were assigned to paired cerium centers, Ce3 and Ce4 centers were assigned to cerium centers in a complex with various defective states at grain boundaries and the boundaries between nanolayers in nanoceramics.

The complication of the absorption and PL spectra of ceramic samples compared to a single crystal is associated in [8,21] with the presence of cerium ions located in defective positions, namely, localized on grain boundaries or dislocations.

Studies have revealed that single-crystal samples under the action of gamma rays begin to color already at doses of 10^5 rad, and ceramic samples are radiation-resistant compared to crystals. They do not take on color when gamma-irradiated to a dose of 10^8 rad. Under the action of gamma irradiation with a dose of 10^8 rad , the intensities of GL in single crystals decrease (Fig. 1, curve 3), while in nanoceramics they increase (Fig. 1, curve 4). Earlier, a similar result was found in [22], but the reason for this phenomenon was not explained. In the present work, it was found that, under the action of irradiation, ceramic samples not only remain colorless, but even significantly improve their luminescent properties.

It is known [23–29] that metastable Frenkel pairs of defects created during irradiation in various solid materials (metals, alloys, semiconductor and dielectric materials) lead to a change in the properties of the irradiated material. During irradiation, such unstable pairs of defects are formed with a frequency 1–2 orders of magnitude greater than stable defects, and therefore have time to have a significant impact on the processes of radiation-stimulated migration of point defects, phase transformations, and the overall evolution of radiation damage. As one of the characteristic phenomena associated with unstable radiation defects, one can point to the "radiation shaking" of the crystal, which is similar in its consequences to the effect of elevated temperatures on materials. However, unlike thermal fluctuations, "radiation shaking" is expressed even more clearly [24,25,28, 29]. Using KBr and LiF ionic crystals as an example, it was shown that when samples are irradiated with pulsed electron beams at high temperatures (above 700 K), the diffusion coefficient increases by a factor of 10–10^3 compared to the thermal diffusion coefficient [27,28]. The essence of this phenomenon lies in the fact that during the creation and annihilation of Frenkel pairs of radiation defects, as a result of the resulting local change in the volume in the crystal, waves of elastic stresses arise. The interaction of these waves with existing point defects can lead to activationless migration of interstitial atoms and their annihilation with the corresponding vacancies, which does not lead to the accumulation of structural defects, but, on the contrary, to their elimination and transfer of the material to a more equilibrium state compared to the initial state [24,25,29].

The proposed mechanism was confirmed by the results of numerous computer [30,31] and real physical [32-38] experiments. It has been elucidated that there is a so-called effect of low doses (D=10^3–10^7 R), in which, in contrast to high doses, the crystal structure is rearranged and ordered due to the release of energy stored in the crystal as a result of chain reactions of defect recombination initiated by ionization. The transition of a nonequilibrium, more disordered material to an equilibrium state is accompanied by an improvement in a number of its physical properties: a change in the concentration of traps, an increase in conductivity [35,38], an increase in the lifetime of minority charge carriers [36] and etc.

We assume that when ceramic samples, which are characterized by a more disordered structure at boundaries between nanocrystals and twin regions, are irradiated with gamma rays, the crystal lattice orders due to "shaking" by irradiation, which leads to an increase in the intensity of gamma luminescence in the ordered regions of ceramics.

IV. CONCLUSION

The ceramic BaF_2:Ce samples are more radiation resistant than the crystals and do not take on color under gamma irradiated up to a dose of 10^8 rad.

The intensity of gamma luminescence in ceramics is higher than that of a crystal. After irradiation, the luminescence intensity in crystals decreases, and in ceramics it increases, which is due to the fact that when irradiating crystals, radiation defects are effectively created due to the nonradiative decay of electronic excitations, and in ceramics, due to the "shaking" of the crystal lattice by irradiation, their defective structure is ordered.

By irradiation with gamma rays, an efficient cerium phosphor based on optical fluoride ceramics was obtained.

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