NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (6), P. 752–756

X-RAY LUMINESCENCE OF BaF_2:Ce^{3+} POWDERS

S. Kh. Batygov, M. N. Mayakova, S. V. Kuznetsov, P. P. Fedorov
A. M. Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia
ppfedorov@yandex.ru

PACS 61.46

We studied the mechanism for the formation of cerium-activated barium fluoride scintillation ceramics and especially X-ray luminescence of its powdered precursors, prepared by co-precipitation of barium and cerium fluorides from aqueous solutions. We have found that the Ce^{3+} luminescence, which is typical for cerium (III)-containing ceramics and single crystals, was not observed for such polycrystalline precursors, and the intensity of barium fluoride's own luminescence decreases with increasing amounts of the cerium dopant in the specimens. We have interpreted our results as two-phase precipitation of barium hydrofluoride ($BaF_2 \cdot HF$) and cerium fluoride, respectively. Cerium (III) became incorporated in fluorite-type barium fluoride lattice only later, in the course of ceramics synthesis by the hot-pressing technique.

Keywords: Fluoride powder, nanoparticles, scintillators, X-ray luminescence.

Received: 30 October 2014

1. Introduction

The study of fluoride nanoceramics is one of the most promising areas of modern photonics [1–3], and barium fluoride is one of the most interesting and actively studied fast scintillators [3–8]. BaF_2 ceramics and single crystals exhibit two types of emission: a broad excitonic line with maximum near 300 nm (slow luminescence, $\tau = 600 - 800$ ns), and a short-wavelength line at 220 nm, corresponding to the superfast luminescence core-valence transitions ($\tau = 0.8$ ns). Addition of CeF_3 to the BaF_2 matrix leads to the transfer of exciton energy to cerium ion and powerful Ce^{3+}-luminescence at 300 – 350 nm [7, 9–12]. Because BaF_2:Ce^{3+} ceramics have an enhanced scintillation yield compared to the same composition single crystals [11, 12], we have developed a technology for the further improvement of its optical quality that included precipitation of barium hydrofluoride $BaF_2 \cdot HF$ from aqueous solutions followed by its thermal decomposition with HF evolution. The latter has been found to be an active fluorinating reagent that eliminated oxygen impurities from the batch materials [13, 14]. Thus, the topic of the present paper concerns the influence of cerium doping on the synthesis of barium fluoride scintillation ceramics and its precursors.

2. Experimental

99.99 wt. % pure $Ba(NO_3)_2$, $Ce(NO_3)_3$, HF and doubly-distilled water were used as starting materials. All precipitation experiments were carried in polypropylene reactors at room temperature under air. All samples were prepared by co-precipitation from aqueous solutions [13–15]. Premixed corresponding amounts of starting 0.17 M metal nitrate solutions (Ce/(Ce+Ba) (molar ratios varied from 0.01 to 1%) were treated in a dropwise manner with concentrated aqueous HF under vigorous stirring. The HF content in the formed matrix solution was maintained at about 47 vol. %. Formed precipitates were additionally treated with conc. HF, decanted, thoroughly washed with doubly-distilled water and dried under air at 40 °C.

Further thermal treatment included heating of the synthesized precipitates at 10 °C/min to 550 °C followed by 1-hour annealing at the same (550 °C) temperature under air.

The phase composition of the synthesized samples was determined by X-ray diffraction analysis (Bruker D8 diffractometer, CuKα radiation, TOPAS software for lattice parameter calculations and profile treatment of the X-ray diffraction pattern lines). All sample X-ray-initiated luminescence spectra were recorded at room temperature (KSVU spectrometer, Cu anode, 10 kV , 10 mA).

3. Results and discussion

Typical X-ray diffraction patterns of the synthesized samples are presented in Fig. 1.

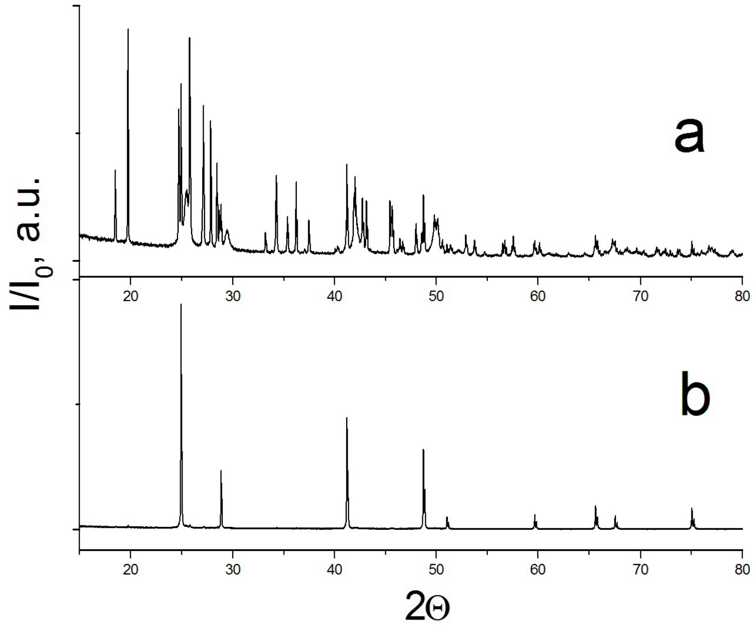

FIG. 1. Typical X-ray diffraction patterns of barium fluoride samples: monoclinic $BaF_2 \cdot HF$ [13, 14] precipitated by HF from aqueous solution at room temperature (a); and the same sample after its washing with water, cubic BaF_2 (b)

All barium difluoride samples had a_0 = 6.189 – 6.200 Å lattice parameters that were in a good agreement with the known literature data for pure BaF_2 [15].

These precipitates did not exhibit any luminescence without additional treatment, but after annealing at 550 °C, intrinsic BaF_2 produced luminescence at 320 nm if excited by X-ray radiation (Fig. 2; for comparison, please see there a similar spectrum of monocrystalline BaF_2, too).

Lines in both spectra have about the same maximum wavelengths (its location for the single crystals is associated with self-trapped exciton irradiation), and luminescence intensity for the powdered BaF_2 batch is comparable to that of single crystals.

The luminescence spectra for cerium-doped BaF_2 batch powders are presented in Fig. 3.

The addition of cerium to BaF_2 samples decreases the intensity of its own line at ca. 320 nm, but – in contrast with cerium-doped single crystals and ceramics – such spectra also lack of Ce^{3+}-related luminescence lines (i.e., lines attributed to Ce^{3+} ions in BaF_2 matrix) (Fig. 4).

0.1% Ce-doped ceramics and single crystals have BaF_2-related luminescence almost completely suppressed, and the only lines visible in the luminescence spectra are those related

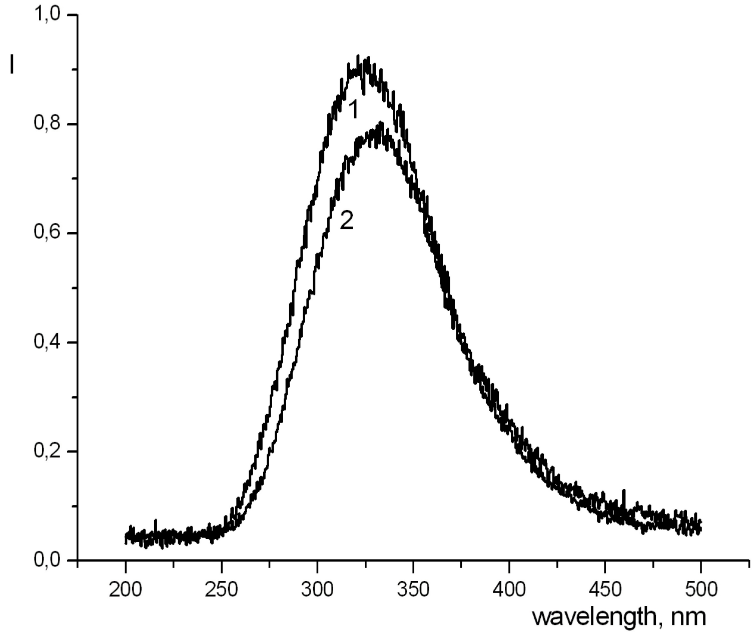

FIG. 2. X-Ray luminescence spectra of intrinsic BaF_2: single crystal (1) and powder (2) (recorded under the same ambient conditions)

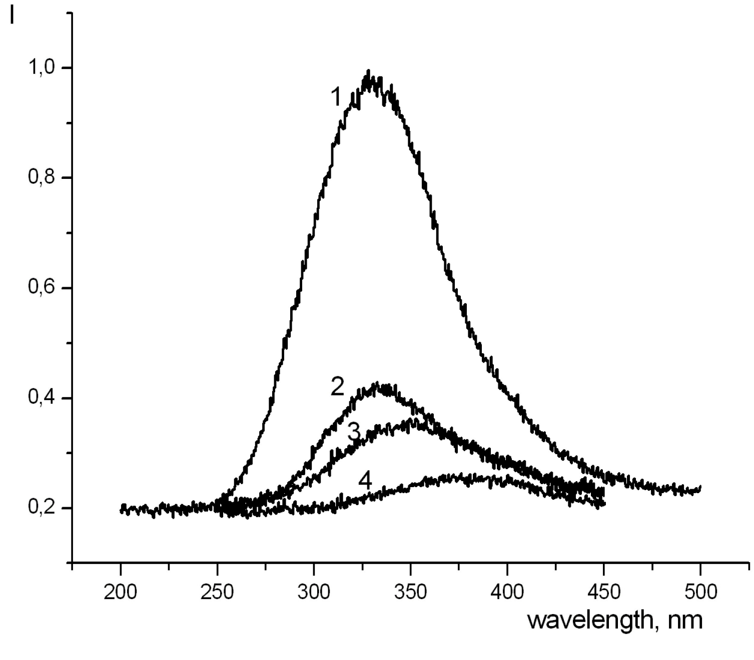

FIG. 3. Luminescence spectra of intrinsic (1) and cerium-doped BaF_2 batch powders: 0.01% Ce (2), 0.1% Ce (3), and 1% Ce (4)

to the $5d-4f$ transitions in Ce^{3+} ions [8–12]. However, our cerium-doped BaF_2 batch samples did not exhibit such Ce^{3+}-related lines, and suppression of the BaF_2-related luminescence line was much less than expected. Also, increasing the cerium concentration in the doped samples caused a shift of the line toward the higher wavelength part of the spectrum (Fig. 3). The negligible influence of cerium dopant on BaF_2 luminescence and lack of Ce^{3+}-related lines in

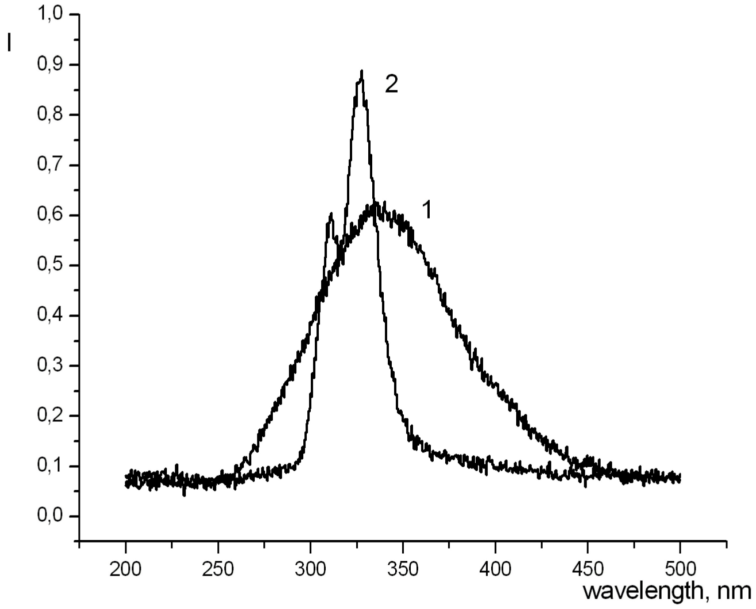

FIG. 4. X-ray luminescence spectra of polycrystalline (1) and ceramic (2) BaF_2 – 0.1% Ce

the recorded spectra may indicate that cerium did not get incorporated in BaF_2 matrix during precipitation (co-precipitation) from aqueous solutions and formed an additional solid phase.

4. Conclusions

1. X-Ray radiation excitation produces luminescence at ca. 320 nm in co-precipitated barium-cerium fluoride powders, which is typical for intrinsic BaF_2 and is usually associated with the auto-localized exciton in intrinsic BaF_2 single crystals and BaF_2 ceramics (intensity of such lines for monocrystalline and polycrystalline (ceramic) BaF_2 is about the same under similar conditions).
2. Doping of BaF_2 with cerium during their co-precipitation from aqueous solutions leads to a decrease in the intensity of the BaF_2-related luminescence line, and there is no cerium-related luminescence line observed (in contrast to the same composition BaF_2:Ce ceramics or single crystals).
3. The latter indicates that co-precipitation of BaF_2 and CeF_3 from aqueous solutions results in the formation of two separate fluoride phases, and cerium only becomes incorporated in fluorite-type BaF_2 crystalline lattice only during hot-pressing ceramics synthesis.

Acknowledgements

This work was supported by the Scholarship of the President of Russian Federation (SP-6467.2013.2) and RFBR grant No. 13-02-12162-ofi-m. Authors thank V. V. Voronov and R. P. Ermakov for their help with X-ray diffraction experiments.

References

[1] F.K. Volynets. Fabrication, structure, and physico-chemical properties of optical ceramics. *Opt. Mekh. Prom.*, **9**, P. 48–60 (1973) (in Russian).

[2] P.P. Fedorov. Fluoride laser ceramics. In: Handbook on solid-state lasers: materials, systems and applications. Ed. by B. Denker and E. Shklovsky. Oxford Cambridge Philadelphia New Delhi, Woodhead Publishing Limited, UK, P. 82–109 (2013).

[3] P.P. Fedorov, S.V. Kuznetsov, et al. Microstructure and scintillation characteristics of BaF_2 ceramics. *Inorganic Materials*, **50** (7), P. 738–744 (2014).

[4] P. Schotanus, P. Dorenbos, C.W.E. van Eijk, R.W. Hollander. Recent development in scintillator research. *IEEE Trans. Nucl. Sci.*, **36** (1), P. 132–136 (1989).

[5] M. Laval, M. Moszynaki, R. Allemand. Barium fluoride-inorganic scintillator for subnanosecond timing. *Nucl. Instrum. Methods*, **206** (1), P. 169–176 (1983).

[6] P.A. Rodnyi. Core-valence transitions in wide-band-gap ionic crystals. *Phys. Solid State*, **34** (7), P. 1975–1998 (1992).

[7] B.P. Sobolev. *Multicomponent crystals based on heavy metal fluorides for radiation detectors*. Barcelona: Inst. d'Estudis Catalans (1994).

[8] D.M. Seliverstov, A.A. Demidenko, et al. New fast scintillators on the base of BaF_2 crystals with increased light yield of 0.9 ns luminescence for TOF PET. *Nuclear Instruments and Methods in Physics Research A*, **695**, P. 369–372 (2012).

[9] P. Schotanus, P. Dorenbos, C.W.E. van Eijk, and R.W. Hollander. Recent development in scintillator research. *IEEE Trans. Nucl. Sci.*, **36** (1), P. 132–136 (1989).

[10] A.J. Wojtowicz, P. Szupryczynski, et al., Radioluminescence and recombination processes in BaF_2:Ce. *J. Phys.: Condens. Matter*, **12**, P. 4097–4124 (2000).

[11] Kh.S. Batygov, L.S. Bolyasnikova, et al. BaF_2:Ce^{3+} scintillation ceramics. *Doklady Physics*, **53** (9), P. 485–488 (2008).

[12] P.A. Rodnyi, S.D. Gain, et al. Spectral-kinetic characteristics of crystals and nanoceramics based on BaF_2 and BaF_2:Ce. *Phys. Solid State*, **52** (9), P. 1910–1914 (2010).

[13] A.A. Luginina, P.P. Fedorov, et al. Synthesis of $BaF_2 \cdot HF$ and BaF_2 from nitric solutions. *Nanosystems: Physics, Chemistry, Mathematics*, **3** (5), P. 125–137 (2012) (in Russsian).

[14] A.A. Luginina, A.E. Baranchikov, A.I. Popov, P.P. Fedorov. Preparation of barium monohydrofluoride $BaF_2 \cdot HF$ from nitrate aqueous solutions. *Mater. Res. Bull.*, **49** (1), P. 199–205 (2014).

[15] P.P. Fedorov, M.N. Mayakova, et al. Co-Precipitation of Yttrium and Barium Fluorides from Aqueous Solutions. *Mater. Res. Bull.*, **47**, P. 1794–1799 (2012).