SCINTILLATION PROPERTIES OF BaF_2:Cd, BaF_2, BaF_2:Ce, BaF_2:Sc, BaF_2:Tm CRYSTALS AND CERAMICS; NEW PHOTOSENSORS FOR THE VACUUM ULTRAVIOLET REGION

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1. Introduction

Research and development of new scintillation materials is mainly triggered by the growing needs of modern medical imaging, high energy and nuclear physics.

Pure BaF_2 crystals are widely applied as scintillation material because of its high density, high radiation resistance and good time resolution due to the fast component (< 1 ns) appearing in the emission bands around 220 and 195 nm. This fast component luminescence is called Auger-free luminescence or cross-luminescence, and it is attributed to the radiative recombination of the F-2*p* valence band electrons with the outmost holes of the Ba-5*p* core band.

However, in addition to the fast component, the BaF_2 crystal has a slow component at 300 nm with a decay time of about 700 ns, which causes deterioration of the time resolution at high counting rates. Suppression of the slow component is a crucial key when applying this crystal to high counting rate experiments in such fields as high energy physics and nuclear medicine.

This work is aimed to develop specimens of BaF_2-based crystals and ceramics doped with different elements in order to improve the light yield of the fast component and to suppress the slow part of the luminescence.

2. Experimental method

BaF_2 crystals were grown by the Stepanov – Stockbarger method, which provides high light transparency in the Vacuum UltraViolet (VUV) region. The optical transparency of our samples was measured with a SF-26 spectrophotometer in the wavelength range from 190 to 600 nm. We used an improved method of ceramics production from the BaF_2 powder with 40 to 60 nm nano particles by hot pressing in the CF_4 environment at a temperature of 1050 °C and under pressure of 200 MPa. The transparency of ceramics at 220 nm is only 11 % lower in comparison to that of single crystals, allowing to use them for measurements in the VUV region. However, such transmittance is insufficient for 20 mm length specimens and requires further improvements.

The luminescence spectra were measured under constant *X*-ray (40 kV) excitation. The registering equipment consisted of a MDR-2 monochromator and a FEU-106 photomultiplier. The obtained spectra were corrected for decreasing of the PMTs sensitivity in the wavelength range from 200 to 600 nm. In measurements of the luminescence kinetics, a pulsed *X*-ray (30 kV) source was used with the pulse duration shorter than 1 ns and a repetition rate of 12 kHz. The registering equipment was arranged according to the standard “start-stop” scheme, the time resolution of the system being better than 50 ps.

3. Results of measurements of optical properties of BaF_2 crystals and ceramics

3.1. Cd-doped BaF_2 crystals

The transmission curves within the range of 200–600 nm for pure BaF_2 and BaF_2:0.1%CdF_2 crystals are identical within the experimental error of 1 % (here and in the following, the percentage of the doped element is given in mol/%). In the case of ceramics, a slight decrease of the transparency in the UV range (200–300 nm) at a level of 3–5 % is observed. Increasing the Cd concentration to 0.3 % has virtually no effect on the sample transparency. The transparency of the BaF_2:0.1%CdF_2 sample is higher by 30 %, relative to that of the BaF_2 single crystal. A comparison of the total *X*-ray luminescence light yield for BaF_2:0.1%CdF_2 crystals and the corresponding ceramics shows that the light yield is 15 % higher in ceramics. A discovery of the strong dependence on the Cd concentration of the light yield in ceramics (clearly visible in Fig. 1) is a subject of interest. Changing the Cd concentration from 0.1 to 0.3 % in the

ceramics reduces the light yield by a factor of 5.4, while in the doped crystal it falls by a factor of 1.3 only. The optical parameters of the BaF_2:0.1%CdF_2 crystals and ceramics, which we determined for the first time, make these scintillators promising from the standpoint of obtaining high light yield for the fast component and reducing the intensity of the slow component relative to that of single BaF_2 crystals [1].

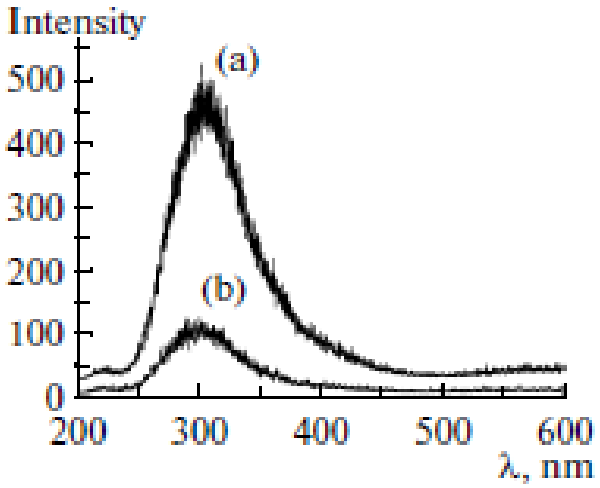

Fig. 1. Influence of Cd doping on the light yield of BaF_2:CdF_2 ceramics: a – 0.1%CdF_2; b – 0.3%CdF_2

3.2. BaF_2 single crystals and ceramics

A comparison of *X*-ray luminescence spectra for single BaF_2 crystals and ceramics shows an increase of the fast component yield in ceramics (as compared to BaF_2 single crystals) of about 12 % and a reduction of the slow component yield by a factor of 3.6 (Fig. 2a, b), which is observed for the first time. We suppose that the suppression of the slow component is caused by the non-irradiative annihilation of excitons on boundaries of nano particles in ceramics. Fitting the experimental data with two exponential decay curve $LY(t) = A_1\exp(t/\tau_1) + A_2\exp(t/\tau_2)$ gives $\tau_1 = 1.77 \pm 0.12$ ns and $\tau_2 = 493 \pm 6$ ns. A similar reduction of the time decay exciton component is observed in BaF_2 crystals doped with Cd [1, 2].

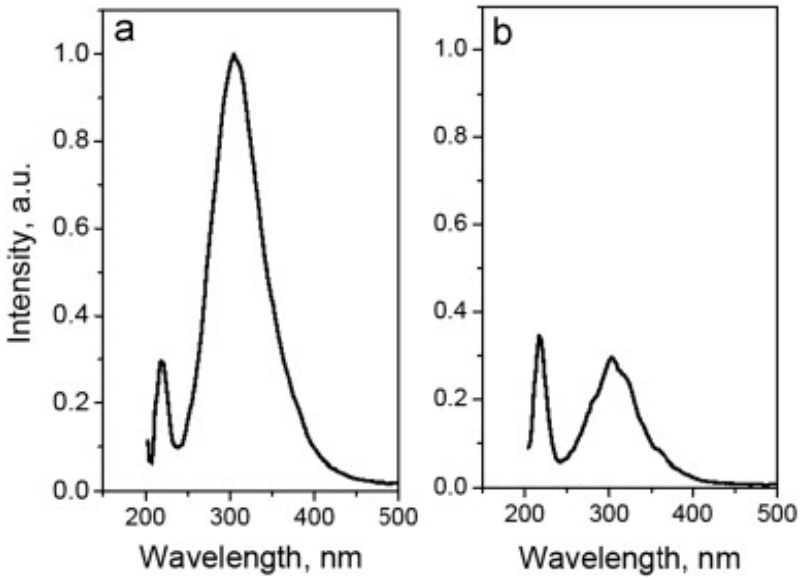

Fig. 2. *X*-ray luminescence spectra of a single BaF_2 crystal (a) and of ceramics (b)

3.3. Sc-doped BaF_2 single crystals and ceramics

BaF_2 single crystals and ceramics were doped with 0.5, 1.0 and 2.0 % Sc. The transparencies of $5 \times 10 \times 15$ mm^3 BaF_2:0.5%Sc and BaF_2:2.0%Sc crystals are close to that of single BaF_2 crystals with a slight absorption line at 290 nm. An increase of the Sc concentration from 0.5 to 2.0 % reduces the transparency at 220 nm by 8–10 %, which does not affect significantly other optical properties of the crystals. Doping the crystals with scandium (1%Sc, Fig. 3a, b) and annealing in CF_4 increase the relative light yield of the fast component by a factor 2.6, in comparison with that of single BaF_2 crystals.

Doping the BaF_2 crystals with scandium (1.0 and 2.0 %) does not change the decay time of the fast component ($\tau_1 = 2.0 \pm 0.5$ ns). The dependence of the light yield upon annealing in the CF_4 atmosphere of ceramics samples of dimensions $4 \times 4 \times 15$ mm^3 with the concentration 0.5 and 2.0 % of Sc was studied. Relative measurements showed an increase of the ratio of the fast to slow components yield by a factor from 1.7 to 2.5, as compared with single crystals [2].

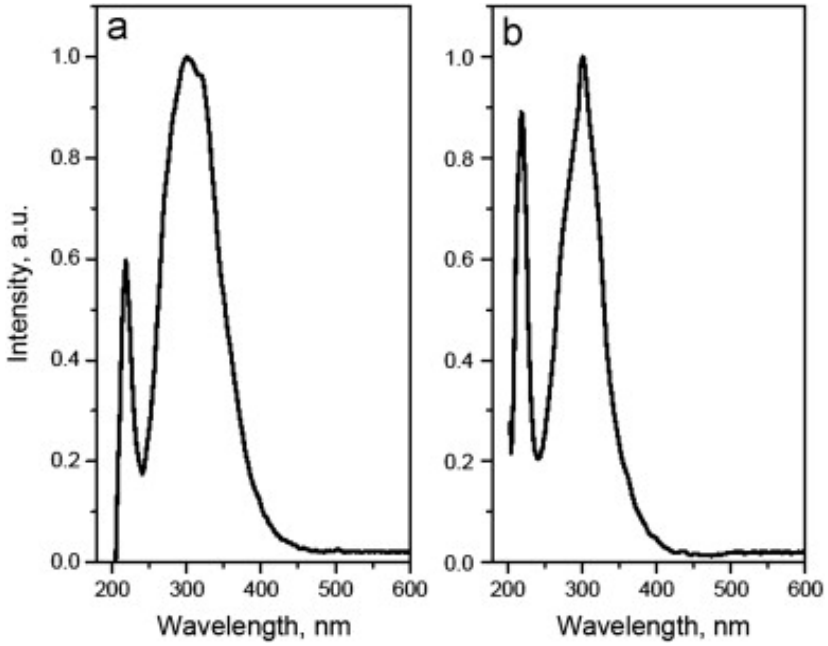

Fig. 3. Light yields of a single BaF_2 crystal without annealing in CF_4 (a) and of a BaF_2 crystal doped by 1%ScF_2 with annealing in CF_4 (b)

3.4. Tm-doped BaF_2 crystals

The main objective of our investigation of BaF_2 crystals doped with 0.5, 1.0, 2.0 and 3.0 % Tm was the development of crystal production technology and then its application to ceramics with the possibility of a four-fold increase of the fast component yield and accordingly a significant reduction of the slow component.

The transmission spectrum of BaF_2:3%Tm is more complicated than a similar BaF_2:Sc spectrum. The spectrum is characterized by three main bands of absorption caused by 4*f*–4*f* transitions in Tm^{3+} ions.

Figure 4 presents *X*-ray luminescence spectra of BaF_2 single crystals, pure and doped with Tm at a concentration of 0.5 %. One can observe an increased yield of the fast component and the corresponding suppression of the slow one, which is typical for all the studied samples. Fitting the experimental data with two exponential decay curve gives $\tau_1 = 1.34 \pm 0.06$ ns and $\tau_2 = 534 \pm 7$ ns [2].

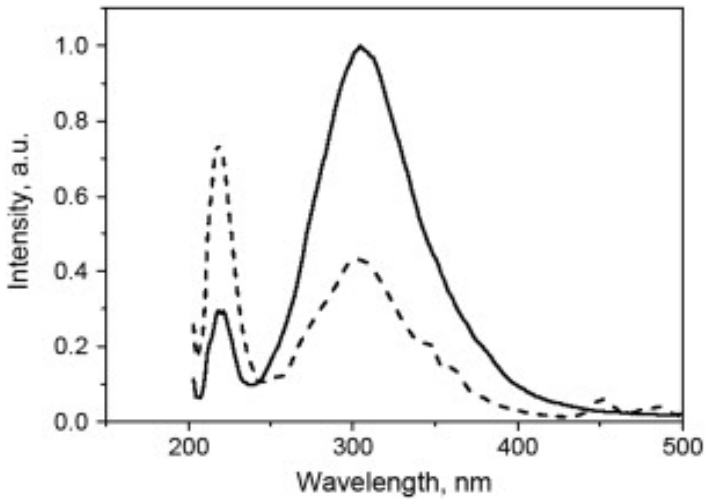

Fig. 4. *X*-ray luminescence spectra of a single BaF_2 crystal (solid line) and a crystal of BaF_2 doped with Tm (dash line). The BaF_2:0.5%Tm crystal has the light yield of the 0.9 ns component 2.4 times larger than that of a single BaF_2 crystal and the slow component yield smaller by the same factor

3.5. Ce-doped BaF_2 crystals

Emission spectra of BaF_2 single crystals and those doped with 0.1 % of CeF_3 are shown in Figs. 4 and 5. The spectrum of the pure BaF_2 ceramics (as well as of the crystals) exhibits a wide band with a maximum near 300 nm, which is caused by self-trapped excitons and a weak band 220 nm relating to the core-valence transitions. In BaF_2:Ce^{3+}, two bands at 308 and 323 nm, typical for Ce^{3+} ions, have been detected.

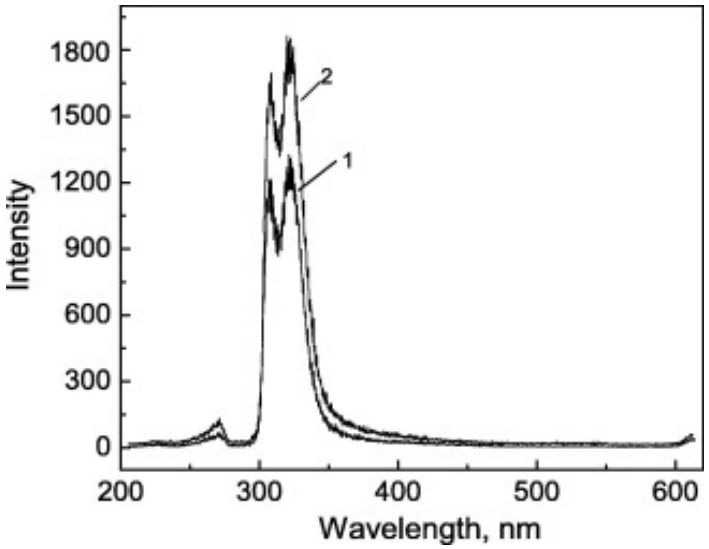

Fig. 5. *X*-ray induced emission spectra: 1 – BaF_2:Ce (0.1 %) single crystal and 2 – BaF_2:Ce (0.1 %) ceramics

It is worth noting that the intensity of the ultrafast component in BaF_2:Ce^{3+} ceramics is slightly larger than that in the standard BaF_2 crystals [3].

4. Photodetectors with AlGaN photocathodes

New photodetectors with photocathodes operated within the VUV spectral range have been developed. $Al_xGa_{1-x}N$ epitaxial films within a full range of composition (x = 0–1) and AlGaN-based heterostructures were grown by plasma-assisted molecular-beam epitaxy. The samples were grown on the annealed and

nitridated c-sapphire substrates, the growth temperature being varied within the range of 650–740 °C. The RF-power in the plasma source, changed within the range of 115–150 W at a constant nitrogen mass-flow of 5 sccm, allowed the *N*-limited growth rates from 0.25 to 0.5 μm/h, respectively. All the heterostructures had 1–1.6 μm-thick AlGaN buffers and *p*-type 20-nm-thick GaN:Mg top layers doped with solid-state Mg effusion cells. To control the AlGaN growth, a phenomenological approach based on simultaneous *in-situ* measurements of the laser interference and high energy electron diffraction followed by *ex-situ* electron probe micro-analysis was used. When the photocathode was grown, it was activated with Cs. The structural and optical properties of the structures were analysed using the scanning electron microscopy, the transmission electron microscopy, the *X*-ray diffraction and photoluminescence spectroscopy.

The Quantum Efficiency (QE) spectrum has an abrupt threshold at the photon energy equal to the GaN band gap. Changing the band gap value, it is possible to suppress the QE in the range of the BaF_2 slow luminescence component. The maximal value of the QE of 0.14 was measured at the wavelength of 230 nm [4].

5. Conclusion

1. The BaF_2 ceramics with the transmission at the wavelength 220 nm close to that of monocrystals can be obtained.
2. The BaF_2 ceramics luminescence spectrum demonstrates stability of the fast component and suppression of the slow one as compared to that of monocrystals.
3. Doping the BaF_2 crystals and the ceramics with different elements causes suppression of the slow component.
4. A photocathode with the quantum efficiency of 0.14 at 220 nm has been developed. The photocathode has an abrupt threshold about the slow luminescence component.

References

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