Temperature Dependence of Ce^{3+} and Pr^{3+} Emission in CaF_2, BaF_2, SrF_2

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Abstract—The paper is devoted to investigation of BaF_2, SrF_2, CaF_2 doped with different concentrations of praseodymium or cerium as scintillator for well-logging. Temperature dependences of light yield at the higher then room temperatures, pulsed-height and emission spectra of fluorides were measured.

Index Terms—Fluorides, light yield, scintillators, well-logging, x-ray emission.

I. INTRODUCTION

SCINTILLATION materials are widely used now in high-energy physics, medicine and radiation protection as detectors of high-energy photons. In addition, scintillators have been used in well-logging. The application of scintillators for logging research requires specific properties of materials: insusceptibility to failure through crystal damage from mechanical and thermal shock and through shifting of the reflective packing around the crystal; thermal stability of light yield and commercial availability. Today, the inorganic scintillators NaJ(Tl), CsJ(Tl), GSO:Ce (Gd_2SiO_5), CsJ(Na), BGO $(Bi_3Ge_4O_{12})$ are used for well-logging applications [1].

Alternative scintillators, having not been widely used in the logging industry but possessing the suitable properties, would be fluorides doped with different rare earths. These materials have been well-known for a long time. For instance, barium fluoride is the fastest known inorganic scintillator (decay time < 1 ns) [2], [3]. Peaks of very fast emission at about 190 and 220 nm so-called core-valence luminescence and a broad peak at about 300 nm were observed in [4]. The latter has decay time about 1 μs and originates in radiative decay of self-trapped excitons. In strontium and calcium fluorides core-valence luminescence is not observed but broad band of self-exciton emission is found at 300 nm [5].

In the series of rare earths cerium (Ce) and praseodymium (Pr) have a particular place. The luminescence of Ce and Pr is fast, efficient, and comparatively free of self-absorption [6]. Emission spectra of fluorides are changed after doping with Ce^{3+} and Pr^{3+}. Two peaks in the 300–400 nm region (5d-4f transitions in cerium) appear in crystals doped with cerium [7]–[9]. In fluorides doped with praseodymium peaks related to 5d-4f emission appears in 200–300 nm region [9]–[11]. The most attention has been focused on cerium-doped barium

fluoride, first accomplished by Czirr and Catalano [12]. Extensive studying of recombination process was carried out by Visser [7], [8]. The charge trapping process influence on the scintillation mechanism first considered for YAG and YAP [13], [14] has been regarded for barium fluoride in [11]–[15]. Scintillation properties of barium fluoride doped with 10% Ce have been already investigated by C. Melcher [16]. The authors concluded that doping the crystal with large cerium concentration improved the thermal stability of light yield and decay time properties but dramatically decreased the light yield of the crystal.

Another way is to dope crystals with low concentrations of rare earth ions because it does not cause large decrease of light yield but improves thermal stability of the light yield of the scintillator. The last observation of $BaF_2 : Ce^{3+}$ was carried out by S. Janus and A. Wojtowicz [15]. They investigated crystals of different sizes (diameter 1,8 cm and thickness from 1,3 mm to 10,2 mm) doped with low concentration of cerium (0,015 mol.%). The maximal light yield was in the sample with thickness 1,6 mm (1169 Ph/MeV). Affect of self-trapped exciton in these crystals was very large. Temperature dependences of light yield in barium fluoride doped with large (1 and more percents) concentrations of cerium was investigated by C. Melcher [16]. It was shown that the crystals had a good thermal stability of light yield, short decay time, but energy resolution was very poor. Authors have concluded that barium fluoride doped with large concentrations of cerium is of potential interest to be used in certain nuclear well logging applications. However, these materials have properties that limit their potential usefulness. Temperature dependence of light yield in barium fluoride doped with praseodymium in the 70–300 K temperature range has been investigated recently in [10], [11].

II. EXPERIMENTAL TECHNIQUE

The crystals BaF_2, SrF_2 and no3, CaF_2 doped with different concentrations of Ce and Pr were grown in vacuum (in graphite crucible by the Stockbarger method). Samples of $8 \times 10 \times 2$ mm dimensions were used. The crystals were polished and covered with a Teflon for pulsed-height experiments. Excitation of X-ray luminescence was made from Pd tube operating at 30 kV and 8 mA. For temperature measurements a chromel-alumel thermocouple was applied. Emission spectra were measured with a VM4 monochromator. With LPA 4902.2 spectrometric amplifier (shaping time 8 μs), FEU-39a PMT tube (Sb-Cs photocathode and quartz window) and self-made preamplifier we measured pulsed-height spectra.
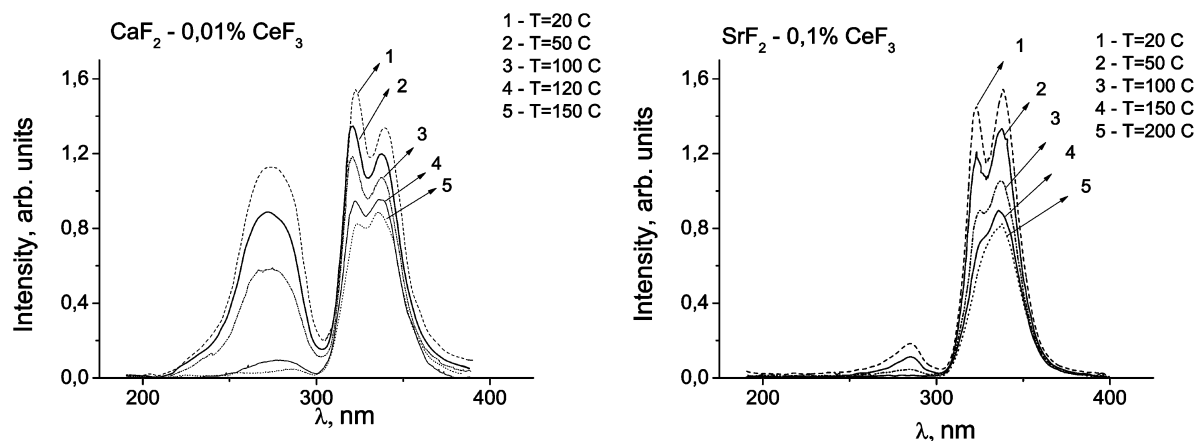
Fig. 1. Emission spectra of CaF_2 and SrF_2 doped with Ce^{3+} at different temperatures.
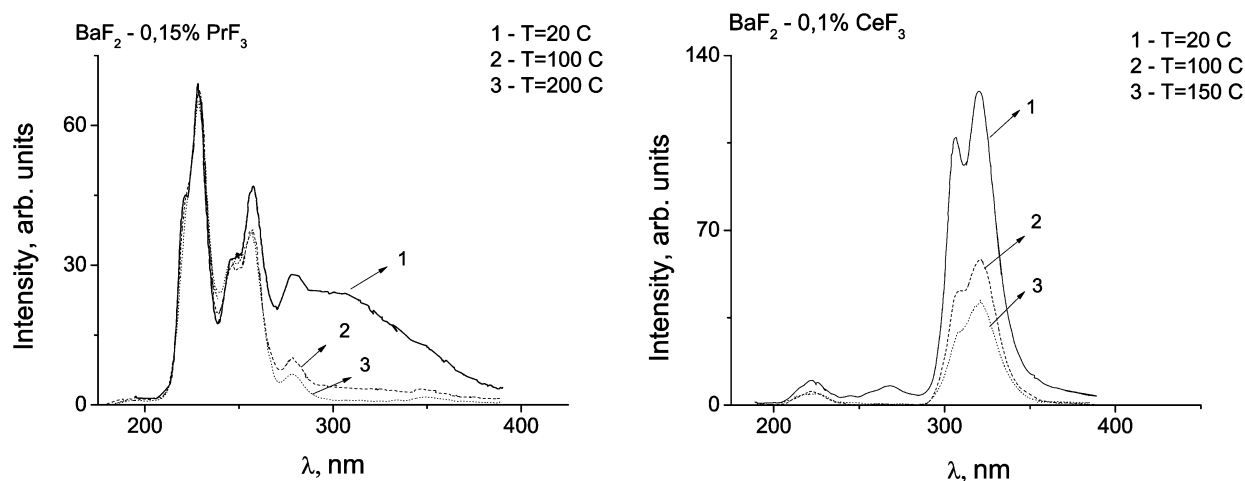

Fig. 2. Emission spectra of BaF_2 doped with Pr^{3+} and Ce^{3+} at different temperatures.

III. RESULTS

We investigated x-ray emission in crystals in the wide temperature range (from room temperature to 200 C). Emission spectra at different temperatures are presented in Figs. 1 and 2. In Fig. 1, spectra of cerium doped calcium and strontium fluorides are shown. Bands of cerium d-f emission are in the 320–335 nm region in SrF_2, there are two narrow bands. The d-f emission in $CaF_2 : Ce^{3+}$ is in the 330–345 nm region. A wide band of STE emission was observed in the 270 nm region.

In Fig. 2, emission spectra of $BaF_2 : Ce^{3+}$ and $BaF_2 : Pr^{3+}$ are shown. Two narrow bands of Ce d-f emission were found in the 300–330 nm region in cerium doped barium fluoride. For $BaF_2 : Pr^{3+}$ d-f emission of praseodymium was observed in the 220–240 nm region. There are five narrow bands. STE emission is a wide band in the 270 nm region.

The spectra have slight changes at the heating. There is a small broading at the 100–200 C temperatures. It is important, that the position of bands and shape of spectra are not changed at heating. Only the intensity of Ce emission and STE emission decrease with increasing temperature. In Pr doped crystals we found that only STE emission decreased.

Temperature dependences of integral light yield (emission spectra integrals) are presented in Fig. 3. In Fig. 3, an emission spectra integrals in SrF_2:Ce, CaF_2:Ce and BaF_2:Ce are shown. Light yield contraction in cerium doped strontium fluoride in the temperature range from the room to 200 C was about 50%. In CaF_2:Ce and BaF_2:Ce the decrease was about 70%. The largest light yield diminution (about 70%) was found in BaF_2:0,01% CeF_3.

In Fig. 3(b), temperature dependences of $BaF_2 : Pr^{3+}$ light yield are compared with integral light yield of exciton emission, which was measured in the range 240–400 nm. The decrease in $BaF_2 : Pr^{3+}$ was about 40–50%.

We measured temperature dependences of light yield in the maxima of Ce^{3+} and Pr^{3+} 5d-4f emission. The results for cerium doped crystals are given in Fig. 4. The largest diminution (about 60–80%) was found in $BaF_2 : Ce^{3+}$. The decrease in $SrF_2 : Ce^{3+}$ was about 20–30%. In calcium fluoride doped with cerium we found a strange behavior of the temperature dependences—light yield increased with temperature. This fact is probably caused by destruction of some thermoluminescent centers, because we did not find that behavior in the integral light yield dependence (Fig. 3(a) curve 2). It requires the following investigation.

In Fig. 5 temperature dependences of light yield in $BaF_2 : Pr^{3+}$ are given. Clear that the Pr emission depends on temperature very weakly.

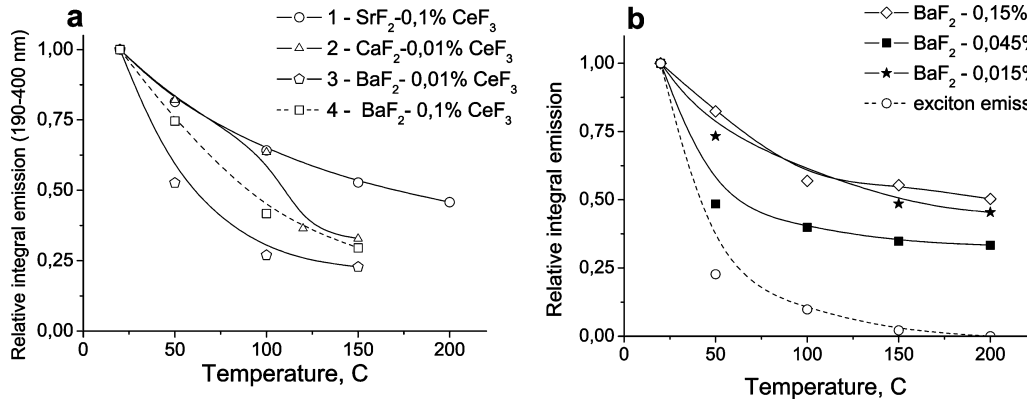Fig. 3. Temperature dependence of integral light yield in the crystals CaF_2; SrF_2, BaF_2 doped with Ce^{3+} (a) (in the range 190–400 nm); $BaF_2 - Pr^{3+}$ and integral light yield of exciton emission (in the range 240–400 nm) (b).
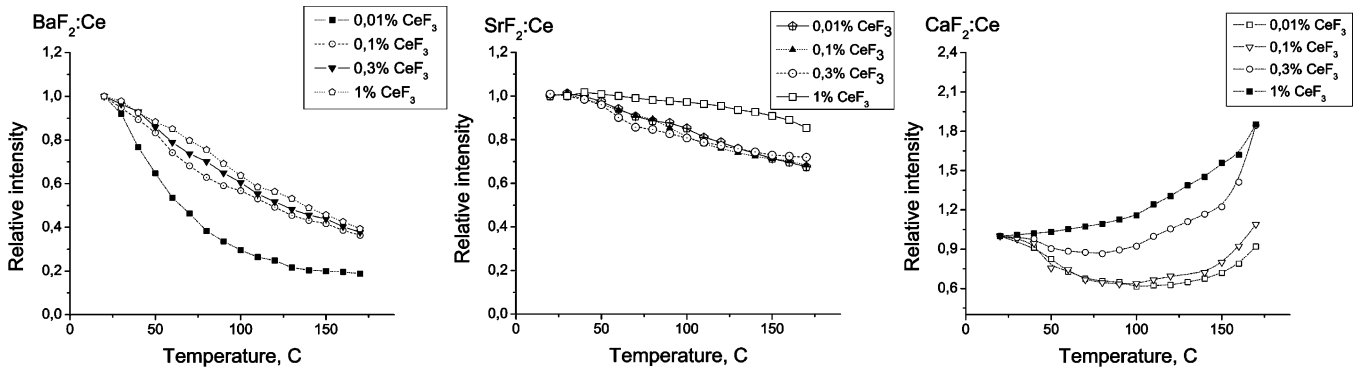

Fig. 4. Temperature dependence of relative light yield in maximum of cerium emission band in CaF_2; SrF_2, BaF_2 doped with different concentrations of Ce^{3+}.
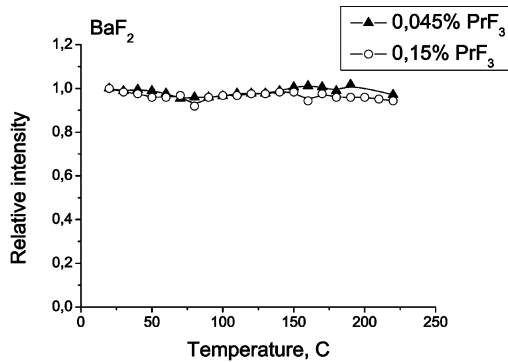

Fig. 5. Temperature dependence of relative light yield in maximum of praseodymium emission band in BaF_2 doped with Pr^{3+}.
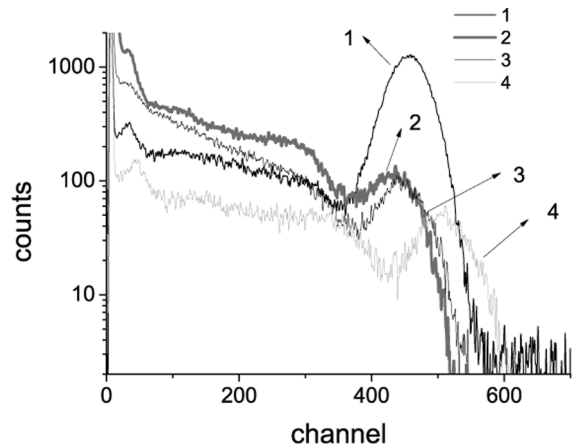

Fig. 6. Pulsed-height spectra (^{137}Cs) of BGO (curve 1); BaF_2:0,1% CeF_3 (curve 2); BaF_2:0,045% PrF_3 (curve 3); pure BaF_2 (curve 4).

We measured pulsed-height spectra (calibration source ^{137}Cs was used) of the samples in comparison with pure barium fluoride and BGO, which was kindly given to us by Ya. Vasil'ev (Institute of Inorganic Chemistry, Novosibirsk, Russia). The results are presented in Fig. 6. Light yield of barium fluorides doped with cerium is almost equal to the light yield of 0,045% Pr^{3+} doped barium fluoride and makes up about 85% from BGO light yield. Strontium fluoride doped with 0,1% cerium has the largest light yield (about 120% from BGO). The light yield decrease in SrF_2- 1% CeF_3 is about 60% with respect to the crystal doped with 0,1% of Ce. In BaF_2- 0,3% PrF_3 the light yield decrease is about 55–60% with respect to the crystal doped with 0,045% of

Pr. Calcium fluoride doped with one kind of the Pr^{3+} or Ce^{3+} ions has the extremely poor light yield.

IV. DISCUSSION

Fig. 3 shows the temperature quenching of full-emission in the range 190–400 nm and quenching of exciton emission in the range 240–400 nm. In x-ray emission spectra of the rare earth doped fluorides broad band of self-trapped excitons was observed. The broad band was quenched with increasing rare earth concentration [16], [17]. As shown in Fig. 3 b, the

TABLE I
PROPERTIES OF SOME SCINTILLATORS FOR WELL-LOGGING

	BaF_2 fast slow	GSO:Ce	NaI:Tl	BGO
Light yield	3 10-16	20	100	13-20
Energy res. @ 662 KeV	22% 9,2%	9,5%	6,7%	9,3%
Decay time, ns	<1 630	60	250	300
Emission maximum, nm	220 310	480	415	480
Eff. atomic number	53	59	51	75
Density, g/cm^3	4,88	6,71	3,67	7,13

exciton emission is also quenched very well with temperature increasing. Therefore it would be promising for well-logging application to use crystals doped with large concentrations cerium or praseodymium. But as pointed in [16], BaF_2 crystals doped with a large concentration (one and more percents) of cerium had extremely poor light yield. We observed this effect in SrF_2 doped with Ce and in Pr doped barium fluorides. Thus mostly the crystals doped with low concentrations cerium or praseodymium are of some interest in well-logging applications. It can be explained as well-known tendency of Ce and Pr for aggregation in these half cation site empty lattices with formation of complex centers [18].

As we can see in Figs. 1 and 2, the shape and position of d-f emission in the rare earth doped crystals are not changed. So the measurements of light yield in maxima of the rare earth emission bands and emission spectra integrals give to us information about quenching rare earth luminescence. Figs. 4 and 5, show the temperature dependences of emission corresponding to 5d-4f transitions in praseodymium and cerium ions. Cerium emission is quenched at heating (Fig. 4). Praseodymium emission is almost independent on temperature, and decrease of integral emission versus temperature (Fig. 3(b)) is caused by quenching of self-trapped excitons. The fact that emission of Pr in BaF_2 crystals is independent on temperature increase is very interesting. It suggests that emission is not excited by transfer of exciton energy to the luminescent center, which was observed in cerium doped fluorides [11]. Probable mechanism of energy transfer in the praseodymium doped barium fluoride is consecutive capture of charge carriers at Pr^{3+}, this also explains the dominance of short decay time (20 ns [9], [10]) in the crystals. The similar effect has been observed in Pr^{3+} doped LuAG crystals [19], [20] at room and lower temperatures. In BaF_2 doped with low concentrations of cerium the prevail transfer mechanism at room and higher temperatures is transfer of exciton energy, the "consecutive capture of charge carriers" mechanism also exists but it is not prevail at these temperatures. However, at lower than room temperatures the latter mechanism is a more preferable [10]. The thermal stability of light yield improves with increase of Pr^{3+} and Ce^{3+} concentration but light yield of the crystals decreases considerably. Comparing thermal stability of cerium with praseodymium doped crystals

we can draw to conclusion that the crystals doped with Pr^{3+} have a better thermal stability properties.

Light yield of barium fluorides doped with cerium is almost equal to light yield Pr^{3+} doped barium fluoride and makes up about 85% from BGO light yield. Strontium fluoride doped cerium has the largest light yield (about 120% from BGO) but it has a long decay time (2 μs).

V. CONCLUSION

In this paper, we investigated the thermal stability of emission at room and higher temperatures. Doping fluorides with the impurities of cerium or praseodymium improves thermal stability of the crystals and makes possible applicability of these crystals in well-logging research. The thermal stability ameliorates with increasing impurity concentration in the crystal. However, the light yield of doped crystals is lower than in pure ones. The best light yield was found in the crystals doped with low concentrations of the rare earth. Crystals doped with Pr^{3+} ions showed the best thermal stability properties, but the light yield is low. Interestingly, the differences between energy transfer to emission centers in crystals doped with cerium and crystals doped with praseodymium have been observed by other authors in other materials. It should be important for understanding of fundamental processes in scintillators.

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