Scintillation properties of Ce^{3+} doped BaF_2 crystals*

R. Visser, P. Dorenbos, C.W.E. van Eijk, R.W. Hollander
Radiation Technology Group, Department of Applied Physics,
Delft University of Technology, Mekelweg 15,
2629 JB Delft, the Netherlands

P. Schotanus
Radiation Detectors and Crystals, Quartz & Silice Holland B.V.,
P.O. Box 168, 3454 Z De Meern, the Netherlands

Abstract

The scintillation properties of cylindrically shaped, $\varnothing 1"x1"$, and 30x30x4.5 mm BaF_2 crystals doped with 0.2, 0.3, 0.5, 0.8, and 1.0 mol% Ce^{3+} have been studied by means of X-ray and gamma ray excitation. Optical transmission, X-ray induced emission, and decay time spectra will be presented. The photoelectron (phe) yield/MeV was measured with an XP2020Q photomultiplier tube. The $\varnothing 1"x1"$, 0.2 mol% doped crystal has a light yield of 1790 phe/MeV which is larger than the total light yield (1570 phe/MeV) of a pure BaF_2 crystal of the same dimensions. The crystal shows two main scintillation decay times of 47 ± 5 ns and 260 ± 40 ns. For the 1.0 mol% doped crystal a light yield of 1210 ± 80 phe/MeV and a dominating decay time of 81 ± 7 ns were observed. The crystals scintillate at wavelengths larger than 300 nm and the scintillation light can be detected with glass windowed photomultiplier tubes.

Introduction

Pure BaF_2 has been applied widely as a scintillation crystal in gamma ray detectors because of its high density and its luminescence at 220 nm and 195 nm with a very short decay time of about 800 ps [1, 2]. In addition to these fast components, BaF_2 has a slow emission component peaking at 300 nm with a decay time of about 700 ns. The intensity of this component can be suppressed considerably, without affecting the fast component, by doping the crystals with a few mol% La^{3+} [3, 4].

The properties of Ce^{3+} ions are quite different from the properties of La^{3+} ions. Ce^{3+} has one electron in the 4f shell which can be excited to the 5d shell; the 4f shell of La^{3+} is empty. The de-excitation of the 5d electron to levels of the $4f^1$ configuration is allowed according to the electric dipole approximation and results in luminescence

with a short decay time. Results obtained for BaF_2 crystals doped with Ce^{3+} have been reported in the recent literature. Czirr et al. [5], Tailor et al. [6], Melcher et al. [7], Woody et al. [4], Rodnyi et al. [8], and Vakhidov et al. [9] have studied crystals doped with Ce^{3+} concentrations between 1 mol% and 30 mol%. These heavily doped crystals show luminescence in the 330 to 370 nm region with a decay time of about 50 ns. Two emission bands near 305 nm and 325 nm have been observed by Vakhidov et al. [10] for crystals weakly doped with Ce. Detailed studies of the scintillation properties of BaF_2 crystals doped with Ce concentrations between 0.1 and 1 mol% have not been published.

Recently we have studied BaF_2 crystals doped with Ce concentrations ranging from 0.002 mol% to 10 mol% [11, 12]. These crystals show interesting scintillation properties. The two luminescence peaks near 305 nm and 325 nm can be observed for Ce concentrations smaller than 0.5 mol%. For concentrations above 1 mol% the emissions in the 330 nm to 370 nm region are observed. The overall emission intensity of crystals doped with about 0.2 mol% Ce^{3+} was almost 60% more intense than the total emission intensity of pure BaF_2 crystals. Preliminary decay time studies revealed an emission component with a decay time of 65 to 85 ns for crystals doped with Ce concentrations less than 1 mol%. The decay time decreases with the Ce concentration down to a value of 45 ns for a crystal doped with 10 mol% Ce. In addition to this relatively fast emission component, we observed a very slow emission with a decay time of about 0.2 ms. This component is maximal for Ce concentrations of about 0.2 mol% and disappears for Ce concentrations larger than 1 mol%.

The crystals mentioned above were rather small, i.e. they were cylindrically shaped with a diameter of 7.5 mm and a thickness of about 4 mm. Only the top and bottom faces of the crystals were optically polished. In order to study whether Ce doped BaF_2 crystals can be employed usefully in scintillation detectors, larger crystals have been grown. In this paper we present results obtained for six cylindrically shaped crystals with dimensions $\varnothing 1"x1"$ and five crystals with dimensions 30x30x4.5 mm. The crystals

were doped with Ce concentrations from 0.0 to 1.0 mol%. All sides of the crystals were optically polished.

Experimental details

Harshaw scintillation crystals grown by the Bridgman technique with nominal Ce concentrations of 0.0 (i.e. pure BaF_2), 0.2, 0.3, 0.5, 0.8, and 1.0 mol% were employed in this work. The growth direction of the original single crystal ingots was perpendicular to the axes of the cylindrically shaped crystals cut from it. This was done in order to minimize the concentration gradient of Ce^{3+} in the crystals. A 30x30 mm and 4.5 mm thick crystal was also cut from each ingot. The optical transmission of the crystals was measured by means of a Hitachi model U3200 spectrophotometer.

An ARC vacuum monochromator (model VM-502) with a 1200 grooves/mm concave holographic grating blazed in first order at 250 nm has been employed to measure the luminescence spectra of the crystals under X-ray irradiation with a wavelength resolution of 4 nm. X-rays from an X-ray tube with a copper anode operating at 35 kV were used to excite the crystals. In order to detect the scintillation light, a Philips XP2020Q photomultiplier (PM) tube was mounted behind the exit slit of the monochromator. The results presented in this work have not been corrected for the transmittance of the monochromator and the quantum efficiency of the photomultiplier tube.

The decay times of the scintillation light from the crystals were determined by the single photon counting technique described by Böllinger et al. [13].

The absolute light output of the crystals was determined by means of photoelectron yield measurements. The crystals were mounted directly onto a Philips XP2020Q photomultiplier tube using an optical coupling compound (General Electric Viscasil) with a viscosity of 60,000 cSt. The sides of the crystal not in contact with the PM-window were wrapped with Teflon foil and Teflon tape. A Canberra, model 1413, spectroscopy amplifier was employed to obtain pulse height spectra of a ^{137}Cs gamma source. The photoelectron yield (phe/MeV) was then calculated from the position of the 662 keV photopeak in the pulse height spectra and the single electron response of the photomultiplier tube. The 662 keV photopeak in the ^{137}Cs pulse height spectra was also employed to determine the energy resolution achievable with a crystal optically coupled to a photomultiplier tube.

Results and discussion

The optical transmission curves of the five $\emptyset 1"x1"$ Ce doped crystals, measured parallel to the axis of the cylinder, are shown in Figure 1. There is about 11% loss in transmission between 340 and 400 nm which is caused mainly by 10% Fresnel reflection losses at the two surfaces of the crystals. The decrease of the transmission at

wavelengths between 320 and 300 nm is caused by 4f-5d absorptions in Ce^{3+} ions. The wavelength for which the transmission of the crystals has dropped to 10% shifts from 305 nm to 326 nm as the Ce concentration increases from 0.2 to 1.0 mol%. A lowering of the energy of the 5d level caused by interactions between Ce^{3+} ions is probably the reason for this shift [11, 12].
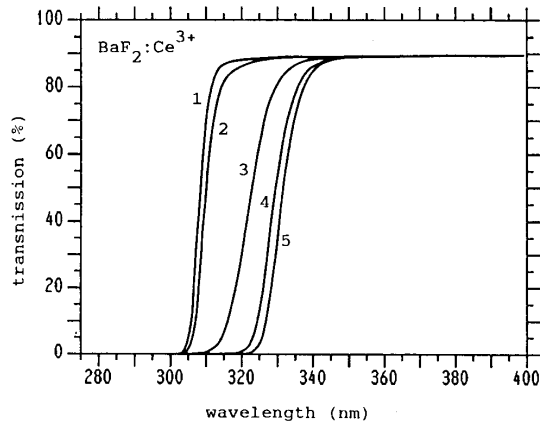

Figure 1: Optical transmission spectra of $\emptyset 1"x1"$ Ce^{3+} doped BaF_2 crystals. Spectrum 1) 0.2 mol% Ce; 2) 0.3 mol% Ce; 3) 0.5 mol% Ce; 4) 0.8 mol% Ce; 5) 1.0 mol% Ce.

Figure 2 shows the emission spectra of the $\emptyset 1"x1"$ Ce doped crystals excited by means of X-rays. The dashed curve shows the emission spectrum of the $\emptyset 1"x1"$ pure BaF_2 crystal. Its luminescence peaks at 195, 220, and 300 nm. The 0.2 mol% doped crystal shows a clear emission peak at 323 nm with a shoulder on the left side of the peak. This shoulder is caused by an emission band located at 304 nm which has been suppressed due to self absorption in the crystal. The major part of the BaF_2 host luminescence is absorbed and quenched by the presence of the Ce^{3+} ions, only weak host crystal luminescence remains between 200 nm and 300 nm. For the crystals doped with 0.8 and 1.0 mol% Ce, the emission at 323 nm has almost disappeared and the emission at 304 nm and the host lattice luminescence have disappeared completely. New emissions appear in the 340 nm to 390 nm region for these two crystals. They are probably caused by 5d-4f transitions in Ce ions with 5d levels shifted towards lower energies due to interactions with other nearby Ce ions. The emissions at 304 nm and 323 nm are attributed to 5d-4f transitions in Ce^{3+} ions with no other Ce ions in their vicinity [11, 12].

We observed that most crystals had obtained a color ranging from light pink to red at the spot where the crystals were X-ray irradiated. The coloration, which was not observed for the 0.2 mol% doped crystal, increases with the Ce concentration and with the total X-ray dose. The
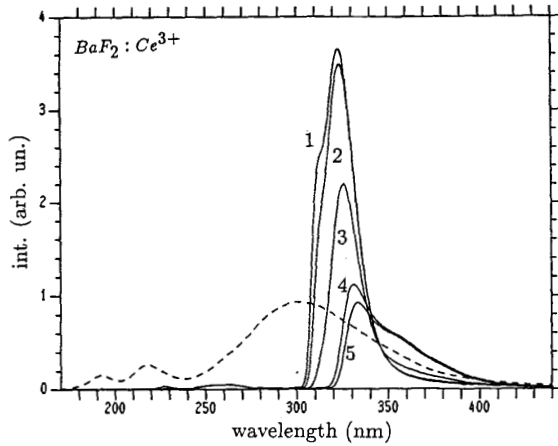
Figure 2: X-ray induced emission spectra of Ø1"x1" Ce doped BaF₂ crystals. Spectrum 1) 0.2 mol% Ce; 2) 0.3 mol% Ce; 3) 0.5 mol% Ce; 4) 0.8 mol% Ce; 5) 1.0 mol% Ce. The dashed curve shows the emission spectrum of a Ø1"x1" pure BaF₂ crystal.

same coloration had been observed for La^{3+} doped BaF_2 crystals [3] and has been studied in more detail by Woody et al. [4] and Vakhidov et al. [9]. In order to test whether the coloration influences the scintillation properties, we exposed the crystals with 0.2, 0.5, and 1.0 mol% Ce for 15 minutes to the X-rays from the X-ray tube; 4 mJ X-ray energy is then absorbed by the crystal per square mm within a depth of about 0.1 mm. This corresponds with a total X-ray dose of 10^4 gray. The emission spectra recorded after the exposure were about 5% less intense than the emission spectra recorded before the exposure. Five percent is also the reproduction accuracy of the emission spectra obtainable with our experimental set-up. We conclude that the Ce doped crystals are sensitive to radiation damage but it does not have a drastic influence on the scintillation properties under ordinary excitation conditions.

Figure 3 shows the decay time spectrum of the 30x30x4.5 mm BaF_2 crystal doped with 0.5 mol% Ce. Three decay time components can be observed in this spectrum. A small very fast component with a decay time of about 800 ps is present in the first two ns after time zero. This component is caused by the cross luminescence in the host material BaF_2. The intensity, compared to pure BaF_2, is very low because of absorption by Ce^{3+} ions. The decay time spectrum, apart from the very fast component mentioned above, was fitted with a sum of two exponential decay curves, $(A_1/\tau_1)\exp(-t/\tau_1) + (A_2/\tau_2)\exp(-t/\tau_2)$. The components have decay times $\tau_1=75\pm4$ ns and $\tau_2=340\pm40$ ns and a relative intensity of $A_1/A_2=0.77\pm0.03$. Two decay components were also observed for the other four 30x30x4.5 mm crystals; the results have been compiled in Table 1. Results obtained for cylindrical Ø7.5x4 mm BaF_2

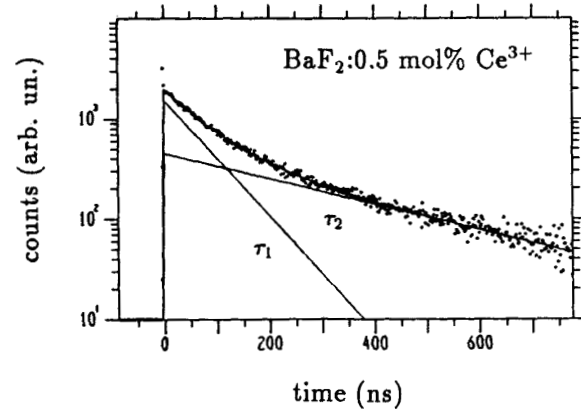**Figure 3:** Decay time spectrum of a 30x30x4.5 mm BaF_2 crystal doped with 0.5 mol% Ce^{3+} measured with single photon counting techniques.

crystals doped with 2.1, 4.6, and 10 mol% Ce^{3+} have been added in Table 1 for completeness.

Table 1: Compilation of results obtained from decay time measurements on 30x30x4.5 mm BaF_2 crystals doped with 0.2, 0.3, 0.5, 0.8, and 1.0 mol% Ce^{3+} and on Ø7.5x4 mm BaF_2 crystals doped with 2.1, 4.6, and 10 mol% Ce^{3+}.

conc. (mol%)	τ_1 (ns)	τ_2 (ns)	A_1/A_2
0.2	47 ± 5	260 ± 40	0.40 ± 0.08
0.3	52 ± 2	300 ± 30	0.49 ± 0.07
0.5	75 ± 4	340 ± 40	0.77 ± 0.03
0.8	91 ± 6	290 ± 50	2.0 ± 0.8
1.0	81 ± 7	340 ± 100	1.8 ± 0.6
2.1	53 ± 5		
4.6	49 ± 7		
10	45 ± 1		

The decay time τ_1 increases from 47 ns to 91 ns and decreases to 45 ns as the Ce concentration increases from 0.2 mol% to 0.8 mol% and to 10 mol%. The component with decay time τ_2 was only observed for Ce concentrations up to 1 mol%. Its decay time is about 300 ns and does not change significantly with the Ce concentration. The relative intensity, A_1/A_2, changes with the Ce concentration. A_2 is 2.5 times larger than A_1 for the 0.2 mol% doped crystal but it is 1.8 times smaller than A_1 for the crystal doped with 1.0 mol% Ce^{3+}. The luminescence spectrum of the 1.0 mol% doped crystal is therefore dominated by a component with a decay time of $\tau_1=81\pm7$ ns and the

spectrum of the 0.2 mol% doped crystal by a component with a decay time $\tau_2 = 260 \pm 40$ ns.

The relatively fast luminescence components with decay times τ_1 and τ_2 can be attributed to 5d-4f transitions in Ce^{3+} ions. The decay time will then be determined by the rate of transfer of excitation energy to the Ce ions and the 5d-4f transition rate.

We did not observe scintillation components with decay times larger than 100 μs for the $\emptyset1"x1"$ Ce doped crystals. This is quite different from results published recently for Ce doped crystals with dimensions $\emptyset7.5x4$ mm [11, 12]. Measurements on these crystals revealed the presence of a scintillation component with a very long decay time of about 0.2 ms. The intensity of this component was 500 phe/MeV for crystals doped with about 0.2 mol% Ce^{3+}. The component, which disappears for Ce concentrations larger than 1 mol%, was attributed to scintillation mechanisms with a very slow transfer of excitation energy to the Ce^{3+} ions. The slow transfer rate was attributed to the presence of intrinsic or extrinsic electron and hole traps in the doped crystals. The presence of foreign impurities might be responsible for the appearance of the slow scintillation component. It is also possible that the thermal history of the crystal influences the intensity of the slow component.

Table 2: Compilation of the photoelectron yield/MeV and the energy resolution at 662 keV of $\emptyset1"x1"$ pure and Ce doped BaF_2 crystals determined by means of a spectroscopy amplifier with a shaping time of 0.5 and 4.0 μs. There is a 7% error in the values for the photoelectron yields.

conc.	phe/MeV		$\Delta E/E$ (%)	
	0.5	4.0	0.5	4.0
(mol%)	μs	μs	μs	μs
0.0	1100	1570	10.4 ± 0.4	9.5 ± 0.4
0.2	1230	1790	11.7 ± 0.4	11.3 ± 0.4
0.3	1060	1520	12.0 ± 0.5	12.5 ± 0.5
0.5	1080	1440	12.1 ± 0.5	15.0 ± 0.8
0.8	980	1230	15.2 ± 0.8	20.0 ± 1.0
1.0	970	1210	17.4 ± 1.0	23.5 ± 1.0

The absolute scintillation intensities of the crystals were determined by means of photoelectron yield measurements. The results obtained for the $\emptyset1"x1"$ Ce doped crystals together with the results obtained for a pure BaF_2 crystal with the same dimensions have been compiled in Table 2. There is a 7% error in the presented photoelectron yields. The second column shows the yield in photoelectrons/MeV determined with a Canberra, model 1413, spectroscopy amplifier with a shaping time of 0.5 μs. We measured a yield of 1230 phe/MeV for the crystal doped with 0.2 mol% Ce^{3+}, which is larger than the total photoelectron yield of the pure BaF_2 crystal measured under

the same conditions. The yield decreases with increasing Ce concentration to 970 phe/MeV for the 1.0 mol% doped crystal. For comparison, Woody et al. [4] reported a value of 888 phe/MeV for a 1 mol% Ce^{3+} doped BaF_2 crystal with dimensions $\emptyset25x19$ mm. This value was obtained by means of a LeCroy QVT using a 1μs long gate.

The photoelectron yield/MeV measured with a shaping time of 4 μs has been compiled in the third column of Table 2, and is significantly larger than the yield measured with a shaping time of 0.5 μs. The difference amounts to 560 phe/MeV for the 0.2 mol% doped crystal and to 240 phe/MeV for the 1.0 mol% doped crystal. The increase of the photoelectron yield can not be explained from the results presented in Table 1. The values of the decay times τ_1 and τ_2 are smaller than 0.5 μs, and we expect a difference of at most 10% between the photoelectron yields measured with a shaping time of 0.5μs and 4μs. Probably, there is a third emission component with a decay time of several μs, and with an intensity which decreases with increasing Ce concentration.

The photoelectron yields measured with a shaping time of 4 μs corresponds well with the yields of Ce doped crystals with dimensions $\emptyset7.5x4$ mm presented elsewhere [11, 12]. The yields are reasonably large compared to other scintillation crystals. A pure BaF_2 crystal of the same dimensions has a yield of 1570 phe/MeV. Moszynski et al. [14] reported a value of 555 phe/MeV for a $\emptyset2x3$ cm BGO crystal optically coupled to an XP2020Q photomultiplier tube. Anderson et al. [15, 16] reported values of about 400 and 800 phe/MeV for a 1-cm cube CeF_3 and a 1-cm cube BGO crystal, respectively.
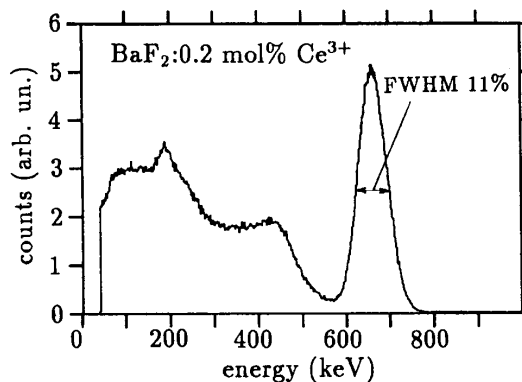

Figure 4: The ^{137}Cs pulse height spectrum measured with a $\emptyset1"x1"$ BaF_2 crystal doped with 0.2 mol% Ce^{3+} and optically coupled to an XP2020Q photomultiplier tube. A spectroscopy amplifier with a shaping time of 4 microsecond was employed.

Figure 4 shows the ^{137}Cs pulse height spectrum measured with the 0.2 mol% Ce^{3+} doped $\emptyset1"x1"$ crystal op-

182

tically coupled to an XP2020Q photomultiplier tube. The energy resolution, $\Delta E/E$, at 662 keV was determined from the width (FWHM) of the 662 keV photopeak and is 11.3 ± 0.4 %. Results obtained from the pulse height spectra of the other four Ce doped crystals and pure BaF_2 are compiled in Table 2. The energy resolution of the 0.2 mol% Ce doped crystal is, despite its larger photoelectron yield, almost 2% worse than the resolution observed with the pure BaF_2 crystal. The FWHM of the photopeak increases with the Ce concentration especially when a shaping time of 4 μs is employed. This increase and the difference with pure BaF_2 crystals can not be explained from the statistical spread in the photoelectron yield. Self absorption and possible concentration gradients of Ce^{3+} in the crystals are probably responsible for a large contribution to the energy resolution.

Conclusions

BaF_2 crystals doped with Ce concentrations smaller than 1 mol% show interesting scintillation properties. The slow and the fast scintillation components of pure BaF_2 crystals disappear completely by doping with a few tenths of a mole percent Ce^{3+}. New emissions caused by 5d-4f transitions in Ce^{3+} ions appear at wavelengths above 300 nm. Several properties make these crystals interesting for applications in scintillation detectors. i) The gamma ray stopping power of the crystals is the same as for pure BaF_2 crystals. ii) The photoelectron yields/MeV of the crystals have values located between values reported for BGO crystals and pure BaF_2 crystals. iii) The dominating decay time component of the scintillation light, which depends on the Ce concentration, is smaller than 100 ns for Ce concentrations larger than 0.6 mol%. This is shorter than the decay time of BGO (300 ns), NaI(Tl) (230 ns), and the slow component of BaF_2 (730 ns) [3, 16]. iv) The Ce doped crystals scintillate at wavelengths larger than 300 nm and the scintillation light can be detected very well with photomultiplier tubes with a glass window.

Acknowledgements

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