Luminescence and Scintillation Properties of BaF₂-Ce Transparent Ceramic

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Abstract: Cerium doped Barium Fluoride (BaF₂-Ce) transparent ceramic was fabricated and its luminescence and scintillation properties were studied. The photoluminescence shows the emission peaks at 310 nm and 323 nm and is related to the 5d-4f transitions in Ce³⁺ ion. Photo peak at 511 keV and 1274 keV were obtained with BaF₂-Ce transparent ceramic for Na-22 radioisotopes. Energy resolution of 13.5% at 662 keV is calculated for the BaF₂-Ce transparent ceramic. Light yield of 5100 photons/MeV was recorded for BaF₂-Ce(0.2%) ceramic and is comparable to its single crystal counterpart. Scintillation decay time measurements shows fast component of 58 ns and a relatively slow component of 434 ns under 662 keV gamma excitation. The slower component in BaF₂-Ce(0.2%) ceramic is about 200 ns faster than the STE emission in BaF₂ host and is associated with the dipole-dipole energy transfer from the host matrix to Ce³⁺ luminescence center.

Keywords

Barium Fluoride, Transparent ceramic, Scintillation, Photo peak, Luminescence, Scintillation decay time

1. Introduction

High light output, high density and short decay time are the basic requirements of a scintillator for gamma ray spectroscopy [1-4]. Single crystal scintillators are preferred over organic scintillators due its high density and better energy resolution. While inorganic scintillators like $\text{LaBr}_3\text{-Ce}$ are promising, inorganic single crystals are difficult to grow in large size and thereby expensive [5]. Recently transparent polycrystalline ceramic has emerged as a cost effective alternative to single crystals [6, 7]. Transparent polycrystalline ceramics are easy to fabricate in large volume, can be heavily and homogeneously doped with active ions, and are relatively inexpensive [8-10]. Foremost, ceramics in general are mechanically stronger than the single crystals. One drawback of the traditional ceramics for scintillation application was its opacity [11]. However, with the developments in sintering technique and nanotechnology, optical transparency of ceramics have significantly improved, paving the way for scintillation applications [12].

Pure Barium Fluoride (BaF_2) is known as fast scintillator. BaF_2 single crystal exhibits two emission bands. Fast component is in the UV region around 195-220 nm with the decay time of 600-800 ps and a relatively slow self-trapped excitons (STE) emission peaking at 310 nm with the decay time of 630 ns [13-15]. To detect the fast component it is necessary to use a photomultiplier tube with quartz entrance window. However, only about 15% of the photoelectrons are produced by the fast component and 85% decay through the slower component [16]. Several rare earth doping has been

used to suppress the slow emission and improve the time resolution of BaF₂ [17-20]. However, this method resulted into quenching of both the slow and fast emission [16]. Another way is to transfer the slower STE emission into fast Ce³⁺ emission through Ce³⁺ doping. In the past, some work has been done on Ce³⁺ doped BaF₂ crystal. For examples, Dorenbos et al. reported the fast Ce³⁺ emission in BaF₂-Ce³⁺ crystal under X-ray excitation, with maximum intensity for Ce³⁺ concentration of about 0.2 mol% [15]. Visser et al. reported the scintillation properties and decay time of Ce³⁺ doped BaF₂ crystals with the quenching of slower BaF₂ emission [21, 22]. However, very few studies have been reported on optical and scintillation properties of Ce³⁺ doped BaF₂ ceramics [23, 24]. Moreover, there is no report on the generation of photo peak with BaF₂-Ce transparent ceramic. Due to the growing interest in ceramic scintillators it is worthwhile to study the scintillation properties of BaF₂-Ce ceramics. In this paper we fabricated 0.2 mol% Ce³⁺ doped BaF₂ ceramic of dimension of about Ø10 X 1 mm² and studied its luminescence and scintillation properties. The pulse height spectra obtained with BaF₂-Ce transparent ceramic shows photo peak with Na-22 and Cs-137 radioisotopes with full width half maximum (FWHM) energy resolution of 13.5% at 662 keV.

2. Experimental

2.1 Fabrication of BaF₂-Ce(0.2%) transparent ceramic

The Ba(NO₃)₂ and KF solutions were prepared according to the ratio of Ce_{0.001}Ba_{0.999}F_{2.001}, using deionized water as a solvent. Ce(NO₃)₃·6H₂O and PEG2000 were then dissolved into the Ba(NO₃)₂ solution. The KF solutions were then dropped into the mixed solution at a rate of 2 ml/min. After the completion of the precipitation reaction, the mixed solution was left for 24 hours. The precipitates were then washed using deionized water and filtered 5 times. The resulting precipitates were then dried at 100 °C for 24 hours. The dried powders were then ground and compressed into

disc compacts of 10 mm × 5 mm under a uniaxial pressure of 200 MPa. The compacts were further carried out under cold isostatic pressure at 200 MPa for 3 minutes. Finally, the compacts were sintered in the VSF vacuum furnace at a vacuum degree of 1×10^{-3} Pa, and the heating rate was kept at 10 °C /min. The furnace chamber is made of high temperature stainless steel and the internal chamber is made with the fiber graphite. The heating element is made of Si-Mo. The sintering temperature was set at 1000 °C for 2 hours at first, and was then raised up to 1300°C for the remaining 6 hours. The sintered samples were ground by abrasive paper and then polished using diamond spraying abrasives.

2.2 Characterization

Phase composition of BaF₂-Ce ceramic was studied using X-ray diffractometer (D/MAX-RB, Cu target, 50 kV voltage, 100 mA electric current, 4 DHS/min scanning speed). The photoluminescence emission (PL) and excitation (PLE) were measured on a SHIMADZU RF-5301 PC Spectrofluorometer. The emission from the sample was also investigated using X-ray induced optical luminescence (XEOL) technique. The scintillation response to gamma 662 KeV (Cs-137) and 511 KeV (Na-22) was measured using a super bi-alkali Hamamatsu PMT R6231-100 biased at 900V. PMT output was further amplified with Hamamatsu preamplifier C6438 and shaped with a spectroscopy Ortec amplifier Model 671. Multi-channel analyzer was a Canberra MP11. Scintillation timing was measured using gamma excitation (Cs-137) and PMT at 900V and output of the preamplifier applied to a digital oscilloscope (Picotech). Decay time was obtained by exponential fitting of the experimental data. Area under the pulse timing graph compared with the corresponding pulse obtained with a NaI(Tl) scintillator under identical conditions is used for LY (light yield) estimation.

3. Results and Discussion

Fig. 1 shows the XRD pattern of BaF₂-Ce(0.2%) nanoparticles and transparent ceramic. All the peaks are in agreement with the pure cubic phase of BaF₂-Ce (JCPDS 04-452). No other phases are detected in both the nanoparticles and the ceramic sample, indicating the absence of secondary phases. The photoluminescence emission and excitation spectrum of BaF₂-Ce(0.2%) ceramic is shown in Fig. 2. The photoluminescence excitation (PLE) spectrum shows a peak at 300 nm and a shoulder at around 280 nm. The photoluminescence measurement of BaF₂-Ce(0.2%) ceramic shows two emissions with peak at 310 nm and 323 nm, when excited with both 279 nm and 300 nm. Unlike pure BaF₂, the fast component with peak at about 195-220 nm is not observed in BaF₂-Ce ceramic. The emission at 310 nm is superimposed with the STE emission observed in pure BaF₂. The emissions at 310 nm and 323 nm has been reported in several Ce³⁺ doped fluorides scintillators caused by the transitions from the bottom of the 5d band to the ²F_{5/2} and ²F_{7/2} energy levels of the 4f¹ configuration of Ce³⁺ ions [22, 23, 25-28]. To further investigate the luminescence in BaF₂-Ce ceramic, we obtained the X-ray excited optical luminescence (XEOL) of BaF₂-Ce ceramic as shown in Fig. 3. The advantage of XEOL is that it allows one to detect all the emissions in the sample. In XEOL, X-ray penetrate through the entire sample generating charge carriers which can recombine or transfer their energy emitting light. XEOL spectrum obtained with X-ray excitation energy of 5250.3 eV shows the emissions at 310 nm and 323 nm in BaF₂-Ce ceramic while the fast component of pure BaF₂ is suppressed. The quenching of fast BaF₂ emission in BaF₂-Ce ceramic suggest the emission at 310 nm which is superimposed with the slower STE emission of pure BaF₂ is associated with the Ce-doping.

To further understand the origin of 310 nm and 323 nm emissions in BaF₂-Ce ceramic, the scintillation decay time was measured under 662 keV gamma excitation as shown in Fig. 4.

Scintillation decay times were calculated by exponential fitting of the experimental data. Scintillation decay measurements exhibits a bi-exponential decay with a fast component of 58 ns and intensity of 37% and a slower component of 434 ns and intensity of 63%. Decay times obtained are similar to the value reported for Ce³⁺ doped BaF₂ single crystal [22]. The fast component of 58 ns is assigned to the 5d-4f transition of Ce³⁺ ion. This decay time is typical of Ce³⁺ luminescence in a variety of environments [15, 23, 26, 28-30]. Slower decay component of 434 ns is about 200 ns shorter than that of STE emission in BaF₂ host. Moreover, the intensity of slower component (63%) in BaF₂-Ce ceramic is quenched compared to 85% in pure BaF₂ as reported. The shorter decay time of 434 ns in BaF₂-Ce ceramic compared to about 630 ns in pure BaF₂ might be the result of dipole-dipole energy transfer from the host lattice to the Ce³⁺ luminescence center. The dipole-dipole energy transfer from the donor (BaF₂ host lattice) to an acceptor (Ce³⁺ luminescence center) is associated with the decrease in luminescence intensity and decay time of the donor in the presence of an acceptor [31, 32]. In dipole-dipole energy transfer process, the efficiency of energy transfer (E) is related to the decay time of the donor (BaF₂ host lattice in this case) by equation (1) [32, 33].

$$E = 1 - \frac{\tau_{DA}}{\tau_D} = 1 - \frac{F_{DA}}{F_D} \quad (1)$$

Where, τ_{DA} and τ_D are the decay time of the donor in the presence and absence of an acceptor (Ce³⁺ in this case) respectively. F_{DA} and F_D are the fluorescence intensity of the donor in the presence and absence of the acceptor respectively.

All this suggest the partial transfer of STE emission from BaF₂ host lattice to the Ce³⁺ luminescence center in BaF₂-Ce transparent ceramic.

There are very few reports on the scintillation properties of BaF₂-Ce ceramics [23, 24] and to the best of our knowledge no reports on gamma photo peak generation with BaF₂-Ce ceramic scintillator. The photo peak in the gamma spectrum is related to the origin of gamma source. For application in gamma spectroscopy, it is desired that the scintillator produce photo peak with a good energy resolution. To study the possibility of using BaF₂-Ce ceramic for gamma spectroscopy, we have acquired the pulse height spectra of gamma rays from a Na-22 and Cs-137 radioisotopes as shown in Fig. 5. The photo peaks at 511 keV, 662 keV and high energy 1274 keV from Na-22 and Cs-137 radioisotopes can be observed in the pulse height spectrum obtained using BaF₂-Ce(0.2%) ceramic of dimension Ø 10 X 1 mm². and The energy resolution of 13.5 % at 662 keV was calculated using the full width at half maximum (FWHM) obtained from the Gaussian fit of the full energy peak area. The scintillation light yield of BaF₂-Ce(0.2%) ceramic was estimated by comparing the integrals of scintillation response of BaF₂-Ce(0.2%) with that of NaI(Tl) applying a spectral correction factor which includes the spectral emission of BaF₂-Ce(0.2%), NaI(Tl) as well as spectral sensitivity of PMT (Hamamatsu R6231-100). The light yield of 5100 photons/MeV was obtained for BaF₂-Ce(0.2%) ceramic and is comparable to the light yield of 5000-7000 Photons/MeV reported for BaF₂-Ce single crystals [1, 34]. The possibility of photo peak generation combines with the ease of fabrication and mechanical strength makes BaF₂-Ce transparent ceramic an alternative to costly single crystal scintillators.

4. Conclusions

BaF₂-Ce(0.2%) transparent ceramic of dimension Ø 10 X 1 mm² was fabricated and luminescence and scintillation properties were studied. The pulse height spectra of radioisotopes Na-22 obtained with BaF₂-Ce transparent ceramic exhibits 511 keV, and 1274 keV photo peaks. The pulse height spectrum of Cs-137 shows the 662 keV photo peak. The energy resolution of 13.5% at 662 keV

was calculated using the FWHM value from the Gaussian fit of the full energy peak area. The scintillation decay data showed the fast component of 58 ns associated to Ce^{3+} transitions and a slower component of 434 ns related to dipole-dipole energy transfer from BaF_2 host lattice to the Ce^{3+} luminescence center. This also shows that the slower STE emission in BaF_2 might have transferred to the relatively faster Ce^{3+} luminescence. Overall, $\text{BaF}_2\text{-Ce}(0.2\%)$ transparent ceramic showed similar luminescence and scintillation properties as observed in its single crystal counterpart. Since, transparent ceramics have advantages such as low fabrication cost, mechanically stronger and easiness of fabrication; it could be an attractive alternative to $\text{BaF}_2\text{-Ce}$ single crystal for scintillation related applications.

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Figure Captions:

Fig. 1. XRD pattern of BaF₂-Ce(0.2%) nanoparticles (a) and transparent ceramic (b).

Fig. 2. Photoluminescence emission and excitation spectrum of BaF₂-Ce (0.2%) ceramic. Inset shows the transition of Ce³⁺ ions in BaF₂-Ce.

Fig. 3. X-ray excited optical luminescence spectrum of BaF₂-Ce (0.2%) ceramic.

Fig. 4. Scintillation decay time of BaF₂-Ce (0.2%) ceramic.

Fig. 5. Cs-137 and Na -22 gamma spectrum of BaF₂-Ce (0.2%) ceramic. Inset shows the photo of BaF₂-Ce (0.2%) transparent ceramic of dimension Ø 10 X 1 mm².

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figure 1

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