

## Optical Analysis of RE<sup>3+</sup> (= Eu<sup>3+</sup>, Sm<sup>3+</sup> & Dy<sup>3+</sup>): BaTiO<sub>3</sub> Ceramic Powders

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Ferroelectric materials Ba<sub>0.95</sub>RE<sub>0.05</sub>TiO<sub>3</sub> (RE=Eu<sup>3+</sup>, Sm<sup>3+</sup> & Dy<sup>3+</sup>) containing certain rare-earth ions as the luminescent ions were prepared by a conventional solid state method. Structural analysis of these materials has been carried out by using both XRD and FTIR spectral measurements. By measuring the excitation, emission spectra and lifetimes of the prominent emission bands, luminescence performance of these optical materials has been investigated.

**Key Words:** RE<sup>3+</sup>; BaTiO<sub>3</sub>; Optical Analysis

### 1. Introduction

Ferroelectric compounds with perovskite structure ABO<sub>3</sub> have attracted a great deal of interest due to their promising and potential applications [1-4]. It has acquired more importance due to its excellent dielectric properties[5-6]. These materials have significant uses in microelectronics and optoelectronics as micro-capacitors, micro-sensors, optical-switches[7]. It has been an encouraging ferroelectric material with a high dielectric constant and hence it has been widely used in manufacturing electronic components such as multilayer ceramic capacitors (MLCCs), PTC thermistors, piezoelectric transducers and other types of electro optic devices[8].

BaTiO<sub>3</sub> possesses a large band gap energy and it is about 3.38 eV when the light's polarization is parallel to the c-axis and it is about 3.27 eV when the polarization is in perpendicular direction to the c-axis. On the other hand, rare earth ions could invert electron shell structures so that the optical transition would occur in the inner shell instead of the outer shell. As a result, the rare earth ions show sharp absorption or emission bands[9-10]. Rare earth ions are trivalent in nature most of the compounds and in the present case which occupy Ba sites in BaTiO<sub>3</sub>. Charge equilibrium in the system could be compensated by electrons, A-site Ba vacancies, B-site Ti vacancies or the 3d<sup>1</sup> (Ti<sup>3+</sup>) mode, are due to the different preparation techniques and ratios of starting chemical compositions[11]. Rare earth doped materials display usage in a wide variety of applications, including phosphors, X-ray imaging and scintillators[12]. In literature, very limited work has so far been reported on the optical analysis of BaTiO<sub>3</sub> having certain luminescent ions as the active ions by replacing Ba<sup>2+</sup> ions. Hence, we have undertaken this piece of work in the present study,

to investigate the emission properties of RE<sup>3+</sup>:BaTiO<sub>3</sub> ceramic powders.

### 2. Experimental Studies

#### 2.1 Sample Preparation

Barium Titanate ceramic powder has been synthesized by a solid state reaction by using BaCO<sub>3</sub> and TiO<sub>2</sub> chemicals in high purity. The overall reaction involves the initial formation of BaTiO<sub>3</sub> at BaCO<sub>3</sub>/TiO<sub>2</sub> grain boundaries, those could later react with BaCO<sub>3</sub> and these could result in with the formation of Ba<sub>2</sub>TiO<sub>4</sub>. Finally, the formation of BaTiO<sub>3</sub> could be achieved by a reaction between Ba<sub>2</sub>TiO<sub>4</sub> and TiO<sub>2</sub> at the optimum conditions [13].

To prepare BaTiO<sub>3</sub>:RE<sup>3+</sup> ceramic powders, BaCO<sub>3</sub>, TiO<sub>2</sub> and RE<sub>2</sub>O<sub>3</sub> chemicals were chosen as the starting materials and were weighed based on the stoichiometric formula relating to the present work. These chemicals were mixed and finely powdered using an agate motor to obtain homogeneous mixtures and were further grounded by adding suitable amount of solvent ethanol. It was heated at 600°C for 2 hours and cooled to the room temperature. The mixture was again grounded by adding a few drops of Poly Vinyl Alcohol (PVA) as a binder solvent. After thoroughly grinding this mixture (BaTiO<sub>3</sub>:RE<sup>3+</sup>), it was heated at 950°C for three hours each and cooled to the room temperature.

#### 2.2 Measurements

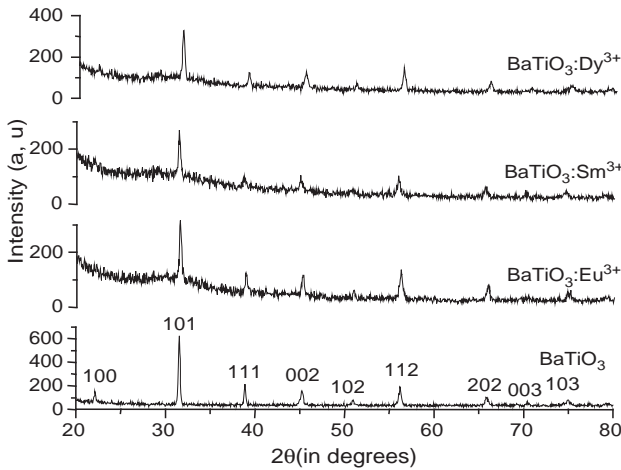
X-ray powder diffraction (XRD) measurements of these ceramic powders were carried out on a XRD 3003 Seifert Model with CuK<sub>α</sub> line of  $\alpha=1.5406$  Å with an operating voltage of 40 kV and current 20mA. In the present work, the 2θ value was varied between 20° and 80° in steps of 0.02°/s. Both the excitation and emission spectra of the BaTiO<sub>3</sub>:RE<sup>3+</sup> powders were recorded on a SPEX Fluorolog-2 fluorimeter (Model-II) with a Xe-arc lamp (450W) with datamax software to acquire the spectral

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data. For the prominent emission bands thus measured, the lifetimes were obtained with a phosphorimeter attachment and flash lamp (Xe) to the main system with a computer controller while measuring the decay curves. FTIR spectra were measured on a Thermo Nicolet-5700 Spectrophotometer using KBr pellet technique in the range of 4000-400  $\text{cm}^{-1}$ .

### 3. Results and Discussion

Single phased tetragonal  $\text{BaTiO}_3$  ceramic powders were obtained for both reference and (0.05%) rare earth ions in the system chosen here. The tetragonal  $\text{BaTiO}_3$  phase has been obtained in powders upon heating at 950°C for 3 hrs in each case. Relative increase of XRD lines intensities of  $\text{BaTiO}_3:\text{RE}^{3+}$  are shown in Fig 1. From the XRD features of undoped and doped  $\text{BaTiO}_3$ , the lattice parameters (a, c in Å) of the materials are changing as we could see in the Table 1, with regard to cell volume change ( $\text{Å}^3$ ) without affecting the crystal structures due to the doping of rare-earth ions in  $\text{BaTiO}_3$ . The details of variation of values of a, c, c/a and cell volume are given in Table 1.



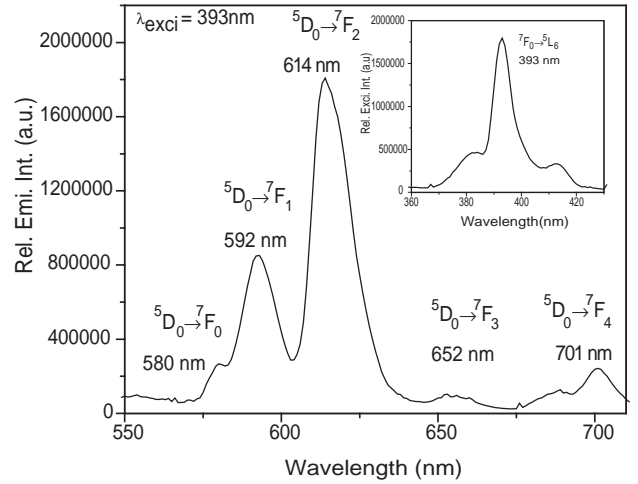
**Fig. 1:** XRD patterns of a reference ( $\text{BaTiO}_3$ ) and rare-earth ions doped ( $\text{RE}^{3+}:\text{BaTiO}_3$ ) ceramic powders

**Table 1**

Sample Type	Crystal parameters			
	a	c	c/a	Cell volume
$\text{BaTiO}_3$	4.0091	4.0061	0.9993	64.39
$\text{BaTiO}_3:\text{Eu}^{3+}$	9.2303	14.3572	1.5554	1223.22
$\text{BaTiO}_3:\text{Sm}^{3+}$	9.0688	16.7101	1.8426	1374.30
$\text{BaTiO}_3:\text{Dy}^{3+}$	11.3310	12.8226	1.1316	1646.30

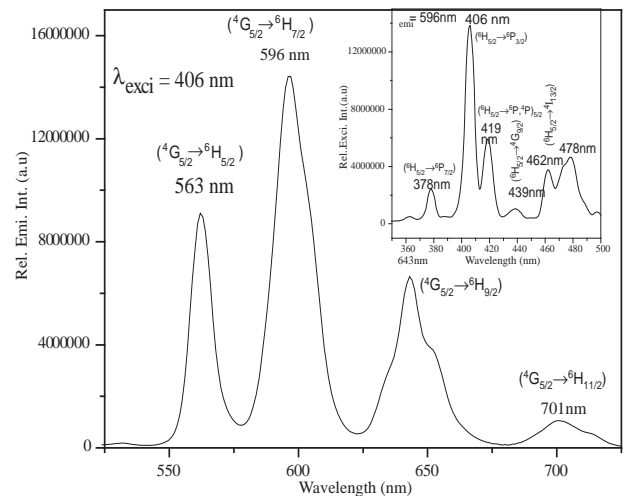
Further, it is observed that an increase in cell volume could inversely be found proportional to the atomic radii of rare earth dopants ( $\text{Eu}=208$  pm,  $\text{Sm}=180$  pm and  $\text{Dy}=178$  pm). The XRD analysis was done with a well-known POWD program [14] and the results have revealed that a tetragonal single-phase nature exists in both the undoped and rare-earth ions doped  $\text{BaTiO}_3$ .

Emission spectrum of  $\text{BaTiO}_3:\text{Eu}^{3+}$ (0.05%) ceramic powder has been shown in Fig 2 with an excitation at



**Fig. 2:** Excitation (350-500 nm) and emission (550-710 nm) spectra of  $\text{Eu}^{3+}:\text{BaTiO}_3$  ceramic powder

393 nm ( ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ ) and from this figure, we could find the emission transitions of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  (580 nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  (592 nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (614 nm),  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  (652 nm) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (701 nm). Among these five emission bands, the red emission ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) at 614nm is a hypersensitive transition with  $\Delta J=2$ , hence it is more intense [15-18]. The excitation band that is located at 393nm ( ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ ). Emission and excitation spectra of  $\text{BaTiO}_3:\text{Sm}^{3+}$ (0.05%) are shown in Fig 3 with four emission bands of  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$  (563 nm),  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$  (596 nm),  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$  (643 nm) and  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$  (701 nm) with an excitation at 406 nm ( ${}^6\text{H}_{5/2} \rightarrow {}^6\text{P}_{3/2}$ ). As shown in Fig. 3, both the excitation and emission bands have been labelled appropriately with the electronic transitions [19]. In Fig. 4, the excitation and emission spectra of  $\text{BaTiO}_3:\text{Dy}^{3+}$ (0.05%) are shown with an excitation at 387 nm ( ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{13/2}$ ). From this figure, two emission bands such as  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$  (478 nm) and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  (575 nm) have been observed respectively. Excitation bands at 387 nm, 395 nm, 426 nm and 450nm are assigned to the electronic transitions of  ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{7/2}$ ,  ${}^4\text{I}_{13/2}$ ,  ${}^4\text{G}_{11/2}$  and



**Fig. 3:** Excitation (350-500 nm) and emission (525-710 nm) spectra of  $\text{Sm}^{3+}:\text{BaTiO}_3$  ceramic powder

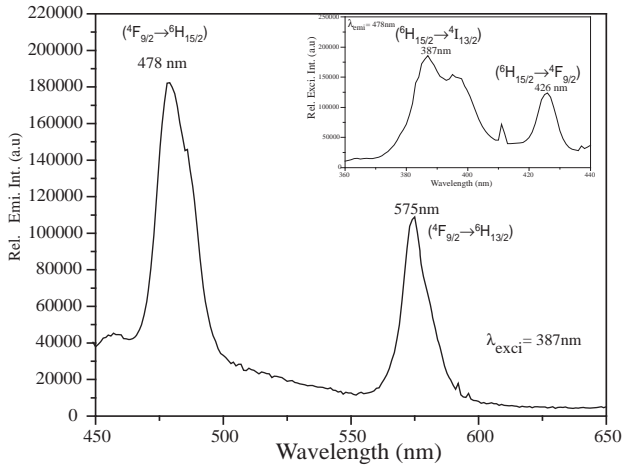


Fig. 4: Excitation (360-440 nm) and emission (450-650 nm) spectra of  $Dy^{3+}:BaTiO_3$  ceramic powder

$^4I_{15/2}$  respectively. Substitutional trends in the host, by the dopant ions have been well explained in literature [20]. The decay curves of prominent emission bands of  $BaTiO_3:Eu^{3+}$ ,  $BaTiO_3:Sm^{3+}$  and  $BaTiO_3:Dy^{3+}$  ceramic powders are shown in Figs 5-7 respectively. FTIR spectra

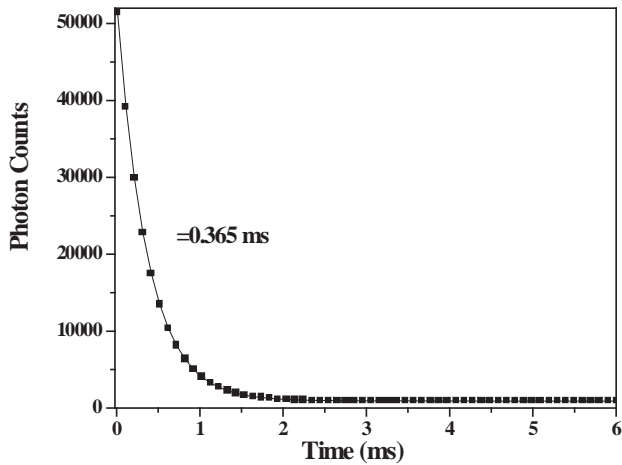


Fig. 5: Decay curve of  $^5D_0 \rightarrow ^7F_2$  (614 nm) of  $Eu^{3+}:BaTiO_3$  ceramic powder at  $\lambda_{exci} = 393$  nm

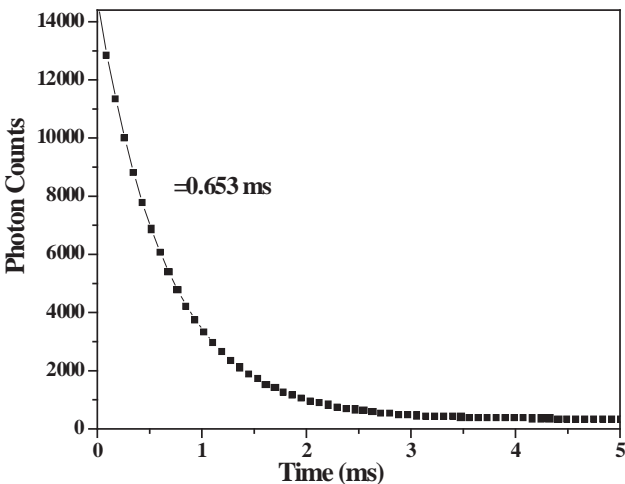


Fig. 6: Decay curve of  $^4G_{5/2} \rightarrow ^6H_{7/2}$  (596 nm) of  $Sm^{3+}:BaTiO_3$  ceramic powder at  $\lambda_{exci} = 406$  nm

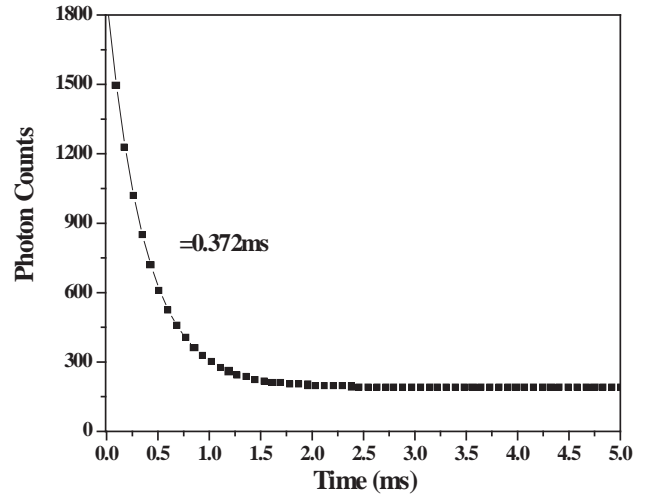


Fig. 7: Decay curve of  $^4F_{9/2} \rightarrow ^6H_{15/2}$  (478 nm) of  $Dy^{3+}:BaTiO_3$  ceramic powder at  $\lambda_{exci} = 387$  nm

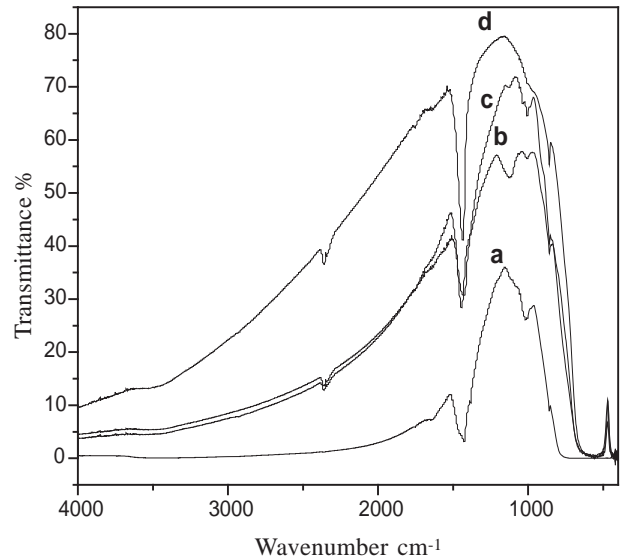


Fig. 8: FTIR spectra of (a)  $BaTiO_3$  (b)  $Eu^{3+}:BaTiO_3$  (c)  $Sm^{3+}:BaTiO_3$  & (d)  $Dy^{3+}:BaTiO_3$  ceramic powders

of reference  $BaTiO_3$  and  $BaTiO_3$  doped with  $Eu^{3+}$ ,  $Sm^{3+}$  and  $Dy^{3+}$  ions are shown in Fig 8 in order to understand the existence of various Ti-O and antisymmetric stretching vibrations of  $CO_3$ . A band at  $2360\text{ cm}^{-1}$  could be attributed to the Ti-O vibrations and another band at  $1440\text{ cm}^{-1}$  to the antisymmetric stretching vibrations of  $CO_3$  [21]. The bands of the double band stretching vibration near  $940\text{--}980\text{ cm}^{-1}$  have disappeared, a new C-O stretching absorption band has been observed at  $1050\text{ cm}^{-1}$  [22]. Regarding a band at  $866\text{ cm}^{-1}$  is due to a vibrational mode of  $CO_3^{2-}$  anions, which indicates the absorption of  $CO_2$  content by the samples [22].

#### 4. Conclusion

In summary, it is concluded that we have successfully analyzed both the structural and emission properties of  $Eu^{3+}$ ,  $Sm^{3+}$ , and  $Dy^{3+}$  doped  $BaTiO_3$  ceramic powders.

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