Synthesis and characterization of rare earth activated barium zirconate ceramic

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Abstract. This paper reports synthesis of rare earth doped BZO perovskite ceramic by facile solid state reaction synthesis route. The phosphor confirms its nanocrystalline structure with high order purity and homogeneity. Characterized by XRD, SEM, EDX, FTIR and TL, a complete investigation of its structural, morphological and thermoluminescent properties is done. The kinetic parameters estimated using peak shape method confirms the second order kinetics of synthesized ceramic powder. With the emerging global concern regarding UVR exposure protection, the BZO perovskite ceramic are emerging as dynamic alternatives for TL mapping.

1. Introduction
With distinct refractory properties, good chemical resistance, high dielectric constant and good structural integrity, ceramic materials have emerged as potential candidate for automotive, sensing, optoelectronics and refractory applications. Perovskite structured ceramic materials with a general chemical formula ABO₃ form a wide range of alkaline earth metal zirconates widely used in manufacturing of MLCC, frequency filters, batteries, thermal barrier coatings and sensors [1]. Barium zirconate, Ba₁₂Zr₁₀O₃₇, is a perovskite electroceramic material with a high MP (> 2600°C), wide band gap (> 4 eV) and high dielectric constant (~ 50). On doping with rare earth (RE) impurities, the perovskite material show drastically amended physical, chemical, optical, thermal, electrical and magnetic characteristics [2]. Prepared via facile solid state reaction synthesis route, the environmental friendly barium zirconate ceramic with crystalline nature and irregular morphology is obtained. The synthesized ceramic material is also subjected to thermoluminescent analysis in order to confirm its suitability as TL phosphor. The TL phosphors have emerged as the most suitable, sensitive and precise means for radiation detection [3]. The characteristics of a phosphor that makes it worth efficient are - Linear dose response, Spatial resolution, Sensitivity, Fading, Directional dependence, etc. TL phosphors make use of the phenomena of Thermoluminescence which is nothing but Thermally Stimulated Luminescence. This phenomena involves thermal stimulation of the material which is pre-exposed to some type of radiation, so as to get visible light emitted as the output. The name of this process is a misnomer because thermal treatment is given as stimulation and not as excitation. In proper words, Thermoluminescence can be defined as Thermally Stimulated luminescence (TSL) [4].

2. Synthesis
The Synthesis of desired perovskite is done here using solid state reaction synthesis route which is the typical, easy, environment friendly and less sophisticated method [5]. BaCO₃, ZrO₂, Eu₂O₃ and Tb₂O₃
are taken here as the starting materials in stoichiometric ratio. All chemicals consumed here were of Sigma Aldrich with homogeneity and high purity (>99.99%). The Solid State reaction synthesis route involves two sub processes- Calcination and Sintering [6]. In the process of Calcination, BaCO$_3$ get thermally decomposed to BaO and CO$_2$, when heated at 1000 °C for 2 hrs. This BaO obtained here combines with ZrO$_2$ to form BaZrO$_3$ in the process of Sintering. During Sintering the firing of rare earth impurities, Eu$_2$O$_3$ and Tb$_2$O$_3$, in the host lattice also takes place when heated at 1350°C [7]. The RE doped BZO phosphors with Eu$^{3+}$ varying from 0.1-2 mole % and keeping Tb$^{3+}$ fixed as 1 mole % are considered here for characterization [8].

3. Characterization results and interpretation

3.1. XRD analysis

XRD analysis is carried out using X-ray diffractometer system PANalytical - XPERT-Powder, which employs X-ray beam of wavelength 0.154nm (Cu-K-alpha) with copper as anode source. The observed X-ray pattern matches with the JCPDS card no. 06-0399 with the reflection peaks recorded at 30.59°, 44.04°, 54.88° and 61.99° corresponding to (110), (200), (211) and (220) planes respectively (in Figure 1) [9]. To estimate the crystallite size Debye Scherrer Formula is used:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

Where, \( D \)= Average crystallite size, \( \lambda \)=Wavelength of X-rays, \( \beta \)=Full width at half maximum FWHM, \( \Theta \)=Angle of incidence, \( K \)=Scherer constant (0.9 - spherical particles) [10].

So, for given sample, \( K=0.9 \), \( \lambda=0.154 \) nm, \( \beta=0.0061394 \) and \( 2\Theta=30.59^\circ \). The synthesized phosphor is orthorhombic with average crystallite size as 23.404 nm [11].

![Figure 1. PXRD pattern of Eu$^{3+}$, Tb$^{3+}$ doped BaZrO$_3$ phosphor.](image)

3.2. SEM and EDXS analysis

In order to extract the topographical and compositional information of synthesized phosphor, SEM analysis is done using Oxford’s SEM Analyser. The SEM micrographs show highly agglomerated clusters with spherical morphology of grain size nearly 68 nm (in Figure 2(a)). This confirms crystalline nature of prepared perovskite phosphor. The EDXS analysis also confirms its desired composition (in Figure 2(b)) [12].
3.3. FTIR analysis
The FTIR is done here for functional group analysis of the synthesized phosphor. In FTIR synthesized phosphor irradiated with infrared radiation and the respective vibrational modes are studied. The sharp peaks obtained at 505–597 cm$^{-1}$, which correspond to vibrational stretching of Zr–O. The peak at 1466.73 cm$^{-1}$ corresponds to existence of carbonate CO$_3^{2-}$ group. The strong peak at 1126.67 cm$^{-1}$ corresponds to Ba–O bonding (in Figure 3). The IR spectra confirm the formation of the BaZrO$_3$: Eu$^{3+}$, Tb$^{3+}$ phosphor [13].

![FTIR spectra of Eu$^{3+}$, Tb$^{3+}$ doped BaZrO$_3$ phosphor.](image)

3.4. Thermoluminescence characteristics analysis
The TL analysis is carried out here by recording TL thermograms of the prepared phosphors when subjected to 10 minutes UVC exposure of 254 nm. Thermoluminescence Reader TL10091 is used here for TL mapping. The heating strips are programmed to heat the samples with a constant heating rate of
5°C/sec up to a maximum temperature range of 500°C. This analysis is done so as to estimate the various trapping parameters of the phosphors synthesized that contribute towards the observed TL emission. The kinetic parameters like activation energy $E$ (eV), order of kinetics and trap depth are computed from the recorded glow curves using Peak shape method [14]. The most intense peak is obtained for Eu$^{3+}$(1 mol%) and Tb$^{3+}$(0.5 mol%) doped BaZrO$_3$ phosphor which is shown in Figure 4.

![Figure 4](image)

**Figure 4.** (a) Recorded TL glow curve and (b) Deconvoluted TL glow curve of Eu$^{3+}$, Tb$^{3+}$ doped BaZrO$_3$ phosphor.

The average kinetic parameters estimated using peak shape method are: $\tau =30.50$, $\delta =32.50$, $\omega =63.0$ and $\mu =0.5158$ [15]. The synthesized phosphors show second order of kinetics with the average activation energy as 0.419 eV clearly indicating that the irradiated electrons get trapped in shallow traps with less trap depth and hence, require less activation energy to stimulate them resulting into TL emission.

4. Conclusion
This work investigated the TL characteristic of Eu$^{3+}$ and Tb$^{3+}$ BaZrO$_3$ nanophosphor synthesized by Solid State Synthesis route. The synthesized phosphor reports nanocrystalline size of 23.404 nm with orthorhombic structure. The SEM analysis confirms spherical morphology of the particles forming agglomerated nanoclusters with grain size of 68 nm. The FTIR spectra confirm the compositional characteristics of the nanophosphor. The TL glow curves recorded here proves the nanophosphor appropriate for UVR exposure assessment with second order of kinetics and low value activation energy $E_{\text{eff}}$.

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