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Effect of UV Irradiation on Thermoluminescence Properties of Perovskite Structured Pure and Europium Doped Barium Zirconium Titanate

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Abstract— *The $BaZr_xTi_{1-x}O_3$: Eu^{3+} phosphors have been synthesized the conventional solid state reaction method. Mechanoluminescence (ML) and thermoluminescence (TL) in barium zirconium titanate (BZT) system with Europium as dopant is reported for the first time. The BZT system belongs to perovskite family. The samples are prepared in a high temperature furnace at a temperature of 1200°C. The powder X ray diffraction (XRD), Scanning electron microscopy (SEM) techniques are used to characterize the samplesthoroughly according to their structure, composition, morphology and optical properties. The XRD patterns confirm the crystalline perovskite type cubic structure. Also, highly agglomerated, porous and regular shaped particles are seen by FESEM. The optical properties of the prepared samples are studied and discussed in terms of TL. The TL glowcurves so obtained for the different samples for different irradiation time are analysed by the well-known Peak Shape method.*

Keywords— *Perovskite, Thermoluminescence, BZT, solid state reaction, optical properties, XRD, FESEM*

1. INTRODUCTION

Materials science is the branch of physics which deals with group of materials having properties that are technologically important. One such group of materials are the well known perovskite structured (ABO_3) materials. Titanates with the perovskite structure constitute an attractive class of materials in which multiple functions can be integrated [1]. Titanates have been found to be optimal candidates in field emission displays (FED) and plasma display panel (PDP) devices. These are resistant to high density electron irradiation, the luminescent efficiency and thermal conductivity can be maintained under prolonged coulomb loading [2]. So many works have been published on lead (Pb) based compounds (perovskites) like $PbTiO_3$ and $PbZr_xTi_{1-x}O_3$ etc. But because of the toxic nature these compounds are found unsuitable and not eco friendly. Barium titanate is a material with very good ferroelectric, piezoelectric and dielectric properties. It belongs to the perovskite family having ABO_3 structure. The ideal perovskite is a corner sharing cubic network of BO_6 octahedra with A cations occupying the 12 co-ordinate position between 8 BO_6 octahedra [3]. Barium Titanate ($BaTiO_3$) is the mother material of this family. It is well known that the dopant ionic radius is the main parameter determining the substitutions in the $BaTiO_3$crystal lattice [4]. A simple substitution of Ti^{4+} (ionic radius 74.5 pm) with Zr^{4+} (atomic radius 86 pm) results in several interesting features[5]. As reported earlier the addition of rare earth ions to the mother material also enhances the luminescence properties[6]. In this research work we tried our best to present the result about the luminescence behavior of Europium (Eu) doped $BaZr_{0.25}Ti_{0.75}O_3$ powders prepared by solid state reaction method at different time of UV irradiation.

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2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

$BaZr_{0.25}Ti_{0.75}O_3$: Eu^{3+} (Eu= 0.01, 0.05, 0.1, 0.5, 1 mole percent) powders of various composition were prepared by the conventional high temperature solid state reaction method. Stoichiometric amount of $BaCO_3$ (AR grade), ZrO_2 (Ar grade), TiO_2 (AR Grade), Eu_2O_3 (AR Grade) were taken as starting materials. All the chemicals were thoroughly mixed and grinded in agate mortar in presence of acetone. Then after the powder is calcined at 1200°C in a high temperature furnace for 6hrs.

2.2 Characterisation Techniques

The obtained calcined powder was characterised by XRD and FESEM. The phase purity and surface morphology can be observed through these techniques. The thermoluminescence glow curve measurements were performed using Nucleonix TLD Reader at heating rate of 3°C/S. Before the TL measurements the samples were exposed to UV irradiation for different intervals of time.

3. RESULTS AND DISCUSSIONS

3.1 XRD

Fig.1 shows the XRD patterns of the powders. XRD patterns reveals the formation of phase pure samples except one additional peak due to the formation of $BaZrO_3$. The high temperature diffusion is one of the reason for the formation $BaZrO_3$. The average grain size of the powders is calculated by using the well known

scherrer's formula. The average size calculated is found to lie in the range of 30-50nm.

3.2 FESEM

Fig.2 shows the FESEM micrographs of $BaZr_{0.25}Ti_{0.75}O_3$: Eu^{3+} samples. Little agglomeration in the particles can be seen in all the micrographs. The particles donot posses uniformity in size. Also uniformity in shape is not observed.

3.3 TL Studies

TL is the thermally stimulated emission of light following the absorption of energy from radiations (here it is UV irradiation). The radiations cause displacement of electrons within the crystal lattice of the substance. Upon heating, the trapped electrons return to their normal lower energy positions, releasing energy in the process[7]. The TL glowcurves of the powdered samples with different Eu compositions for different time length of UV irradiation is shown in Fig.3 and Fig.4. both the curves are smooth and have avery clear peak. No significant change in the TL intensity is seen when the time of irradiation changes from 5min to 20min. Also the peak temperature for all the samples in both the cases is similar. The peak of the TL glowcurve is seen close to 120°C to 125°C.

The TL glowcurves are analysed by the well known peak shape method. The glowcurves are analysed in terms of peak temperature and trapping parameters. Table.1 and 2 represents the values of T_m, ω, μ, E corresponding to the samples irradiated for 5min and 20 min respectively. Here, T_m, represents peak temperature, E is activation energy. ω and μ are kinetic parameters.

$\omega = (T_2-T_1)$°C and $\mu=(T_2-T_m)/(T_2-T_1)$

Where, T_1 and T_2 are half intensity temperatures on both the sides of the peak. In table.1 and table.2 system 1,2,3,4,5,6 corresponds to BZT with 0, 0.01,0.05,0.1,0.5 and 1 mole percent concentration of Eu.

3.4 ML Studies

Table 1: Kinetic parameters for 5min UV irradiation

system	*Tm(°C)*	*ω*	*μ*	*E(eV)*
1	125	93	0.41	0.27
2	118.2	84.6	0.45	0.36
3	112.3	86	0.45	0.34
4	111.5	87.3	0.49	0.39
5	120.8	86.5	0.44	0.34
6	123.2	95.5	0.41	0.26

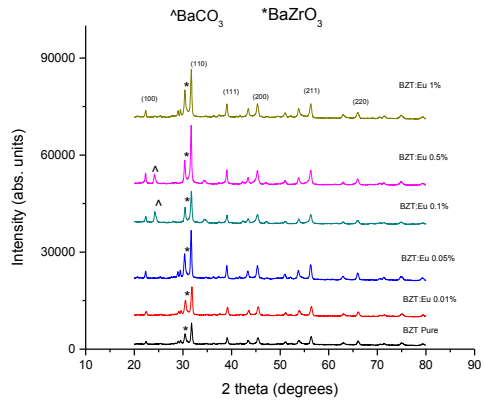

Fig. 1: XRD patterns of $BaZr_{0.25}Ti_{0.75}O_3$: Eu^{3+} (0,0.01,0.05,0.1,0.5,1 mole percent)

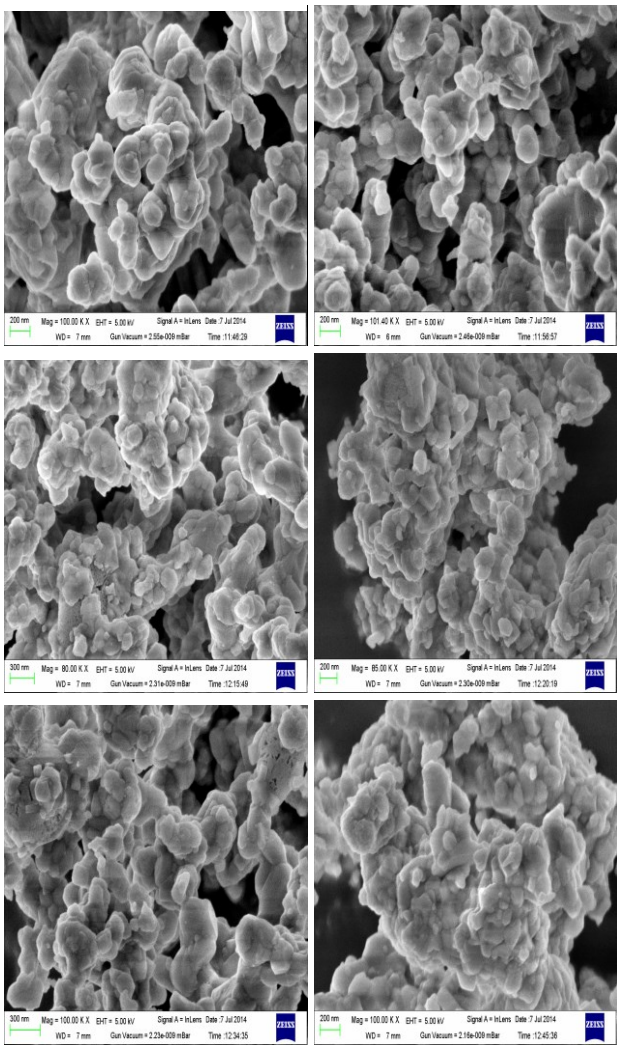

Fig. 2: FESEM micrographs of $BaZr_{0.25}Ti_{0.75}O_3$: Eu^{3+}

Table 2: Kinetic parameters for 5min UV irradiation

system	*Tm(℃)*	*ω*	*μ*	*E(eV)*
1	125.5	89.4	0.4	0.27
2	115.9	84.5	0.45	0.35
3	113.4	82.2	0.46	0.38
4	116	87.3	0.46	0.35
5	118.4	87.5	0.44	0.33
6	125.5	92	0.41	0.28

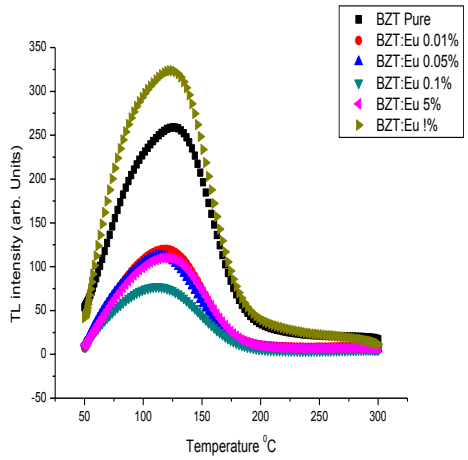

Fig. 3: TL glowcurves of $BaZr_{0.25}Ti_{0.75}O_3$: Eu^{3+} for 5 min UV irradiation

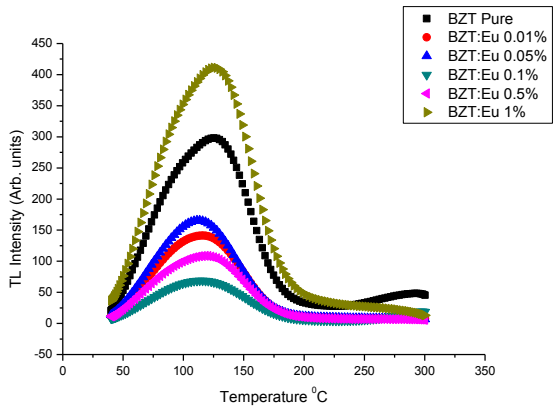

Fig. 4: TL glowcurves of $BaZr_{0.25}Ti_{0.75}O_3$: Eu^{3+} for 20 min UV irradiation.

The ML studies of the BZT: Eu^{3+} system are conducted without and under UV irradiation but, the samples didnot show any results. The reason for this may be concentration quenching in BZT at and above 25 mole percent of Zr in the mother material $BaTiO_3$.

4. CONCLUSIONS

BZT: Eu^{3+} samples were successfully synthesised by solid state diffusion method. Confirmation of perovskite cubic structure is done by XRD. FESEM images shows agglomeration of particles. The activation energy calculated from the TL glowcurves lies in between 0.25 – 0.4 eV.

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