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Thermo and mechanoluminescence studies of BZT phosphor

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ABSTRACT

Mechanoluminescence (ML) and thermoluminescence (TL) in barium zirconium titanate (BZT) is reported for the first time. The BZT powder sample, belonging to perovskite category is synthesized using solid state reaction technique. The sample is prepared at a temperature of 1200 °C. The obtained specimen is thoroughly characterized paying particular attention to their structure, composition, morphology and optical properties. The surface morphology and structural properties are analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns confirm the formation of crystalline perovskite type cubic structure. Also, highly agglomerated, porous and regular shaped particles are seen by SEM. The optical properties of as prepared sample is presented and discussed in terms of ML and TL. The ML intensity is found to be maximum for the sample irradiated for 10 min. More than one maxima in TL glow curve reveals that the traps are distributed in separate groups at different depths and corresponding values are calculated using initial rise method.

1. Introduction

Ferroelectric materials exhibit important multifunctional properties such as ferroelectric, dielectric, pyroelectric and electro-optic properties. They are being used to fabricate various optoelectronic and microelectronic devices such as microsensors, microactuators, electronic modulators, etc. [1,2]. It is well known that $BaTiO_3$, $CaTiO_3$ and $SrTiO_3$ are three typical ferroelectric materials. Their solid solutions have been and continue to be of interest for investigation, not only because of their various applications, but also for their interesting dielectric and ferroelectric behaviors. These materials belong to perovskite category of materials represented by general formula ABO_3, where big 'A' cation can be classified as network modifiers and small 'B' cation as network formers [3]. The ideal perovskite, ABO_3, is a corner sharing cubic network of BO_6 octahedra with 'A' cations occupying the 12 coordinate positions between 8 BO_6 octahedra. Recently, structurally disordered ABO_3 perovskites such as $SrTiO_3$, $CaTiO_3$, $BaTiO_3$, $PbTiO_3$, $SrZrO_3$, $Pb(Zr,Ti)O_3$ (PZT) and $Ba(Zr,Ti)O_3$ (BZT) have been investigated in several papers due to their optical properties at room temperature (RT). Till 1970s rare earth (RE) doped perovskite type oxides were actively investigated for their ferroelectric, phase transitions and semiconducting properties but after that spectroscopic investigation of RE ions doped perovskite type oxides faded out due to their lower luminescence efficiency [4]. The so called universal "green-luminance" of perovskite-type materials such as titanates is well established. When these materials are excited by wavelengths above the band-gap energy, the titanates on single crystal show luminescence at RT [5]. It is suggested that these mechanisms include self trapped excitons (STE), recombination of electron–hole polarons and a charge transfer vibronic exciton, donor acceptor recombination and transitions in MeO_6 complexes [4]. Leonelli and Brehner put forward a model that explains the mechanism of visible emission in which the electrons form small polarons, while the holes interact with the polarons to form STEs [6]. In these crystals, a broad luminescence band is usually observed at low temperatures and this behavior is associated with the presence of imperfections or defects into the band-gap [3]. Among above materials, BZT has been attracting much attention owing to its various promising electrical and optical properties in different forms. As, it is derived from two perovskite lattices namely $BaTiO_3$ and $BaZrO_3$, the zirconium substitutions into the titanium lattices enhance the dielectric and piezoelectric properties [7]. Moreover, Zr^{4+} ion is chemically more stable than Ti^{4+} ion and has a larger ionic size to expand the perovskite lattice. Therefore, the substitution of Ti by Zr would depress the conduction by electronic hopping between Ti^{4+} and Ti^{3+} and it would also decrease the leakage current of the $BaTiO_3$ system. It is worth mentioning that recently, BZT was chosen as an alternative material to PZT in the manufacture of bulk ceramic or thin films because it is highly stable and lead free [8].

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The ML effect is a light emission induced as a result of some mechanical action on a solid. The ML effect can be produced through either destructive means (grinding, rubbing, stretching, biting, cleaving) or non-destructive means (ultrasonic, stress, vibration or through other means) [9]. Until now, destructive mechano-luminescent (DML) effects have been extensively observed in various inorganic and organic materials [10]. However, due to non-repeatability of destructive ML response, it is difficult to obtain practical devices based on application of DML effects [11]. On the other hand the TL from ferroelectric materials has been almost untouched as far as perovskite kinds of materials are concerned especially in BZT. Recently, Shivaram et al. [12] reported the TL properties of $CaTiO_3$ nanophosphor. They compared the TL results of $CaTiO_3$ nanophosphor synthesized by three different routes namely solution combustion (CS), modified solid state reaction (MSS) and solid state (SS) methods. They observed TL behavior using gamma irradiation.

With the development of newer technologies, several kinds of chemical synthesis techniques such as co-precipitation [13], sol–gel [14], reverse micro emulsion [15] and combustion method [16] have been employed to prepare BZT and its phosphors. Comparatively speaking, above methods are suitable to synthesize the phosphor with smaller sizes but often difficult to achieve well-defined morphologies. The optical properties of luminescent materials not only are closely related to its native crystal structure but also to its morphology. The preparation of BZT in perovskite form at high pressure was also reported recently [17]. Among these, solid state reaction (SSR) has been an interesting method for preparing precursor powders [18].

Several reports have been dedicated to the synthesis, characterization and PL properties of BZT but its ML and TL behaviors are still rarely reported. As far as known to us, this paper is a very first attempt to explore the possibility of BZT to be used as a versatile luminescent material.

2. Experimental

2.1. Sample preparation

For preparing powder sample, stoichiometric amounts of barium carbonate ($BaCO_3$), titanium dioxide (TiO_2) and zirconium dioxide (ZrO_2) are used as raw materials. All these materials, supplied by Merck Chemicals are of analytical purity. The mixture of above chemicals is grinded continuously in an agate-pestle mortar (diameter-5″) for 3 h. After proper grinding, the crushed material is transferred into a rectangle shaped alumina crucible with comparatively larger volume within which chemical reaction takes place. Thereafter, the mixture is placed into a digitally controlled furnace and calcined at a temperature of 1200 °C for 6 h. The advantage of using rectangular crucible is that the entire material can be supplied uniform heat inside the furnace. In this paper, we present and discuss the results of ML and TL studies carried out for BZT. To the best of our knowledge and what literature survey suggests, there has not been done much work on these properties of ferroelectric materials especially BZT.

2.2. Measuring instruments

The materials are weighed using Shimadzu ATX 224 single pan analytical balance and the sample is calcined in a digital furnace at a temperature of 1200 ± 5 °C. The crystalline structure, size and phase composition of the sample are examined by Bruker D8 Advance X-ray diffractometer (detector-Si trip Lynx EYE) using Co-K_α radiations (λ = 1.790 Å) at 36 kV tube voltage and 20 mA tube current at RT in the 2θ range from 10° to 80°. For qualitative analysis, X-ray diffractograms are recorded at a scan speed of 2θ/min giving a step size 0.05° and the step time 0.7 s. The morphology of as prepared sample is studied using JEOL JSM-6380 scanning electron microscope (SEM). The TL spectra at different temperatures are recorded using Nucleonix make TLD reader (model I 1009 h), where samples are excited with UV radiation at 365 nm wavelength for different times. The heating is performed from RT up to 400 °C and heating rate under thermal stimulation is varied 3 °C/s.

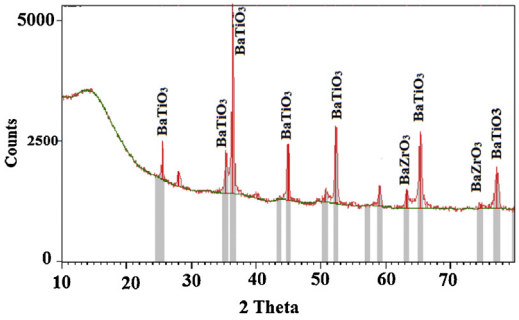

Fig. 1. X-ray diffraction pattern of pure $Ba[Zr_{0.1}Ti_{0.9}]O_3$.

The ML was monitored by an indigenous set-up having RCA 931 photomultiplier tube (PMT) positioned below the Lucite plate and connected to a digital storage oscilloscope (Scientific 300 MHz, SM 340). Loads of different masses are dropped from a particular height.

3. Results and discussion

3.1. Characterization

3.1.1. X-ray diffraction

The crystalline phases of powder sample are identified by XRD. The typical XRD pattern of pure $Ba[Zr_{0.1}Ti_{0.9}]O_3$ is presented in Fig. 1. The assignment of diffraction lines is made by comparison with JCPDS files of barium titanate oxide (cubic, JCPDS 72-0215), and barium zirconium oxide (JCPDS 74-1299) and the evaluated and reported values of parameters like lattice interval, lattice constant and Miller indices. The unit cell parameters of BZT are $a = b = c = 4.0577$ Å with a perovskite type cubic structure and space group *Pm-3m*. A similar finding for BZT synthesized by the polymeric precursor method (PPM) was reported by Cavalcante et al. [3]. The lattice parameters are calculated using the least square refinement from the X'Pert High Score program. Here, it is worth mentioning that for the $Ba[Zr_xTi_{1-x}]O_3$ samples with small increment of zirconium content, i.e., $0.00 < x < 0.02$; it was not possible to identify the crystalline phase due to the close proximity of the diffraction angles [9,17].

The average grain size (g.s.) of the powder grains is estimated using Scherer's formula [12]

$$\text{g.s.} = K\lambda/\beta \cos\theta \quad (1)$$

where λ is the wavelength of X-rays, β is the full width at half maxima (FWHM) of the peak, K is a constant and θ is the Bragg's angle. The average grain size calculated using Eq. (1) is found to be approximately 7.0 Å. The corresponding XRD data are summarized in Table 1.

3.1.2. Scanning electron microscopy (SEM)

The SEM micrograph of pure $Ba[Zr_{0.1}Ti_{0.9}]O_3$ sample calcinated at 1200 ± 5 °C is shown in Fig. 2. As is evident from the figure, the phosphor prepared by SSR method shows highly agglomerated and regular shaped particles. Moura et al. [18] observed an increase in