$BaTi_{0.97}Fe_{0.03}O_3$ Ceramic Material: A study of structural and electrical properties

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***Abstract* - The ferroelectric compound barium titanate ($BaTiO_3$) has a perovskite type structure. It is an essential material for dielectric applications. From application point of view, doped $BaTiO_3$ ceramic materials inherit great potential for electric and electronic devices. Herein, the Fe doped $BaTiO_3$ is reported. It was synthesized by solid-state reaction route. The structural, vibrational and electric properties of $BaTiO_3$ were studied using X-ray powder diffraction (XRD), Raman spectroscopy and Polarization (P-E loop) characterizations. The study of XRD pattern of Fe doped $BaTiO_3$ reveals that the sample has acquired single phase tetragonal structure with space group *P4mm*. The Raman spectra obtained at Room temperature for Fe doped $BaTiO_3$ display signature Raman modes witnessing tetragonal structure. The P-E hysteresis loop of Fe doped $BaTiO_3$ displays a good behaviour with definite saturation and remnance of polarization however the cut in loop reveals the sample exhibits leakage.**

***Index Terms* - Perovskite structure, $BaTiO_3$ ceramics, XRD, Polarization.**

1.INTRODUCTION

In the field of electro-ceramics and microelectronics, barium titanate ($BaTiO_3$) is a very attractive material due to its rich features. It inherits high dielectric constant and low loss values. These properties makes it an excellent choice for many applications, which include capacitors, energy storage devices, photonic crystals and multilayer capacitors. Its properties can be enhanced via doping thereby it founds wide range of applications in semiconductors, ultrasonic transducers, positive temperature coefficient resistors (PTCR), piezoelectric devices etc. It is regarded as the integral member of the ferroelectric ceramic family. Furthermore, the features of the sample are enhanced by means of the synthesis route and sintering regime exploited [1-4].

$BaTiO_3$ has attracted the interest of researchers due to their ubiquitous properties. Recently, investigations into the incorporation of impurities (i.e., transition metals) in the $BaTiO_3$ is also reported to inherit ferromagnetic properties when transition metal impurities are incorporated giving rise to their multifunctional characteristics [5].

$BaTiO_3$ exhibits perovskite structure viz. ABO_3, where A represents Ba^{2+} and B represents Ti^{4+}. It has a centro-symmetric cubic crystal structure (*Pm*3*m* space) above the Curie temperature, T_C ~ 130°C. The transition temperature T_C can be broadened via doping at B-site which disturbs TiO_6 octahedra [6,7]. At lower temperature, T~ 400 K, the sample acquires tetragonal crystal structure due to the ionic displacement of the titanium (Ti)-ion. This results ferroelectric features of the sample [8,9]. It also exists in orthorhombic phase at 0 °C and rhombohedral phases at below -90 °C and above 1460 °C it exists in hexagonal phase.7

The transition metals Fe preferentially substitute on the Ti4+ site. The usual mechanism of charge compensation for this ion involves the creation of a stoichiometric amount of oxygen vacancies, so it behaves as acceptor dopants. It is suggested that the ionic radius, dopant concentration, sintering atmosphere and Ba/Ti molar ratio all play crucial roles. The properties of $BaTiO_3$ can thus be modified through the incorporation with various ions. One of the important issue is stability in addition to the conductivity via doping by transition metals. Transition metal, Fe doping meets the requirements in general thereby introduces semiconducting behavior in $BaTiO_3$ which is usually an insulator at room temperature.

2.EXPERIMENTATION DETAILS

2.1. Synthesis

Fe doped $BaTiO_3$ sample was synthesized by a conventional solid state reaction method. The raw materials used were $BaCO_3$, TiO_2 and Fe_2O_3. All the materials were of analytic grade with 99% purity from Loba Chemicals Limited. Stoichiometric amounts of raw materials were mixed via 7h mechanical grinding using Mortar-pestle in the acetone medium to ensure proper distribution of the constituents in the sample. The sample was then calcined at 1300^{o}C in a muffle furnace for a time duration of 7h. The sample was reground for 2 hours to get fine powder. The fine powder was mixed with polyvinyl alcohol (PVA) as binder. Then, it was transformed into circular discs of 10mm at a pressure of 6tonnes pre inch. The pellets were sintered at 1350^{o}C for 5h. In the final step, the sintered compact discs were polished with silver paste to get better electrical contacts.

2.2. Characterizations

The identification of crystal structure and type of phase were investigated in terms of room temperature X-ray powder diffraction (XRD). The data collection with a scanning rate 2° and a step size of 0.02° over the angular range 2θ (20° - 90°) was carried out employing Bruker D8 Advance X-ray diffractometer with CuKα1 (1.5406 Å) radiation. The LABRAM-HR spectrometer with a 488 nm excitation source equipped with a Peltier cooled charge coupled device detector was exploited to record the inelastic Raman spectra of Fe doped $BaTiO_3$. The electrical polarization versus field (P–E loop) measurement was performed on commercial ferroelectric loop tracer from M/s Radiant Instruments, USA.

3. RESULTS AND DISCUSSION

3.1. X- ray diffraction data analysis

The XRD pattern of solid state produced $BaTi_{0.97}Fe_{0.03}O_3$ ceramic material is displayed in Figure 1. The clean and noise free type of XRD pattern reveals the sample is single phased. The analysis of XRD data reveals the sample has crystalized in tetragonal structure exhibiting space group of P4mm [10]. Within the limits of experiment, no trace of secondary phase is witnessed. The lattice parameters calculated were $a = b = 4.01Å$ and $c = 4.023Å$

From the XRD pattern of $BaTi_{0.97}Fe_{0.03}O_3$, it can be concluded that the sample is highly crystalline. The higher crystallinity acquisition of the sample may be attributed to the higher temperature treatment of the sample. Here in the XRD pattern, the sharpness and hence the higher intensity witness the fact. Furthermore the sample exhibits the higher average crystallite size. This prediction can be made on the basis of the fact that full width at half maximum (FWHM) of the sample is narrow.' The average crystallite size of the sample was calculated using Scherer's formula viz. $t = k\lambda / [\beta\cos\theta]$, 't' is thickness of the crystallite, λ is wavelength of X-ray used (1.5406 A °), $k = 0.9$ is a constant (shape factor), θ is the angle of diffraction and β is the FWHM, we calculated average crystallite size and the determined value were was found to be 102 nm.

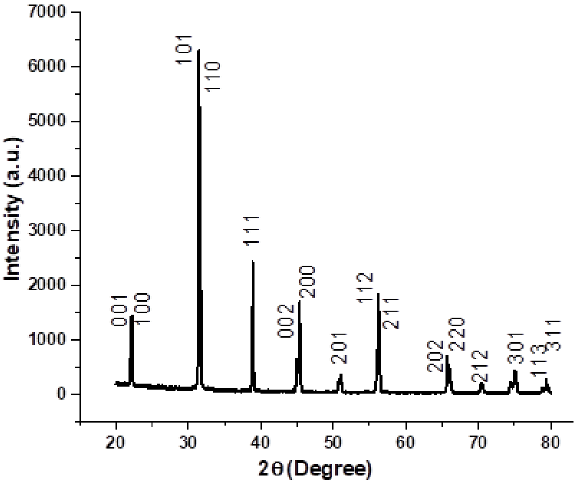

Figure 1: XRD pattern of Fe doped $BaTiO_3$

3.2 Raman analysis

To emphasize further on the desired sample formation, we carried out Raman inelastic spectral carried out the Raman spectroscopic measurement. We recorded Raman spectrum in the range of 100 cm^{-1} – 1000 cm^{-1}. Raman spectra of Fe doped BTO recorded at room temperature is displayed in Figure. 2. Group theory predicts eight Raman active modes for tetragonal phase of $BaTiO_3$ denoted as 4E (TO+LO) + 3A1 (TO+LO) + 1B1 (TO+LO) [11]. The Raman spectrum depict the phase formation via the display of fingerprint bands. The indication of the tetragonal phase is the appearance of mode of vibration at 307 cm^{-1} is an. Related to characteristic of A1 symmetry, the Raman modes appear at 245 cm^{-1}. The asymmetric mode at 520 cm^{-1} also corresponds to the transverse optical (TO) phonon mode.

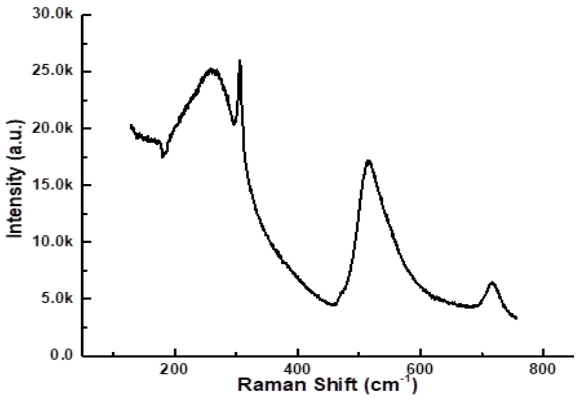

Figure 2: Raman Spectrum of Fe doped BaTiO$_3$

The mode of vibration at 307 cm^{-1} is assigned to the [B1, E(TO+LO)] which is fingerprint Raman mode indicating the tetragonal phase formation inferring an asymmetry of TiO$_6$ octahedra with the structure of BaTiO$_3$. The highest frequency longitudinal optical (LO) mode with A1 symmetry is presented by mode of vibration at 720 cm^{-1} [A1(LO), E(LO)]. Thus Raman spectral analysis also confirms the XRD results

3.3. FTIR Analysis

The FTIR displays phase formation in terms of the vibration of fingerprint absorption bands. Fig. 3. displays FTIR spectrum recorded in the wavenumber range of 400 cm^{-1} – 4000 cm^{-1}. Due to vibration bands of CO$_2^{3-}$ groups, the absorption bands appear at 860 cm^{-1} and 1440 cm^{-1}. Corresponding to the vibration of Ti–O bonds, the absorption band appears at 400 cm^{-}1. The absorption band about 500^{-1} arise from the vibration of Ba–O bonds. Due to moisture, the band appear at1080 cm^{-1} and 2970 cm^{-1} attributed to the vibration of -OH group [7,10]. All the absorption bands witnessed within the bounds of experimentation confirm the desired phase formation of the sample.

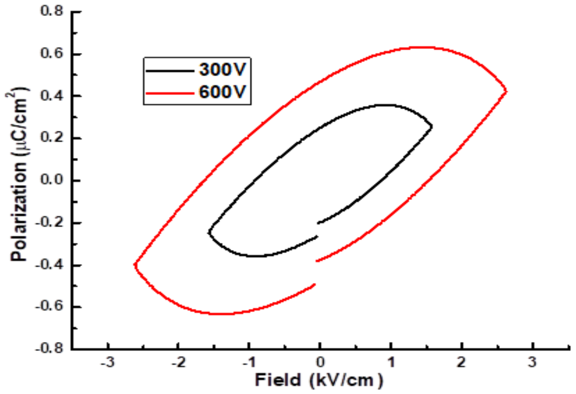

Figure 3: FTIR Spectrum of Fe doped BaTiO$_3$

3.4 Ferroelectric Studies

We studied polarization character of Fe doped BTO samples at room temperature with applied electric. The polarization hysteresis curve as a function of Field is displayed as Figure. 4.

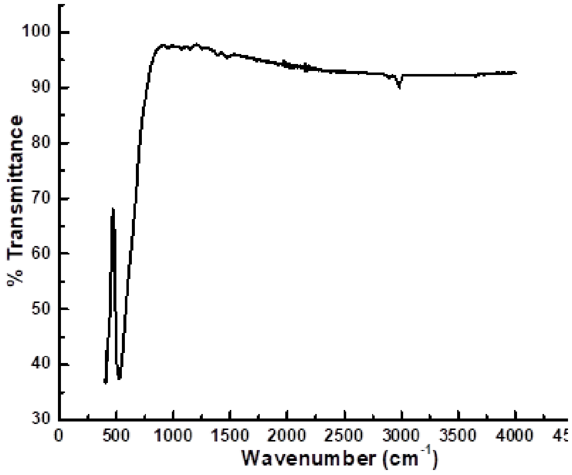

Figure4: Polarization (P-E loop) of Fe doped BaTiO$_3$

The polarization of the sample is depicting a well behaved hysteresis loop with genuine saturation, remnance and coercive field. However the values of the said parameters are low. Furthermore, the loop shows cut which indicates the leakage in the sample. Also, we note that with enhanced field value, the ferroelectric parameters improve. The behaviour can be improved with suitable doping, modification of morphology and on the basis of size dependence [12, 13]. Overall, the sample behaves well and needs further study with dopants from the f-block elements at B-site with respect to concentrations

4. CONCLUSIONS

Fe doped BaTiO$_3$ was successfully prepared by solid-state reaction route. The structural analysis by means of X-ray diffraction reveals that the sample was single-phased and crystalized in tetragonal structure with space group *P4mm*. Raman and FTIR spectral analysis carried out at room temperature further confirms the desired Phase formation. The sample was subjected to the polarization measurements and it was found to exhibit leakage with low value of polarization. Overall, the sample has performed well and need modifications from synthesis and particle size point of view to enhance its feasibility in device applications

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