

THE STUDY OF STRUCTURAL PROPERTIES OF $\text{BiFeO}_3 - \text{PbTiO}_3$ CERAMICS

R.K. Sharma,

Department of Physics,

D.A.V. (PG) College, Dehradun-248001,

Uttarakhand, India

ABSTRACT

BiFeO₃ is an attractive material because of its multiferroic properties, i.e., ferroelectricity with high Curie temperature ($T_c = 820-850$ °C) and antiferromagnetic properties below Neel temperature ($T_N = 350-380$ °C). $\text{PbTiO}_3/x\text{BFO}$ ($x = 0, 0.02, 0.04, \text{ and } 0.06$ wt%) ceramics were successfully synthesized by solid-state mixed oxide method. X-ray diffraction pattern indicate that the addition of BFO in PbTiO_3 causes a slight change in tetragonality. The result also clearly shows that there are no secondary phases. It shows perfect solubility of BiFeO_3 into PbTiO_3 upto the prepared composition.

Keywords: X-ray diffraction, lead titanate modified bismuth ferrite, diffuse phase transition.

INTRODUCTION

BiFeO_3 shows antiferromagnetic G-type spin configuration along the [1 1 1] or [0 0 1] directions in its pseudocubic or rhombohedral structure. BiFeO_3 has a superimposed incommensurate cycloid spin structure with a periodicity of 620Å along the [1 1 0] axis at room temperature. This structure cancels the macroscopic magnetization and inhibits observation of the linear ME effect. The decrease in particle size has been proved to be effective in suppressing this cycloid structure and enhancing the magnetic moment of BiFeO_3 . Interestingly, this ferromagnetic BiFeO_3 exhibits characteristic features in dielectric properties around the magnetic transition temperature, highlighting useful multiferroic behaviour. Spontaneous polarization has always been difficult to obtain in bulk BiFeO_3 -based multiferroics due to the large leakage conductivity

which can significantly interfere with the measurement of ferroelectric hysteresis loops giving rise to artificially large polarization and hampering intrinsic polarization switching. With the growing interest in developing new materials for device applications, a large number of ferroelectric oxide ceramics have been studied covering a wide range of composition. Due to distorted cubic (rhombohedral) structure and morphotropic phase boundary (MPB), it shows high-piezoelectric coefficients useful for many devices. The high spontaneous polarization (P_s) has been reported in the BFO thin films, due to which it is used for high-density memory devices. BiFeO_3 is ferroelectric with a very large spontaneous polarization that points along one of the body diagonal. When an external electric field is applied, the polarization can rotate to another body diagonal direction. The switching path, however, depends on the direction of the electric field and the elastic

constrains that the film experiences. By controlling the growth parameters, we can obtain BiFeO₃ with a single polarization direction. Lead titanate (PT) solid solutions achieved a wide range of application in recent years because of their superior properties. PT has a perovskite structure ABO₃. At ambient temperature, the solid solution between lead oxide, PbO and titanium dioxide present a tetragonal phase. The material has been studied intensively since the discovery of the miscibility of lead titanate and lead zirconate in the 1950s. The excellent properties are related to the existence of the morphotropic phase boundary (MPB) between the tetragonal and the rhombohedral phase. The position of the phase boundary and its thermodynamic background were the subject of numerous studies. Extraordinary high piezoelectric activities are found at the morphotropic phase boundary (MPB) composition corresponding to Pb(Zr_{0.52}Ti_{0.48})O₃. This compound also possesses high spontaneous polarization, high Curie temperature, good thermal stability during operation, high electromechanical coupling coefficient and easy poling, etc. PZT materials are well known for their good piezoelectric properties and are ideal candidates for making sensors and actuators. It is one of the most used industrial piezoelectric material, used as transducers, such as phonograph pickups, air transducers, underwater sound and ultrasonic generators, delay line transducers, wave filters etc. All these applications need generally high piezoelectric constants and low dielectric and mechanical losses in the ceramics. The variation of mechanical losses and elastic modulus as function of temperature and excitation frequency can provide direct information on the energy dissipation and phase transitions in the material.

In this paper, PT/BFO ceramic system was synthesized by conventional solid-state mixed oxide method. Role of added BFO concentration on density, phase evolution, microstructure, dielectric, and ferroelectric properties of PT ceramics were investigated and discussed.

EXPERIMENTAL PROCEDURE

For the synthesis of xBiFeO₃-(1-x)PbTiO₃, we used solid state reaction method. Firstly BiFeO₃ was prepared by rapid sintering method. For this we take pure (99.5%) Bi₂O₃, Fe₂O₃ (Himedia) and mixed them thoroughly in an agate mortar for 3h in acetone media. The powder was then pressed in to pellets by applying pressure by hydraulic press. These pellets were sintered at temperature 870°C for 25 minute then suddenly take these pellets out from furnace and put them on cold(like iron)base. When the temperature of these pellets equal to the room temperature then grind these pellets for 3h to get a fine powder form. Formation of BiFeO₃ was identified by X-ray diffraction (CuK_α) (λ=0.1540598nm). PbTiO₃ was prepared by solid state reaction method. Highly pure (99.9%) PbO, TiO₂ (Himedia) was thoroughly mixed in agate mortar for 3h with acetone. This powder was calcined at temperature 950°C for 2h in a furnace in air atmosphere. Grind this calcined powder and characterized by X- ray diffraction.

For xBiFeO₃-(1-x)PbTiO₃, BiFeO₃ and PbTiO₃ formed as given above were taken, in proper proportion and mixed in to agate mortar for 3h with acetone media. Then ground powder was calcined at temperature 950°C for 2h. Then formation and quality of compound was checked by XRD technique. The X-ray diffraction pattern of the compounds was recorded with CuK_α radiation (0.1540598nm) in a range of Bragg's angle 2θ (20°-60°) at a scanning rate 1° min⁻¹. This calcined powder was ground and then pressed in to pellets of diameter 8-10mm and thickness 0.7-1.2 mm by applying pressure by hydraulic press. These pellets were sintered at temperature 1100°C for 2h in air atmosphere. These sintered pellets were electrode with high purity silver paint on two parallel surfaces and then dried at 250°C for 30min before taking electrical and dielectric measurements. The polarization-electric field (P-E) hysteresis loop of sample was carried out at room temperature by using computer controlled modified Sawyer Tower circuit. The capacitance and dielectric loss of the sample at different frequency

and temperature were measured by using HIOKI 3532-50 LCR meter. Observation of the surfaces of the ceramics was carried out using field emission scanning electron microscopy (FESEM). For this measurement the sintered pellet was used which was gold polished from one side. This side is connected to the aluminium base by silver contact. Grain size of each sample was measured by a mean linear intercept method from SEM micrographs.

RESULTS AND DISCUSSIONS

The X-ray diffraction pattern of $(1-x)\text{PbTiO}_3-x\text{BiFeO}_3$ where $x=0, 0.02, 0.04$ and 0.06 are compared in figure 1. PbTiO_3 powder has composition tetragonal phase while BiFeO_3 powder has rhombohedral structure. The XRD pattern of PbTiO_3 was found in excellent agreement with the reported article. The XRD pattern of $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ is similar to pure

PbTiO_3 . The tetragonal phases were observed in all samples. The peak of PbTiO_3 shifted towards right i.e towards higher 2θ value with the addition of BiFeO_3 as shown in inset of Fig 1. The lattice parameter a increases but c decreases. It shows that $\text{PbTiO}_3/x\text{BFO}$ contain mainly tetragonal phase with reduction in tetragonality (c/a ratio) with increasing percentage of BFO. The slight distortion in XRD pattern may be attributed to the differences in ionic radii of Bi^{3+} [1.17Å], Fe^{3+} [0.55Å] and Pb^{2+} [1.29Å], Ti^{4+} [0.605Å]. There are two possibility that Fe^{3+} can replace Pb^{2+} or Ti^{4+} ion but the ionic radii of Ti^{4+} is much closer to the Fe^{2+} ion than Pb^{2+} , then one can expect that Fe^{3+} preferably replaces the Ti^{4+} ion than the Pb^{2+} ion. Since no secondary phase was observed in these patterns, it indicates high degree dissolution of BFO into PbTiO_3 lattice occurred during sintering process.

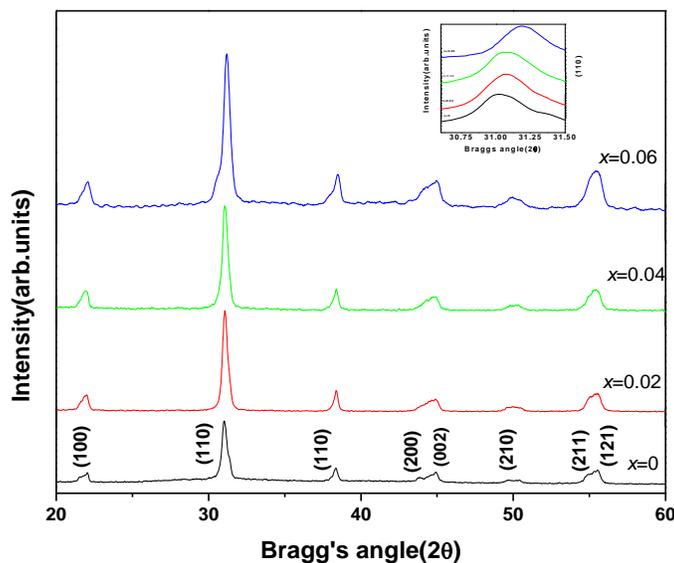


Fig. 1. XRD pattern for $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ with different compositions.

The crystallite size (P) (Fig.2) of all the sample was estimated from the peak broadening β (full width of half maxima) and peak position (2θ) using Scherrer's relation $P=k\lambda/\beta\cos\theta$ ($k=\text{constant}=0.9$, $\lambda=0.15407\text{nm}$) [10]. The crystallite size calculation using the single peak (110) of sintered $\text{PbTiO}_3/x\text{BFO}$ shows that it decreases with increasing percentage of BFO in

PbTiO_3 . The crystallite size is of order of $\sim 22.449\text{nm}$, 21.872nm , 20.324nm and 10.6635nm for $x=0, 0.02, 0.04$ and 0.06 respectively. It is clear from the calculation that for $x=0.02$ and $x=0.04$, the decrease in crystallite size is less than that of $x=0.06$. The decrease in crystallite size results in a decrease of the tetragonal distortion.

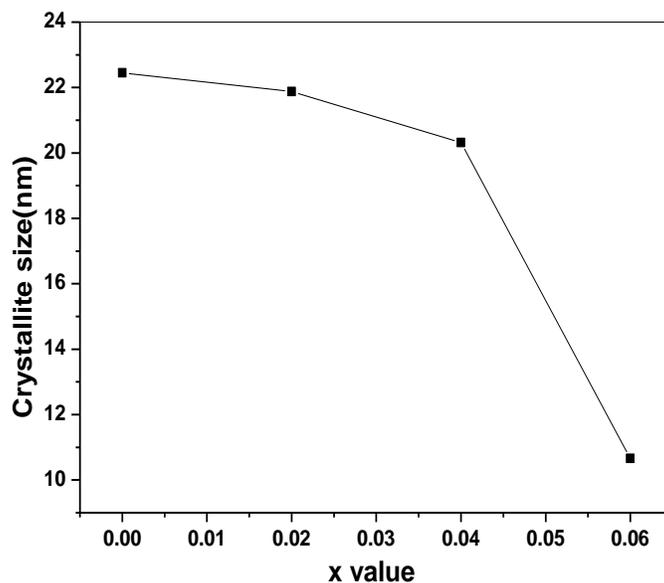


Fig. 2. Crystallite size variation with different value of x in $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$.

The scanning electron micrographs (Fig 3) of the $\text{PbTiO}_3/x\text{BFO}$ for different x value clearly show the mixed microstructures of PbTiO_3 and BFO. These micrographs suggest that the sintered pellets were significantly dense and minor porosity is visible in the material. The average grain size was determined by linear interception method. The grain size is of order of $\sim 2.1\mu\text{m}$, $1.87\mu\text{m}$, $1.657\mu\text{m}$ and $1.572\mu\text{m}$ for $x=0$, 0.02, 0.04 and 0.06 respectively. The grain size decreases with increasing x value. The reduction in the grain size may be due to the grain growth inhibition as a result of solute drag effect. Since

solute diffusion near grain boundary region is usually slower than intrinsic diffusion of host atoms across the boundary plane and becomes rate-limiting for grain boundary movement. This seemed to be the main mechanism governing the observed microstructure similar to those reported in a number of previous work on solid solutions and doped systems, for examples, Nb-added BaTiO_3 and MgO-doped Al_2O_3 . The compositional analysis of $\text{PbTiO}_3/x\text{BFO}$ was determined by EDS and it showed that the atomic ratio of different elements is within instrumental accuracy.

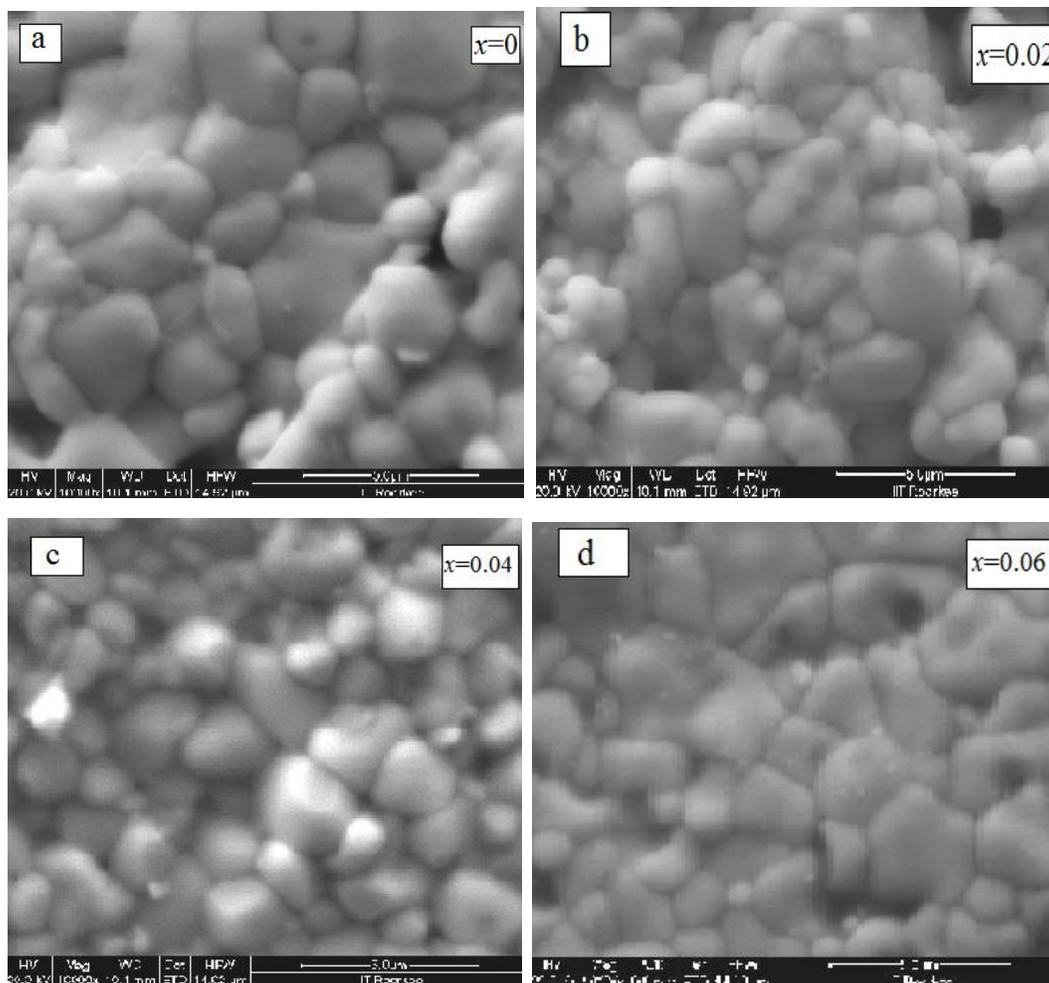


Fig. 3. SEM micrograph of $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ for different values of x .

CONCLUSION

In the present work I have reported the synthesis and characterization of $\text{PbTiO}_3/x\text{BFO}$ ($x= 0, 0.02, 0.04,$ and 0.06 wt%) ceramics which were successfully fabricated by a solid-state mixed oxide method. X-ray diffraction pattern indicates that the addition of BFO in PbTiO_3 causes a slight change in tetragonality. The result also clearly shows that there are no secondary phases. It shows perfect solubility of BiFeO_3 and PbTiO_3 . A new $\text{PbTiO}_3/x\text{BFO}$ system provides useful information for material development.

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