Dielectric Properties of $B_iF_eO_3$ – $P_bT_iO_3$ Perovskite Ceramics

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ABSTRACT

In the present study electrical properties of $P_bT_iO_3$/xBFO (x= 0, 0.02, 0.04, and 0.06 wt%) ceramics which were successfully synthesized by solid-state mixed oxide method. X-ray diffraction pattern indicate that the addition of BFO in $P_bT_iO_3$ causes a slight change in tetragonality. The maximum dielectric constant was found to increase and transition temperature decreased with the increasing percentage of BFO in $P_bT_iO_3$ with diffuse phase transition. PE-loop with increasing remnant polarisation with no significant change in coercive field was observed. So a new $P_bT_iO_3$/xBFO system provides useful information for material development.

Keywords: *dielectric constant, diffuse phase transition, ferroelectricity, Curie temperature*

INTRODUCTION

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. $BiFeO_3$ 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 $BiFeO_3$ 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 ABO_3. 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 morphotopic phase boundary (MPB) composition corresponding to $Pb(Zr_{0.52}Ti_{0.48})O_3$. 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, dielectric, and ferroelectric properties of PT ceramics were investigated and discussed.

EXPERIMENTAL PROCEDURE

For the synthesis of xBiFeO$_3$-(1-x)PbTiO$_3$, we used solid state reaction method. Firstly BiFeO$_3$ was prepared by rapid sintering method. For this we take pure (99.5%) Bi$_2$O$_3$, Fe$_2$O$_3$ (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 BiFeO$_3$ was identified by X-ray diffraction (CuK$_\alpha$) (λ=0.1540598nm). PbTiO$_3$ was prepared by solid state reaction method. Highly pure (99.9%) PbO, TiO$_2$ (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 xBiFeO$_3$-(1-x)PbTiO$_3$, BiFeO$_3$ and PbTiO$_3$ 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$_\alpha$ radiation (0.1540598nm) in a range of Braggs 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 temperatue1100°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 Saywer 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 tetragonal phases were observed in all samples. The grain size is of order of ~2.1μm, 1.87μm, 1.657μm and 1.572μm 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 inhabitation as a result of solute drag effect. Figure 1 and 2 shows the temperature-frequency dependency of relative dielectric constant (ε_r) and dielectric loss of xBiFeO$_3$-(1-x) PbTiO$_3$ respectively. It is observed that the dielectric constant of all the composites increases with rise in temperature. In some temperature region the dielectric constant of the compounds is almost similar but slowly increases with increases

temperature and gain maximum value ε_{max} at Curie temperature and then decreases with further increase in temperature. The higher value of ε_r at lower frequencies is due to simultaneous presence of all types of polarizations (interfacial, ionic, dipolar, electronic, space charge etc.) in the compounds. It is known that higher frequencies, the main contribution to ε_r comes from electronic polarization, as some of the polarizations become in effective, and thus, the value of ε_r decreases on increasing frequency.

The dielectric constant increases with the increasing percentage of BFO. Since BFO is a donor-doped material, this A-site substitution of $PbTiO_3$ resulted in a creation of cation vacancies and reduction in the number of oxygen vacancies in $PbTiO_3$ system. It has been known that oxygen vacancies are the main cause of domain wall clamping which leads to the lowering of dielectric constant . Thus, it seemed that addition of high BFO content caused a reduction of oxygen vacancies and led to enhance dielectric constant compared to that of pure $PbTiO_3$ sample which contained more oxygen vacancies.
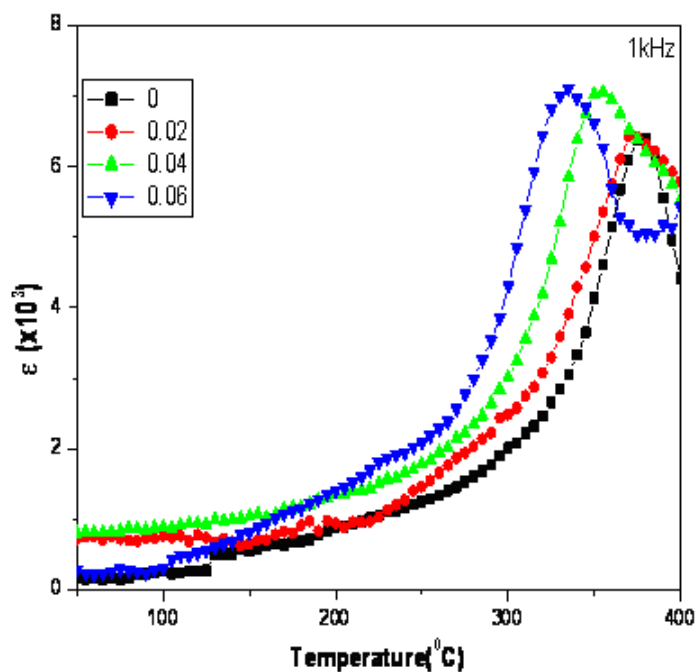

Fig. 1 Variation of dielectric constant as a function of temperature of xBiFeO$_3$-(1-x) PbTiO$_3$ for different value of x.
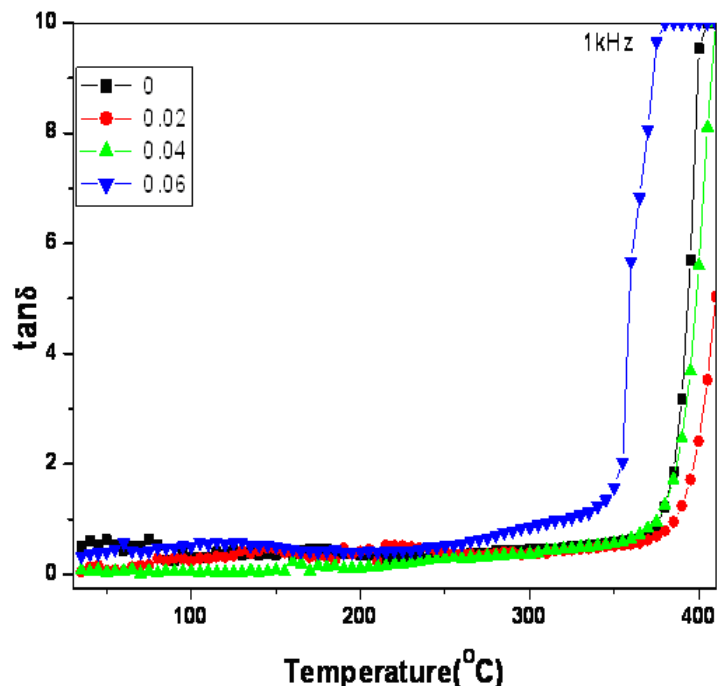
Fig. 2   Variation of dielectric loss as a function of temperature of xBiFeO$_3$-(1-x) PbTiO$_3$ for different value of x.

From this study, addition of BFO into PbTiO$_3$ ceramic could thus significantly improve dielectric constant. It is found that the Curie temperature decreases and the width of the peak increases with increasing percentage of BiFeO$_3$ in PbTiO$_3$. To explain this decreasing curie temperature, the effect of substitution site will have to be taken into account. In the ABO$_3$ perovskite structure the A- and B-site cations are 12 and 6-coordinated, respectively. When a foreign cation is introduced into the perovskite sublattice, the substitution site of the cation is determined mainly by two factors: i.e. charge and size. Bi and Fe are trivalent in BFO and the ionic radii are (r_8=1.17Å) and (r_6=0.55Å) respectively. It has also been reported that the Tc is lowered for all the lead-based compositions whenever A-site (Pb^{2+}) is replaced by another cation regardless of type of cation. The dissipation factor is found to be less at lower temperature for all samples. But at higher temperature almost above transition temperature a sharp increase in dielectric loss was observed. As a general rule, tan δ increases appreciably when the temperature rises. This growth in tan δ is brought about by an increase both in the conduction of residual current and the conduction of absorption current. In actual fact, the rise in temperature and the resulting drop in viscosity exert a double effect on the amount of losses due to the friction of the rotating dipoles, on the one hand, and the increase in the degree of dipole orientation, on the other hand; there is a reduction in energy required to overcome the resistance of the viscous medium. In a polar substance, apart from dipole losses, losses due to electrical conduction, which increase with an increase in temperature, are present. The anomaly corresponding to 380^{0}C which seems to agree with the dielectric measurement of on literature in PbTiO$_3$ correspond to ferroelectric to paraelectric phase transition.

The dielectric constant Fig. 3 (a) is found to decrease with increase in frequency which may be due to inability of the electric dipoles to be in pace with frequency of applied electric field at high frequency. The dielectric loss (Fig. 3 (b)) firstly increases with frequency and then decreases with further increase in frequency. The peak was observed in dielectric loss with frequency, this indicate the presence of some relaxation species even at room temperature.
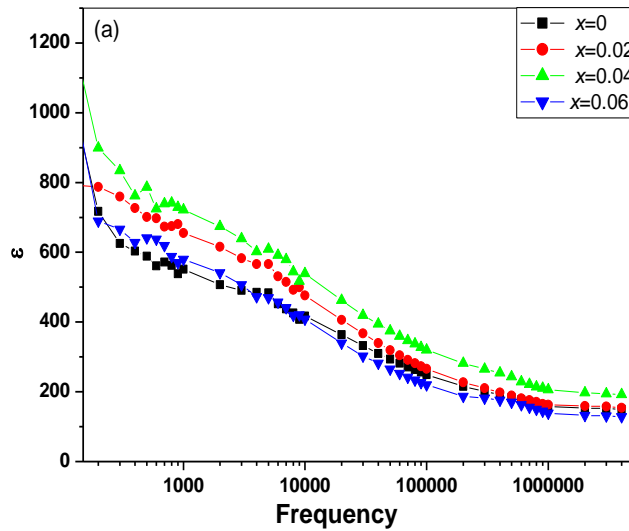
Fig. 3. (a) Variation of dielectric constant as a function of frequency for xBiFeO$_3$-(1-x) PbTiO$_3$ for different value of x.
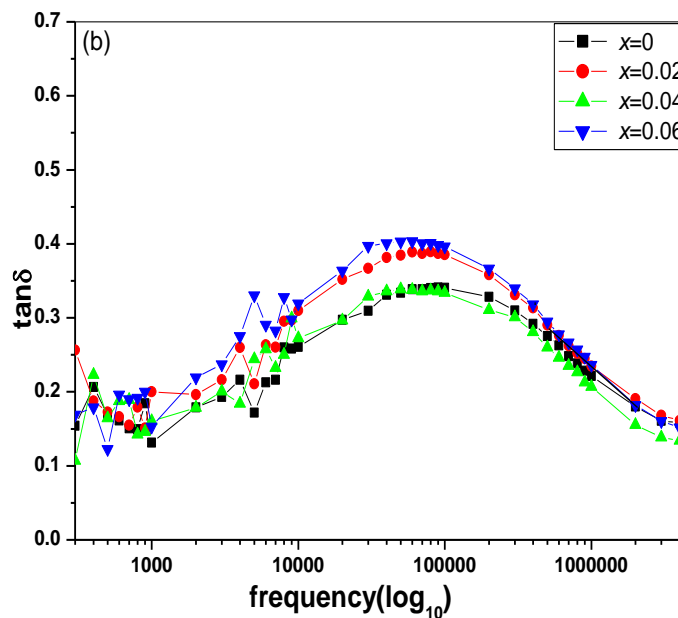

Fig. 3 (b) Variation of dielectric loss, as a function of frequency for xBiFeO$_3$-(1-x) PbTiO$_3$ for different value of x.

Variation of dielectric constant with crystallite size at room temperature and curie temperature in xBiFeO$_3$-(1-x) PbTiO$_3$ and variation of dielectric constant and tanδ with x value at curie temperature is shown in Fig 4 (a) and (b) respectively.
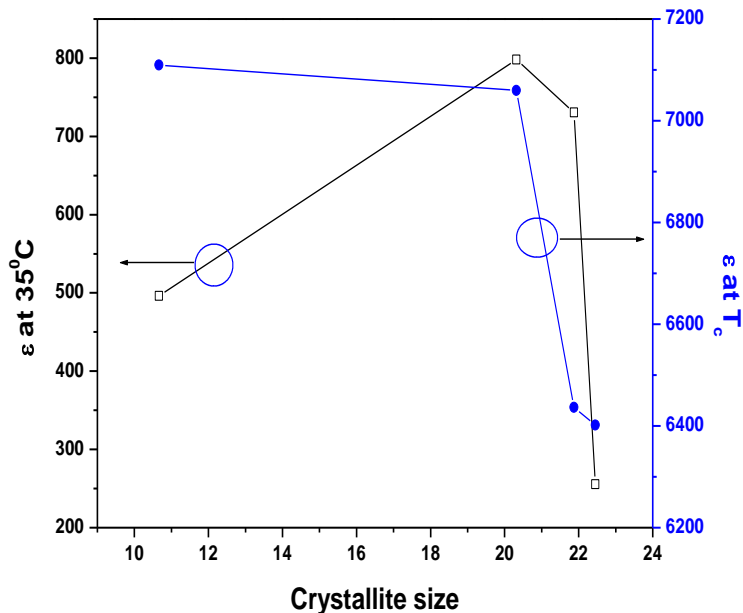
Fig. 4.(a) Variation of dielectric constant with crystallite size at room temperature and curie temperature in *x*BiFeO₃-(1-*x*) PbTiO₃.

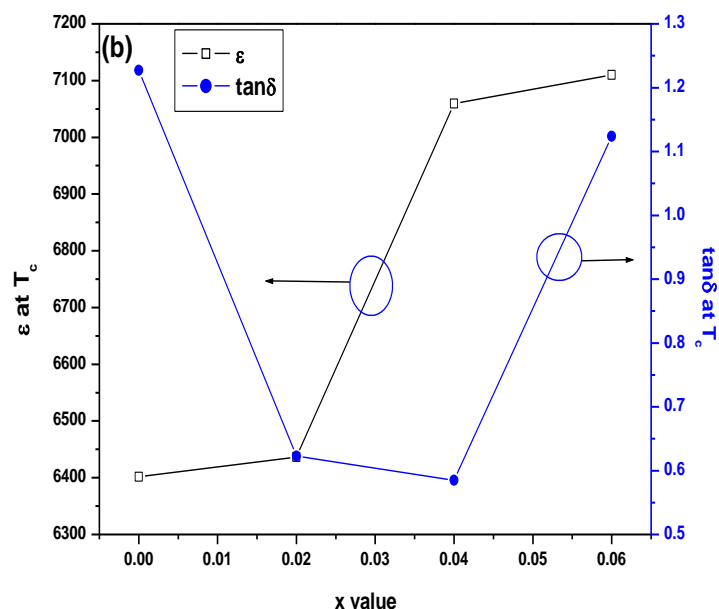**Fig. 4(b) Variation of dielectric constant and tanδ with *x* value at curie temperature.**

PE-loop measurement shows (Fig. 5) that the addition of BiFeO₃ in PbTiO₃ increases the value of remnant polarization and there is no significant change in coercive field. This may be due to increase in density of PbTiO₃ with the addition of BFO. Now we take PE-loop in the presence of magnetic field and found that the remnant polarization slightly changes in magnetic field.

The degree of diffuseness (γ) in the dielectric peak of the material was estimated by using the expression

$$(1/\varepsilon - 1/\varepsilon_{max}) \, \alpha \, (T-Tc)^\gamma$$

where ε and ε_{max} are the dielectric constants at temperature T (T > Tc) and ε_{max} (maximum value of ε at the transition temperature Tc, respectively. This

large value of γ (table 1) confirms the second-order phase transition and the high degree of disorderliness in the material.

A plot (Fig. 6 (a) and (b)) for all the samples unambiguously demonstrates approximately linear behaviour for all doped compositions, and γ does fall into the above range (Table 1). The value of γ for all

the composition confirms that diffuse phase transitions (DPT) occurs in the materials and there is a deviation from the Curie–Weiss type of phase transition. Maximum value of γ was observed for pure 2% BFO in PbTiO$_3$.
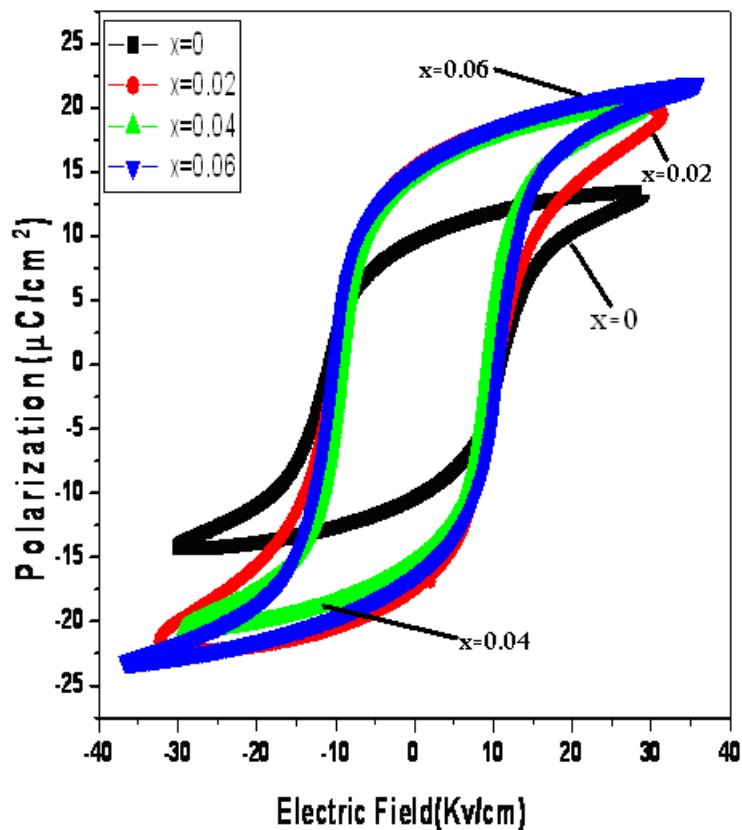

Fig. 5. Variation of Polarization-electric field hysteresis loop for xBiFeO$_3$-(1-x) PbTiO$_3$ where x=0.02, 0.04 and 0.06

It is believed that the ferroelectrics exhibit DPT have microdomains with different Tc and that the local Tc

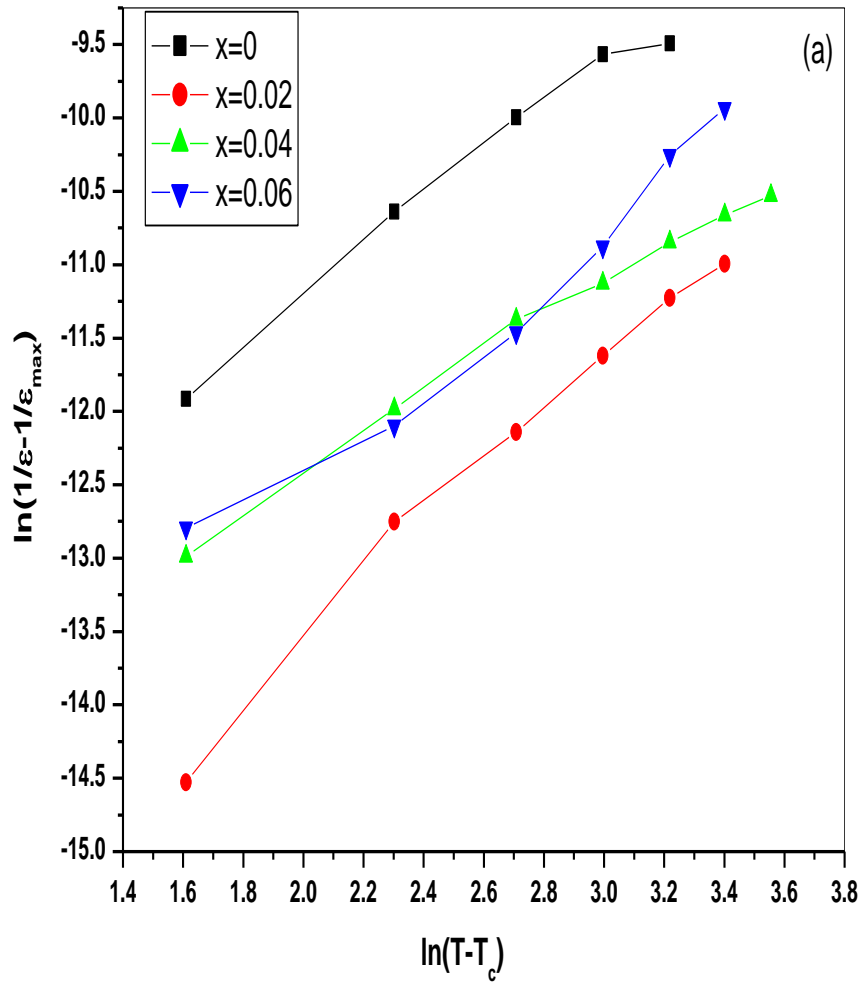distribution causes the peak broadening of dielectric constant.

Fig. 6 (a) : Plot between ln(1/ε-1/ε$_{max}$) and ln(T-Tc) for evaluating diffusivity exponent in *x*BiFeO$_3$-(1-*x*) PbTiO$_3$.
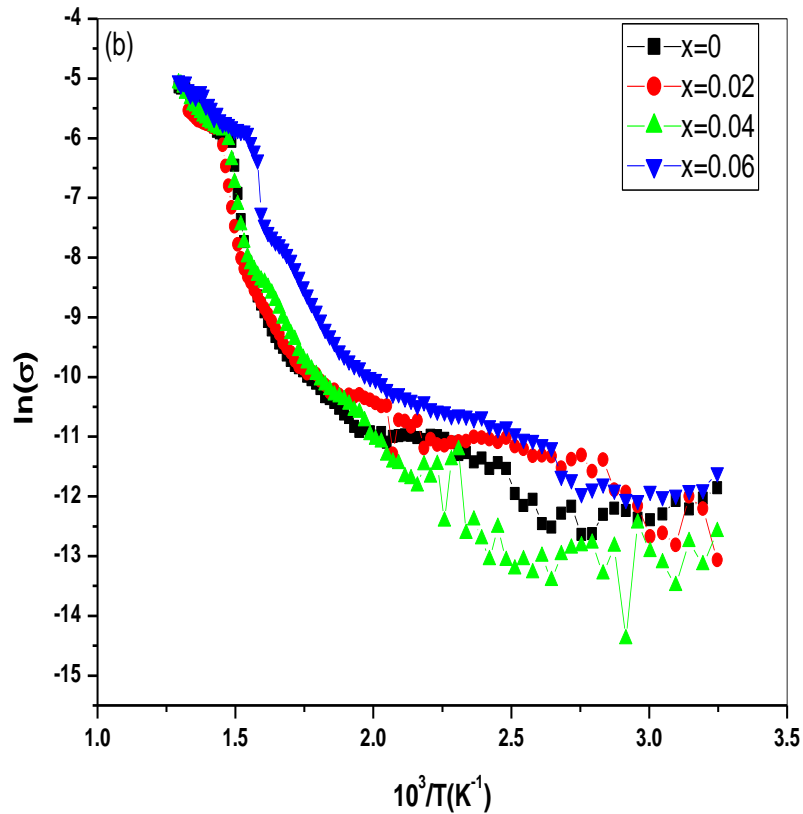
Fig. 6 (b) Conductivity Vs Temperature characteristic for *x*BiFeO₃-(1-*x*) PbTiO₃.

The activation energy Ea can be calculated by making use of this plot and the relation given below:

$$\sigma = \sigma_0 \exp(-Ea/K_B T)$$

The conductivity is given by $\sigma = \omega \varepsilon_0 \varepsilon \tan \delta$, where ε_0 is the vacuum dielectric constant, ω is the angular frequency and K_B is the Boltzmann constant. The calculated values of activation energy at 1 kHz frequency for all the compositions are given in table 1.

Table 1. Electrical properties of xBiFeO$_3$-(1-x) PbTiO$_3$ ceramics

x value	0	0.02	0.04	0.06
a	4.0331	4.0441	4.0475	4.0277
c	4.12678	4.11404	4.08398	4.11570
c/a	1.02323	1.01732	1.009013	1.02185
Grain size(μm)	2.108	1.8749	1.657	1.5719
Crystallite size(nm)	22.449	21.872	20.324	10.6635
Diffusivity exponent γ	1.5598	1.9497	1.2639	1.625
Coercive feild(Kv/cm)	10.9235	10.391	9.1375	10.434
Remanent polarization (μc/cm2)	9.994	16.449	14.954	15.856
Activation energy Ea(eV)	0.34209	0.29628	0.40487	0.3560

CONCLUSION

In the present work I have reported the synthesis and characterization of PbTiO$_3$/xBFO (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$_3$. The maximum dielectric constant was found to increase and transition temperature decreased with the increasing percentage of BFO in PbTiO$_3$ with diffuse phase transition. PE-loop with increasing remnant polarisation with no significant change in coercive field was observed. So a new PbTiO$_3$/xBFO system provides useful information for material development.

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