Structural and Electrical Properties of La doped BiBa(Fe$_{0.6}$Ti$_{0.4}$)O$_3$ Composite Ceramic

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ABSTRACT

The sample La doped BiBa(Fe$_{0.6}$Ti$_{0.4}$)O$_3$ a new member of the ferroelectric family, was synthesized by a mixed-oxide technique at a low temperature of 850^{0}C. Preliminary structural study of the compound at room temperature was done using XRD. Electrical properties of the sample were measured in a wide frequency (10^2-10^6Hz) and temperature range (room temperature-500 ^{0}C). Temperature dependence of dielectric properties (i.e., dielectric constant ε_r and loss tanδ) of the materials has been analyzed at selected frequencies which indicate that compounds have transition temperature well above the room temperature. The temperature dependence of ac electrical conductivity (σ_{ac}) was also studied.

1. Introduction

The polycrystalline lead zirconate titanate [Pb(ZrTi)O$_3$; PZT] ceramics have gained much attention in recent years due to their excellent dielectric, piezoelectric and ferroelectric properties exhibiting tremendous applications in the field of electronics and electro-optics [1-4]. PZT is the solid-state solution of ferroelectric PbTiO$_3$ (T$_c$=490°C) and antiferroelectric PbZrO$_3$ (T$_c$ =230°C) having two ferroelectric phases: tetragonal in Ti-rich composition and rhombohedral in Zr-rich composition [5-6]. The boundary line between these two phases is called morphotropic phase boundary (MPB) at which the electrical and electromechanical properties of the materials enhance to a great extent [7]. The PZT ceramics has perovskite ABO$_3$ structure in which A-site is occupied by Pb^{2+} ions and B-site by Zr^{4+} or/and Ti^{4+} ions. Its physical properties and device parameters can be modified with suitable Zr/Ti ratio, substitution at A or/and B-sites, preparation techniques & conditions, etc [8].

However environment friendly alternatives to the toxic lead containing PZT are needed. To date no MPB piezoelectrics have been developed which has the potential to replace PZT for acoustic material application. Bismuth based materials are considered to be the best alternatives [9-10]. Bismuth ferrite based materials are also of great interest due to their simple perovskite structure and the simultaneous coexistence of ferroelectricity and antiferromagnetism [11-12]. So in the search of an alternative we studied the La doped BiBa(Fe$_{0.6}$Ti$_{0.4}$)O$_3$ Composite Ceramic.

2. Experimental details

The polycrystalline ceramics $BiBa(Fe_{0.6}Ti_{0.4})O_3$ were prepared by high-temperature solid-state reaction technique using ingredient oxides; Bi_2O_3, $BaCO_3$, Fe_2O_3 and TiO_2 (99.9% purity, M/S Loba Chemie, Inc. Bombay, India) in appropriate stoichiometry. The well mixed ingredient oxides in alcohol medium were calcined at an optimized temperature (830°C) for 5 hour. Using polyvinyl alcohol (PVA) as binder, the calcined powders were converted into pellets at $4\times10^6\,N/m^2$ pressure. These pellets were sintered at an optimized temperature (860°C) for 3 hour so as to get maximum density (97% of theoretical density).

Preliminary structural analysis of calcined powders was made from the data obtained using X-ray diffractometer (Rigaku Miniflex, Japan) at room temperature with Cuk_α radiation (λ=1.5405 Å) in a wide range of Bragg's angles 2θ ($20°\leq2\theta\leq80°$) at the scanning rate of 3°/min. To analyze dielectric properties of materials, the smooth flat surfaces of pellets were painted with high quality air-drying silver paint and, then, dried at 150°C for 1 hour to remove moisture. Now dielectric parameters were analyzed from the data obtained by using a Phase Sensitive Multimeter (PSM; Model 1735).

3. Results and discussion
3.1. Structural analysis

The XRD pattern of $BiBa(Fe_{0.6}Ti_{0.4})O_3$ at room temperature are shown in figure.-1(a) and1(b). The average crystallite size (P) of the studied compound was calculated by this method from the broadening of the XRD peaks of different Bragg's angles using Scherrer's equation; $P_{hkl} = K\lambda/\beta_{1/2}\cos\theta_{hkl}$ [13,14] where K (constant)= 0.89, $\beta_{1/2}$ is the half peak width (in radian) and θ_{hkl} is the Bragg angle and was found to be 202 Å. As powder sample has been used, the peak broadening due to mechanical stain, instrumental divergence and other sources were ignored in calculation.
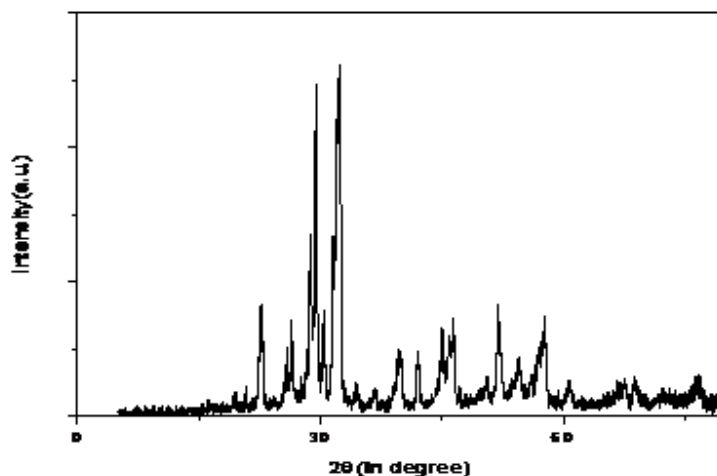

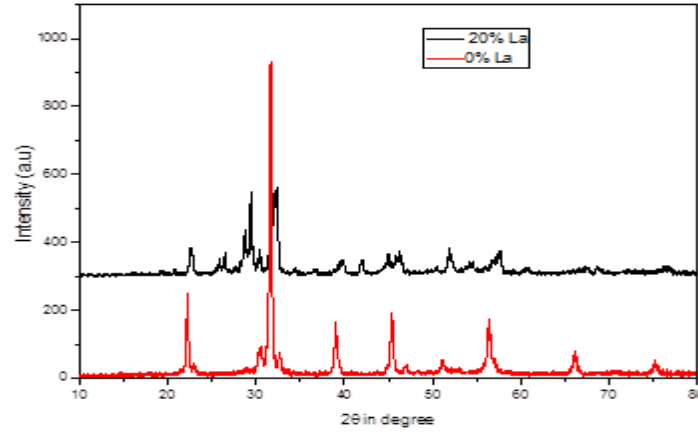**Figure 1(a):** XRD of the sample (20% La)

Figure 1(b): Intensity vs. 2θ graph

And the analysis from figure-1(b) that after doping of La some peaks of the sample is shifted in along with 2θ direction from the parent sample. Red line indicated the parent sample (no La is doping) and black line indicated 20% of La doped.

3.2. Dielectric analysis

The variation of dielectric constant (ε_r) of La doped BiBa(Fe$_{0.6}$Ti$_{0.4}$)O$_3$ with temperature at 1, 10, 50 and 100 kHz is shown in figure-2. The value of ε_r is found to decrease with the increase in frequency which refers to the normal behavior of ferroelectric/dielectric materials. The higher value of dielectric constant at lower frequencies indicates the simultaneous presence of all the types of polarizations (space charge, dipolar, ionic, electronic, etc) [13, 14]. It was observed that the compound undergoes phase transition of diffuse type at 200^{0}C, 195^{0}C, 192^{0}C, 188^{0}C respectively at 1kHz, 10kHz, 50kHz and 100kHz.
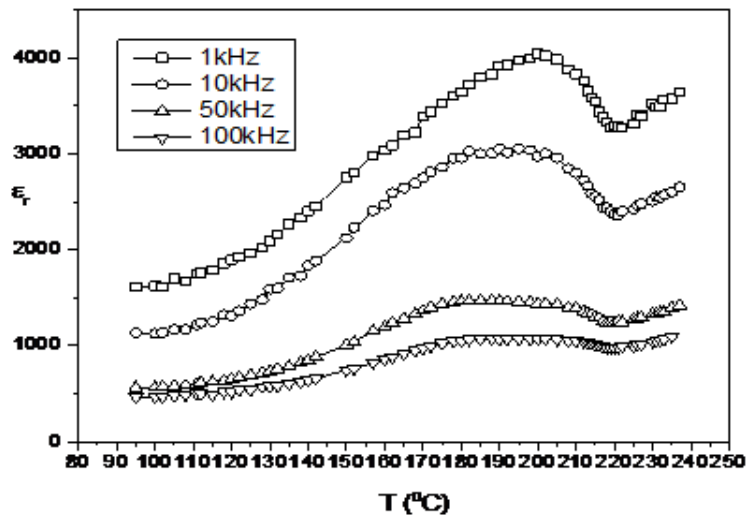

Figure 2: Variation of Temperature vs. ε_r at different frequencies

The smooth switch over of ε_r from low symmetry ferroelectric phase to more symmetric paraelectric phase indicates that the phase transition is of diffuse nature. A particular temperature cannot be regarded as a Curie temperature rather than a region called Curie region is to be considered. The dielectric peak was found to be broadened indicating the existence of diffuse phase transition .The degree of disorder of diffusivity can be estimated by using the empirical relation $\ln\left(\dfrac{1}{\varepsilon_r} - \dfrac{1}{\varepsilon_{max}}\right) = \gamma\ln(T - T_C) + \ln K$, where T is the temperature and K is a constant. This phase transition was confirmed by the appearance of the hysteresis loop (Figure-3) which shows the variation of polarization as
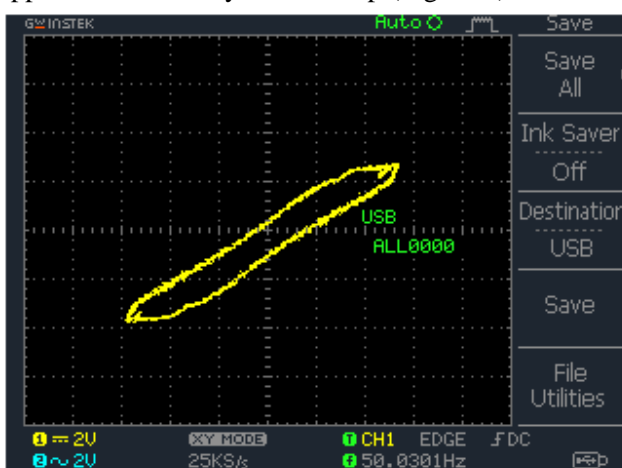

Figure 3: Polarization (P) – Electric Field (E) loop of the sample (20% of La doped)

a function of the applied electric field on the poled sample at room temperature 30^0C. Remnant polarization has been calculated from the taken photograph using Digital Oscilloscope, which is the variation of polarization (μC/cm^2) with applied electric field of kV/cm. We have got a proper Hysteresis loop because of the nature of the material. However even with smaller remnant polarization the existence of ferroelectric properties in the material can be concluded. Careful analysis for the existence of ferroelectric-Para electric phase transition of the whole family is being attempted.

The temperature dependence of dielectric loss (tanδ) of the sample at at 1kHz, 10kHz, 50kHz and 100kHz is also shown in figure-4. It is also observed that the tanδ at high frequencies is much lower than the corresponding values at low frequencies. This kind of dependence of tanδ on frequency is typically associated with loss of energy by conduction process.

Figure-5 shows the variation of σ_{ac} with inverse of absolute temperature (10^3/T) of the compound at different frequencies. The variation of the σ_{ac} over a wide temperature range indicates that the material has thermally activated transport properties obeying Arrhenius equation: $\sigma_{ac} = \sigma_0 \exp(-E_a/K_B T)$, where the symbols have their usual meanings. It is observed that the ac conductivity of the materials increases with rise in temperature, having negative coefficient of resistance. At higher frequencies, the activation energy (calculated from the ac conductivity curve) is smaller than that of lower frequencies (above T_c). This behaviour suggests that the conduction mechanism of this compound is due to the hopping of charge carriers.
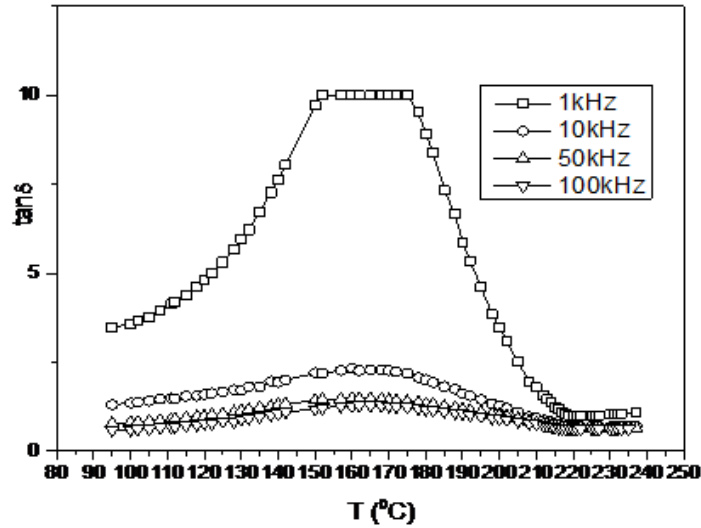
Figure 4: Variation of temperature vs. $tan\delta$ at different frequencies
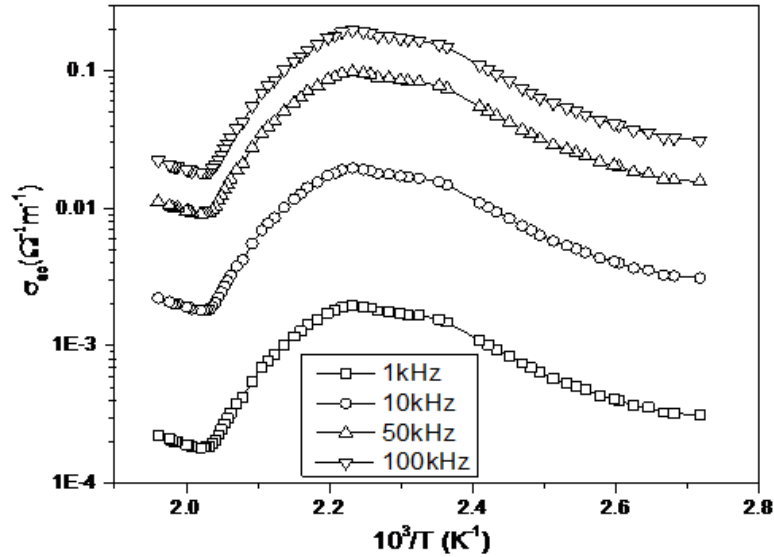

Figure 5: Variation of σ$_{ac}$ with (10^3/T)

4. Conclusions

Polycrystalline ceramics of La doped BiBa(Fe$_{0.6}$Ti$_{0.4}$)O$_3$ were synthesized through the high temperature solid-state reaction technique. From dielectric analysis, we get that the dielectric constant of the material is very high. It has a diffuse type of phase transition. Interestingly the tangent loss of the materials is found to be low up to a very high temperature close to the transition temperature.

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