Electrical Properties of BiFeO$_3$ - BaTiO$_3$ Ceramics

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BiFeO$_3$- BaTiO$_3$ ceramics have been synthesized via solid state reaction method. The X-ray studies of structural parameters reveal that BiFeO$_3$- BaTiO$_3$ (BFO-BT) solid solutions undergo structural transformations from rhombhohedral to cubic system. The unit cell dimensions increases with higher doping of higher ionic radii dopant (BT). The electrical properties for different composition x=0.10,0.15 and 0.30 in (1-x)BFO-xBT ceramics were studied in the frequency range 1kHz-1MHz at room temperature. It is found that the BFO with higher BT concentrations show higher electrical resistivity as well as capacitance. The decrease in electrical resistance and capacitance has been observed with the increase of frequency of the applied field. The larger dispersion in resistivity is due to dominance of intra-well hopping over inter-well hopping indicating a strong dependence of material properties on BT doping.

1. INTRODUCTION

The materials that exhibit coupled electric, magnetic, and structural order parameters and consequentially yield simultaneous effects of ferroelectricity, ferromagnetism, and ferroelasticity are multiferroics [1]. BiFeO$_3$ is ferroelectric (T$_C$ = 863°C) and antiferromagnetic (T$_N$ = 397°C) [2]. It reveals weak magnetism at room temperature due to a residual magnetic moment caused by canting spin magnetic structure [2]. However, the problem of low resistivity has hindered its application in devices with coupled electric and magnetic polarizations. Bulk BFO, especially synthesized through solid solution, exhibits weak ferromagnetic properties at room temperature due to residual moment from a canted spin structure, [3,4] which is believed to be generated from the impurity phase related to Fe phase separation. These ceramic samples show relatively high resistivity and saturated ferroelectric hysteresis loops at room temperature and could be useful for potential applications. Physical and chemical properties of any material are mainly dependent on chemical composition and processing. There is drastic improvement over the past decade on the fabrication of BFO and BFO based ceramics [5-8]. However the electrical properties viz., resistance and capacitance of BiFeO$_3$-BaTiO$_3$ (BFO-BT) solid solutions have not been reported till date. This paper reports on the room temperature electrical properties of BFO-BT ceramics in the frequency range 1kHz-1MHz.

2. EXPERIMENTAL SECTION

All the three samples were synthesized by solid state ceramic route using analytical reagent Bi_2O_3, Fe_2O_3, $BaCO_3$ and TiO_2 having purity (≥ 99.0%). This was carried out in steps to obtain a homogeneous mixture. Stoichiometric amounts were weighed, ground more than 4hrs in an agate mortar. The mixed powders were calcined at 820^oC for 8 hrs. The mixture was mixed with polyvinyl acetate as a binder for granulation. This was then pressed into 1.0 cm-diameter pellets. BFO-BT pellets were sintered at 940^oC for 4 hrs. The rate of temperature increase and cooling of furnace was 5^oC per minute. The sintered pellets were ground and powder X- ray diffraction (XRD) patterns were recorded using an X- ray Diffractometer employing Cu-Kα radiations. The electrical properties were made using Novocontrol Alpha - A High Performance Frequency Analyzer at room temperature in the frequency range 1kHz-1MHz [9].
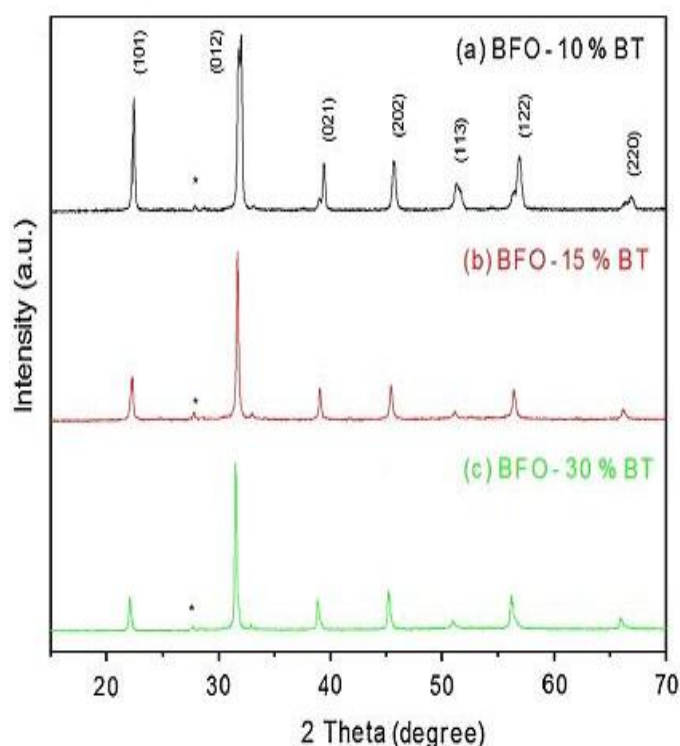
3. RESULTS AND DISCUSSION

Fig. 1:. Room temperature XRD of BFO-BT solid solution.

Figure 1 shows the room-temperature XRD spectra of (1-x)BFO–xBT. XRD pattern of BFO–BT solid solutions (x = 0.10) exhibits splitting in the 2θ peaks and indicates a rhombohedral structure. The splitting behavior of XRD peak gradually disappears with increasing BT and becomes a nearly single sharp peak for BFO–30%BT giving a cubic structure. We have minimized the impurity phase content in BFO ($Bi_2Fe_4-O_9$), indicated

by (*), having XRD peak 2θ (27.9°) in our BFO–(10–30)%BT samples to a negligible amount (<1%) by controlling the loss of Bi$_2$O$_3$. The calculated rhombohedral angle and corresponding lattice parameter [9] for different compositions x=0.10, 0.15 and 0.30 in (1-x)BFO-xBT are shown in Figure 2. From the Figure 2 it is clear that when the BT content is increased in BFO, the lattice parameters increases leading to an increase in volume.
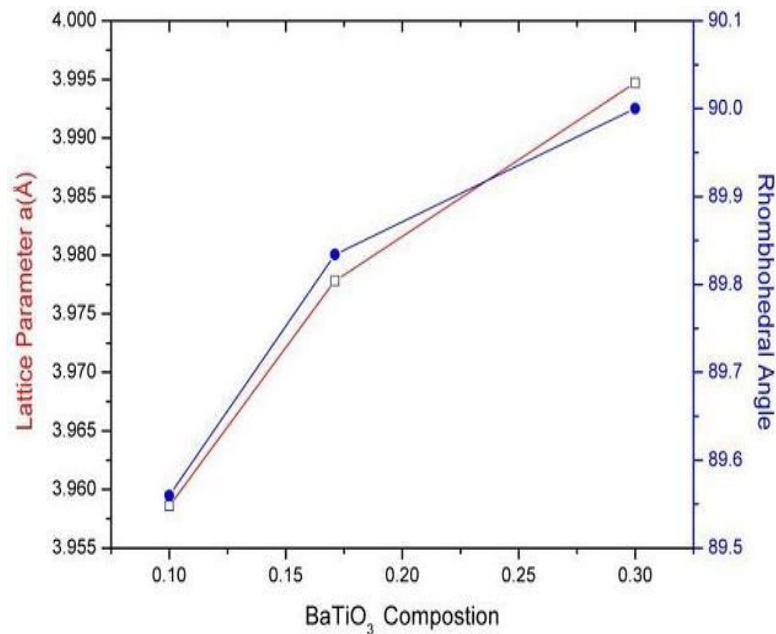

Fig. 2: Variation of rhombohedral lattice parameters and angle with BT content.

This evolution agrees with increasing values of the ionic radius in the A-site, since the radius of Ba^{2+} (1.35Å) is higher than Bi^{3+} (1.03Å). This also agrees with the results reported earlier [10].

The frequency dependence electrical properties viz., resistivity and capacitance are studied at room temperature. The measurements are done in the frequency range 1kHz-10MHz for all BFO-BT solid solutions. The decrease of electrical resistivity or intern the increase in electrical conductivity with the frequency of applied field is shown in Figure 3. It is seen that the value of electrical resistivity increases with increasing concentration of BT. Thus, electrical conductivity of the ferrite material decreases with the concentration of BT. The variation of electrical conductivity can be explained on the basis of verwey and hopping mechanisms [11,12]. The incorporation of BT substitutes Ti^{4+} for Fe^{3+} which compensates the electron deficiency, thus reducing the leakage current and improves the electrical properties. As the Ti^{4+} ion concentration increases, the hopping rate decreases and reduces the probability of acceleration of the charge carriers. The consequent mobility is decreased and thereby the resistivity increases. This dispersion in resistivity with frequency can be explained by Koop's theory [13,14,15]. In this model, the

ferrite grains and grain boundaries have different properties because multilayer condenser raises with frequency and conductivity increases.
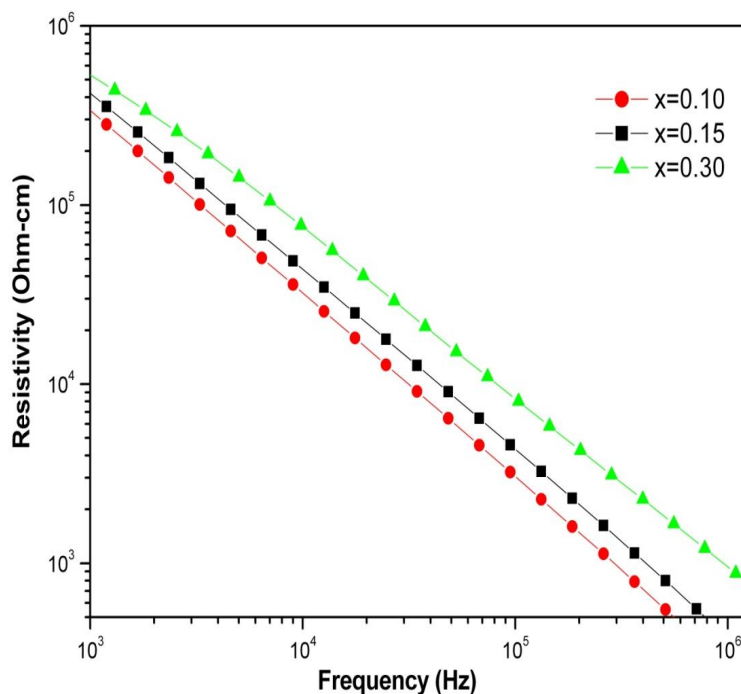

Fig. 3: Variation of resistivity with frequency for different x in (1-x)BFO-xBT ceramics.

Figure 4 shows the variation of capacitance for different x compositions in BFO-BT solid solutions. The increase in capacitance with increase in concentration of BT can be explained on the basis of space charge polarization, presence of higher conductivity phases (grains) in the insulating matrix (grain boundaries) causing localized accumulation of charge under the influence of an electric field. For all compositions the capacitance decreases with increasing frequency. This behavior may be explained qualitatively by the supposition that the mechanism of polarization process in ferrite is similar to that in the conduction process. The electron reaches the grain boundary by hopping and the resistance of grain boundary is relatively more. Electrons pile up at grain boundaries where they produce polarization. When the frequency of applied field is increased the electrons reverse their direction of motion more often which decreases the probability of electrons reaching the grain boundary and as a result polarization decreases, therefore decreasing the capacitance.
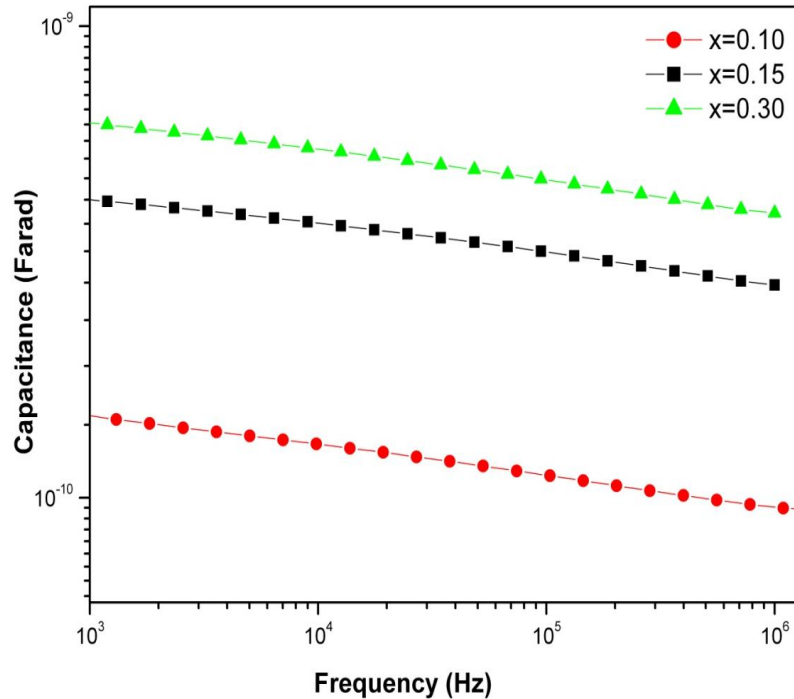
Fig. 4: Variation of capacitance with frequency for different x in (1-x)BFO-xBT ceramics.

The variation in resistivity with frequency is larger than the variation in capacitance with frequency. This dispersive variation is attributed to dominance of intra-well hopping over inter-well hopping [16].

3. CONCLUSION

It is concluded from the studies of structural parameters that BFO-BT solid solutions undergo structural transformations from rhombhohedral to cubic system. The unit cell dimensions increases with higher doping of higher ionic radii dopant (BT). The BFO with higher BT concentrations show higher electrical resistivity as well as capacitance. The decrease in electrical resistance and capacitance has been observed with the increase of frequency of the applied field. The larger dispersion in resistivity is due to dominance of intra-well hopping over inter-well hopping.

Acknowledgments

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