

Structural, Dielectric and Thermal Properties of 0.25BFO-0.75CTO Composite

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Abstract. The ceramic based composite of (1-x) CTO-(x) BFO where x=0.25 was prepared by direct mixing of powders of BFO and CTO prepared by solid state reaction method. The prepared material was characterized using X-ray diffraction. The peaks were well matched with the standard data which confirmed the existence of both orthorhombic phase of CTO and rhombohedral phase of BFO. The Dielectric study was carried out as a function of frequency at RT. Also the Impedance study was carried out as a function of frequency at RT. The dc conductivity has been analysed and activation energy was calculated using the Arrhenius relation. The specific heat, Enthalpy change and weight loss of the compound was measured using STA-6000 Perkin Elmer DTA-TGA.

INTRODUCTION

The concept of product property introduced by Von Suchtelen [1] resulted in appearance of the composite based multiferroic materials in which both the phases co-exist and show their individual property [2]. As there are very few materials in which there exist both ferroelectric and ferromagnetic traits in a single phase material example is Perovskite type BiFeO₃ with T_c=1103K and G-type ferromagnetism at 643K [3]. So the idea of composites has proven a boon in this context. Since CaTiO₃ is an incipient ferroelectric but has high value of dielectric constant and is less lossy [4]. Initially CaTiO₃ was prepared by the solid state reaction at high temperature (1623K) [5] with orthorhombic structure and Pbnm space group at RT [6]. Also CaTiO₃ is thermally stable material [7]. So an attempt has been made to prepare a composite of CaTiO₃ (an incipient ferroelectric) and BiFeO₃ (both ferroelectric and ferromagnetic) by direct mixing of powders of CaTiO₃ and BiFeO₃. Here 25% of BiFeO₃ is added into the 75% matrix of CaTiO₃ and its structural, dielectric and thermal properties were studied.

EXPERIMENTAL

The 0.75CTO-0.25BFO composite was made by direct mixing the powders of CTO and BFO in stoichiometric amount prepared by solid state reaction method. The mixture was then grinded to make it homogeneous and sintered at 850°C. The material was then analysed by the Rigaku Mini flex Ultima IV powder X-ray Diffractometer at a scanning rate of 4 degree/min from 20° to 80°. The mixture was then pelletised and coated with silver paste. Then the Dielectric study was carried out as a function of frequency (at RT) and in air atmosphere using 4275A Multi frequency LCR meter. The dc conductivity was measured from RT to 600K using a laboratory made set up and its activation energy was calculated using Arrhenius relation $\left[\sigma = \sigma_0 \exp \left(-\frac{E_a}{KT} \right) \right]$ Where σ is conductivity in $\Omega^{-1}m^{-1}$, σ_0 is parameter depending on the material, E_a is activation energy in eV, K is Boltzmann constant and T is temperature in Kelvin. The specific heat, Enthalpy change and weight loss of the compound was analyzed in temperature range from 700K to 1200K at a scanning rate of 30 K/min using STA-6000 Perkin Elmer DTA-TGA.

RESULTS AND DISCUSSIONS

Structural Study

Figure shows the RT X-ray diffraction pattern of BFO, CTO and 0.75CTO-0.25BFO. Calcium Titanate and Bismuth Ferrite were prepared using solid state reaction method. The prepared materials peak were matched with the standard data [data file no. ICSD 62149 (CTO) and ICSD 51664 (BFO)]. Composite was prepared using these prepared materials in a definite composition of 25%BFO-75%CTO. The individual peaks of the composite material were matched which confirmed the co-existence of both phases of CTO and BFO in the composite. There are some of the impurity peaks in the material which are of Bi_2FeO_9 and TiO_2 .

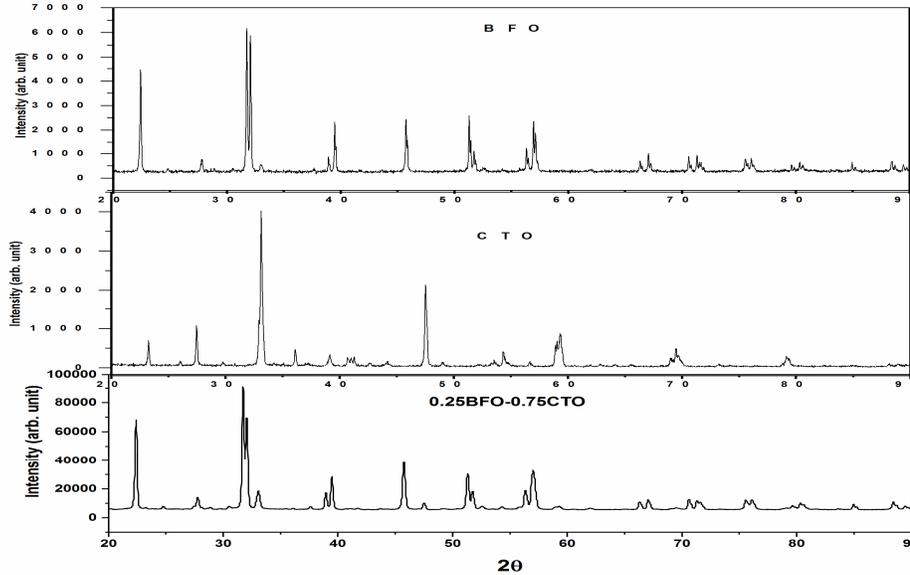
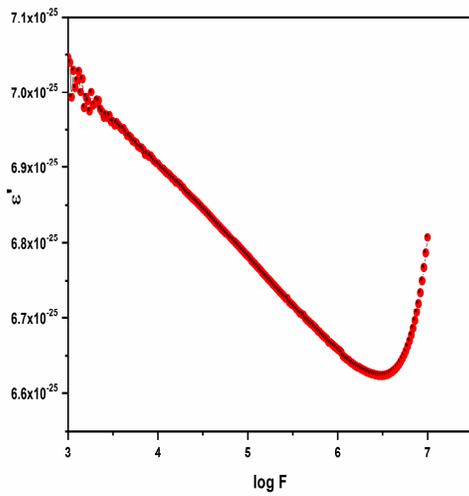


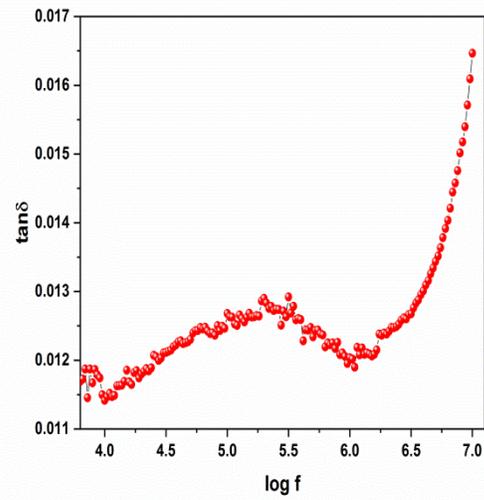
FIGURE 1. X-ray Diffraction pattern of the pristine CTO and BFO compounds and their composites.

Dielectric studies

The Dielectric permittivity and dissipation factor was studied as a function of frequency at RT which is shown in Figure 2(a) and 2 (b). The Dielectric permittivity has highest value (70.5) at low frequency that is due to the orientation of the dipoles. As frequency increases dielectric permittivity decreases up to 3MHz as at high frequency orientation of dipoles cannot follow the frequency. Here dielectric permittivity again increasing with increase in frequency (10MHz) due to extrinsic mechanism such as interfacial polarization arising at the interface of grain or grain boundary [8]. Figure 2(b) shows variation of dissipation factor with frequency. Curve shows two characteristic relaxation time which can be explained on the basis of Debye relaxation mechanism [9].



(a)



(b)

FIGURE 2. (a) Variation of dielectric permittivity with log f at RT and (b) variation of Dissipation factor with log f at RT.

Complex Impedance Study

Figure 3 shows the variation of real part of impedance with frequency at RT. At low frequency the real part of impedance decreases with increase in frequency such that it becomes frequency independent at high frequency (100 KHz - 1 MHz).

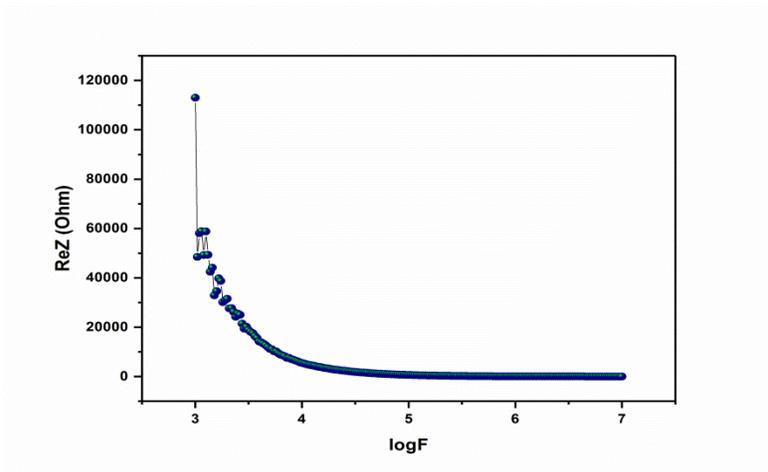


FIGURE 3. Frequency dependence of the real part of impedance at RT.

Figure 4 shows the frequency dependent variation of imaginary part of impedance at RT. The maximum value of impedance is found to be around 4.5 MΩ which decreases to 8KΩ with increase in frequency.

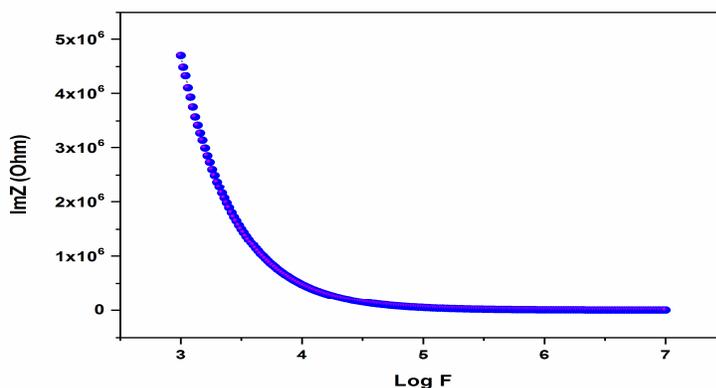


FIGURE 4. Frequency dependence of the imaginary part of impedance at RT.

DC Conductivity

Figure 5 shows that in low temperature region (307K-345K) conductivity decreases, becomes constant in 345K-415K and then increases in temperature range 415K-640K. The activation energy was calculated using Arrhenius relation from the slope of the $\log \sigma_{dc}$ vs. $1000/T$ curve and was found to be -0.44eV in temperature region 307K-345K and 1.01eV in temperature region 415K-640K. The negative value of activation energy shows that with increase in temperature the trapped charge carriers are not able to move hence conductivity decreases. Further the rise in temperature liberates the trapped charge carriers and hence conductivity increases and activation energy becomes positive.

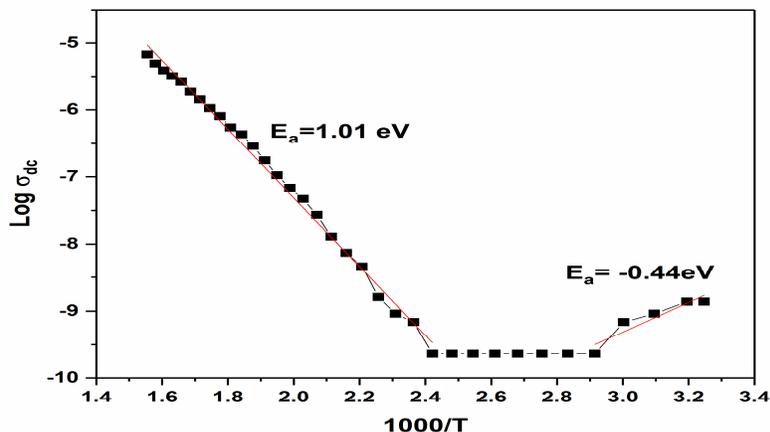


FIGURE 5. $\log \sigma_{dc}$ vs. $1000/T$ curve.

Thermal Study

The heat flow vs. Temperature for the composite is shown in figure 6(a). During heating cycle an exothermic peak is observed at around 1092K which indicates ferroelectric phase transition of BiFeO_3 . During cooling cycle endothermic peak is observed at 1059K which is at low temperature than that of heating cycle. The enthalpy change and Specific heat at constant pressure was calculated and was found to be 3.28 J/g and $0.66\text{ J/g}^\circ\text{C}$ respectively. The amount of heat absorbed during heating cycle was calculated to be 108.05 mJ in the temperature range 1080K to 1100K.

Figure 6(b) shows the percentage weight loss during heating and cooling cycle. The %weight loss was found to be around 2% which is very less. Thus the composite material is thermally stable [10]. The reason may be due to major content of CTO (75%) in the composite.

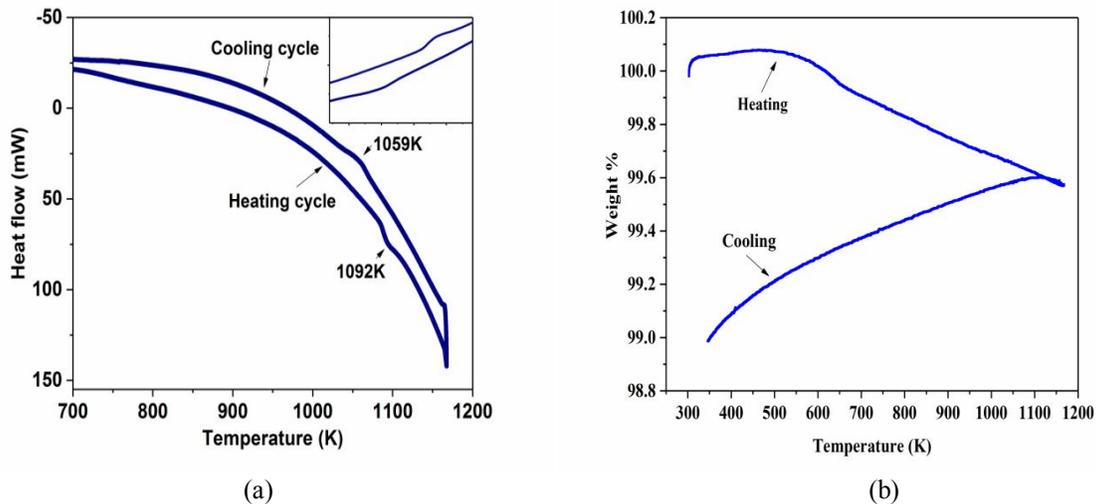


FIGURE 6. (a). Heat flow vs. Temperature and (b) percentage weight loss vs. temperature

CONCLUSION

The composite of 0.75CTO-0.25BFO was prepared by direct mixing of powders of BFO and CTO prepared by solid state reaction method. The XRD revealed the co-existence of both phases of CTO and BFO. CTO exists in orthorhombic phase and BFO exists in rhombohedral phase. The dielectric permittivity study as a function of frequency shows the dispersive nature and the overall behavior can be explained due to grain and grain boundary effects. In low temperature region the dc conductivity decrease with increase in temperature which infers that the material exhibit positive temperature coefficient of resistance and in high temperature region conductivity increases with increase in temperature implying that the material exhibit negative temperature coefficient of resistance. This behavior was observed in pristine CTO. The thermal analysis of the composite shows the ferroelectric transition at 1092K which is same as that of transition temperature of BFO. The enthalpy change and Specific heat at constant pressure was low and found to be 3.28 J/g and 0.66J/g°C respectively. Also the weight loss with respect to temperature was very low this shows that the composite material is thermally stable.

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