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Impedance properties of 0.7($BiFeO_3$)-0.3 ($PbTiO_3$) composite

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ABSTRACT

The polycrystalline sample of 0.7($BiFeO_3$)-0.3($PbTiO_3$) [0.7(BFO)-0.3(PT)] was prepared by a high temperature solid state reaction technique. Studies of structural analysis confirm the formation of the compound with rhombohedral structure at room temperature. The electrical properties (impedance, modulus and conductivity) of the material were analyzed using a complex impedance spectroscopy technique in a wide temperature (225-300 ^{o} C) and frequency (10^2 -10^6 Hz) range. The studied material exhibits a significant contribution of grain (bulk) effect and non-Debye of relaxation process. The bulk resistance decreases with rise in temperature which exhibits negative temperature coefficient of resistance (NTCR) behavior. Electrical modulus study confirms the presence of bulk effect in the material. This compound also exhibits the temperature dependence of relaxation phenomena. The ac and dc conductivity of the materials were found to be increase with increase in temperature. The activation energy of the compound is found to be less than 1eV and suggests the conduction process is of mixed type (ionic-polaronic and singly-ionized oxygen ion vacancies). Copyright © 2013 VBRI Press.

Keywords: X-Ray diffraction; complex impedance, modulus study, conductivity.

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Introduction

Recently, there has been rapid progress in search of new multiferroic materials. Generally, there are four primary ferroic properties, i.e., ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidicity. The material in which any two of four primary ferroic properties coexist is called multiferroic (MF) materials. Further, multiferroic materials provide potential multifunctional devices with the advantage of coupling between the two degrees of freedom based on local off centered distortions and electron spins. Due to the coupling between ferroelectric and ferromagnetic ordering (called magnetoelectric effect), the multiferroics are wide range of applications such as spintronics, multiple state memory, data storage media, sensor, tunable microwave devices etc **[1-3]**.The existence of ferroelectricity and ferro-magnetism in the same phase of MF which allows the observation of both switchable electric polarization and magnetization even in the absence of space-inversion and time-reversal symmetry respectively reported by Fetcher *et al* **[4]**. $BiFeO_3$ (BFO) is one of the most widely studied multiferroic materials because of its magnetoelectric properties (i.e., ferroelectric with a high curie temperature and antiferromagnetic) **[5]**. $BiFeO_3$ has a rhombohedrally distorted perovskite structure with space group R3c **[6]** and high Curie temperature (i.e., T_c = 1123K) **[7]** along with high Neel temperature (T_N=653K) **[8]**. The application of $BiFeO_3$ is due its thermal metastability and electrical conduction due to non-stoichiometry **[9]**. In recent years, tremendous research is going on BFO which shows the co-existence of both ferroelectric and ferromagnetic ordering in the same phase **[10-13]**. BFO has solid solution with many insulating ABO_3 structured perovskite oxides such as $PbTiO_3$ (PT) **[14]** and $BaTiO_3$ (BT) **[15]**. Particularly, the 1-x($BiFeO_3$)-x($PbTiO_3$) (BFO-PT) composite has generated significant interest because it exhibit high piezoelectric coefficient, high dielectric constant, low dielectric loss and Curie temperature in comparison to the conventionally used Pb (Zr, Ti)O_3 **[14]**. Complex impedance study on several structured materials like perovskite and tungsten bronze type have been reported **[16-19]**. Though lots of works related to structural, dielectric and electrical properties have been done on BFO-PT with different composition **[20-23]**, not much work has been reported on impedance properties of studied compound. In the present study, the electrical properties (impedance) of 0.7 ($BiFeO_3$) - 0.3 ($PbTiO_3$) is reported.

Experimental

The polycrystalline sample of 0.7(BFO)-0.3(PT) was prepared by a mixed oxide method at high temperature using high purity ingredients; Bi_2O_3 (99.99 %, Spectrochem Pvt. Ltd., India), Fe_2O_3 (98.5 %, Blulux Lab. Pvt. Ltd., India), PbO (98%, Blulux Lab. Pvt. Ltd., India) and TiO_2 ($\geq$ 99% Merck Specialties Pvt. Ltd., India) in a suitable stoichiometry. The stoichiometrically weighed composition was mixed thoroughly in an agate mortar for 2 h and in alcohol for 2 h. The mixed powders were calcined in a high purity alumina crucible at an optimized temperature of 750 ^{o}C for 6h in an air atmosphere. The process of grinding and calcinations was repeated several times till the formation of the compound was confirmed. Then calcined powder was mixed with polyvinyl alcohol (PVA) which acts as a binder to reduce the brittleness of the pellet and burnt out during high temperature sintering. The fine homogenous powder was cold pressed into cylindrical pellets of 10 mm diameter and 1-2 mm of thickness at pressure of $3.5x10^6$ N/m^2 using a hydraulic press. These pellets were sintered at 800 ^{o}C for 6 h in an air atmosphere. The sintered pellets were polished by fine emery paper to make both the surfaces flat and parallel. To study the electrical properties of the compound, both flat surfaces of the pellets were electrode with air-drying conducting silver paste. After electroding, the pellets were dried at 150 ^{o}C for 4 h to remove moisture, if any, and then cooled to room temperature before taking any electrical measurement. The formation of compound was studied by an X-ray diffraction technique at room temperature with a powder diffractometer (Rigaku Miniflex, Japan) using CuK_α radiation (λ = 1.5405 Å) in a wide range of Bragg's angles $2\theta(20^0 \leq \theta \leq 80^0)$ with a scanning rate of 3^{o}/min. The electrical parameters (impedance and capacitance) of the compound were measured using an LCR meter (HIOKI, Model-3532) in the frequency range of 10^2-10^6 Hz from 25 to 500 ^{o}C.

Results and discussion

Structural properties

The room temperature XRD pattern of 0.7(BFO)-0.3(PT) is shown in **Fig. 1**. Comyn *et al.* **[24]** reported that X-ray diffraction patterns of the same composition show both the rhombohedral and tetragonal forms of the perovskite. They suggested that the diffraction peaks are diminished with increase the sintering temperatures, which implies the reduction of the tetragonal phase present in the material. Therefore, rhombohedral structure of the studied material can be confirmed.

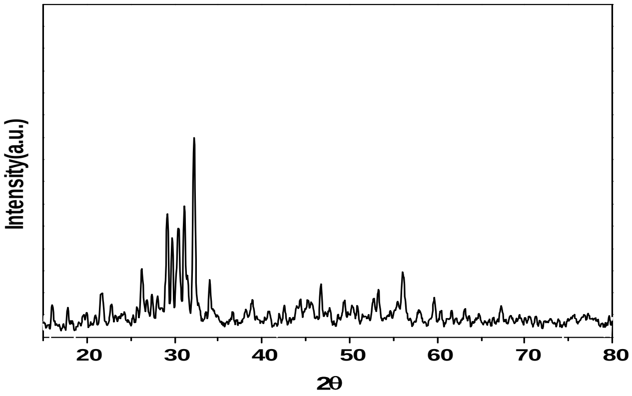

Fig. 1. XRD patterns of 0.7(BFO)-0.3(PT).

Impedance properties

The complex impedance analysis **[25]** is a well known and powerful tool which has been effectively used for probing into dielectric materials and ionic crystals/materials as a function of frequency and temperature. This analysis enable one to resolve the contributions of various processes, such as the bulk effects, grain boundaries and electrode interface effects in the frequency domain. Generally, the data in the complex plane is represented in any of the four basic formalisms. These are complex impedance (Z^*), complex admittance (Y^*), complex permittivity (ε^*), complex electric modulus (M^*), which are related to each other:

complex impedance $Z^*=Z'-jZ''=1/j\omega C_0\varepsilon^*$,

complex electrical modulus $M^*=M'+jM''=1/\varepsilon^*=j\omega C_oZ$,

complex admittance $Y^*=Y'+jY''=j\omega C_0\varepsilon^*$, $\varepsilon^*=\varepsilon'-j\varepsilon''$

and $\tan\delta=\varepsilon''/\varepsilon'=M''/M'=Z'/Z''=Y'/Y''$

where (Z', M', Y' ε') and (Z'', M'', Y'' ε'') are real and imaginary components of impedance, electrical modulus, admittance and permittivity respectively, $\omega=2\pi f$ is the angular frequency and $j=\sqrt{-1}$ the imaginary factor. The complex impedance of "electrode/sample/electrode" configuration can be explained as the sum of a single with a parallel combination of RC (R=resistance, C=capacitance) circuit. Thus, the result obtained using impedance analysis is an unambiguous, and hence provide a true picture of the electrical behavior of the material. The peaks of the high frequency semicircular arc in the complex impedance spectra enable us to calculate the relaxation frequency (ω_{max}) of the bulk material using the equation: $\omega_{max}\tau = \omega_{max}R_bC_b\ 2\pi f_{max}R_bC_b=1$, where R_b= bulk resistance and C_b= bulk capacitance.

Fig. 2 shows the complex impedance spectrum (Z' Vs. Z''), Nyquist plot, of 0.7(BFO)-0.3(PT) at selected temperatures. A single semicircular arc has been observed in a wide temperature range. This indicates that the electrical properties of the material arise mainly due to the contribution of bulk effects only. It is also observed that as the temperature increases the intercept point on the real axis shifts towards the origin which indicates the decrease in the resistive property i.e., called bulk resistance (R_b) of the material **[26-27]**. The electrical process taking place within the material can be modelled (as an RC circuit) on the basis of the brick-layer model **[25]**.

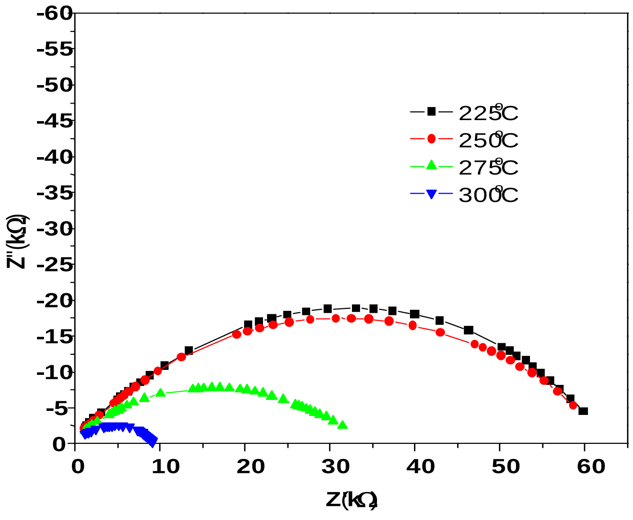

Fig. 2. Complex impedance spectrum (Z′ vs. Z'') of 0.7(BFO)-0.3(PT) at different temperatures.

Fig. 3 shows the variation of Z′ with frequency of 0.7(BFO)-0.3(PT). It is observed that in the low frequency region, the magnitude of Z′ decreases on increasing temperature which show the NTCR behavior as observed in the Nyquist plot. The coincidence of the value of Z' at higher frequencies at all the temperatures indicates a possible release of space charge **[28-29]**. This may be due to the reduction in barrier properties of the materials with rise in temperature which is responsible for the enhancement of conductivity of the materials **[30-31]**. At a particular frequency, Z' becomes independent of frequency. This type behavior is similar to the other material reported by Singh *et. al.* **[32]**.

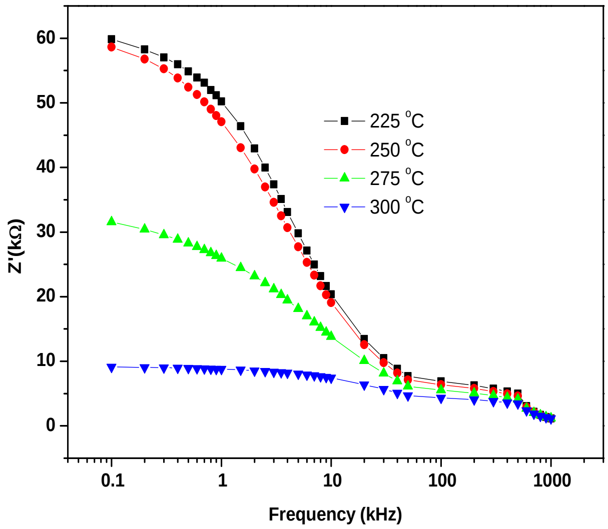

Fig. 3. Variation of Z′ as a function of frequency at different temperatures of 0.7(BFO)-0.3(PT).

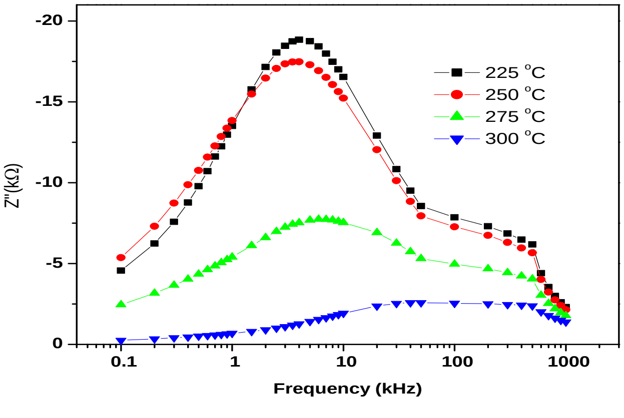

Fig. 4. Variation of Z'' as a function of frequency at different temperatures of 0.7(BFO)-0.3(PT).

Fig. 4 shows the frequency-temperature dependence of Z'' of 0.7 (BFO)-0.3(PT). It exhibits that the peaks of the plot are shifted towards higher frequency side with rise in temperature. Further, the magnitude of Z'' decreases gradually with a shift in peak frequency towards high frequency side, and it finally merges in the high frequency region. This is an indication of the accumulation of space charge in the materials **[33]**. The change in the peak broadening on change in temperature suggests the presence of temperature dependent relaxation processes in the material. This may be due to the presence of immobile species at low temperature and defects at higher temperatures **[34-35]**.

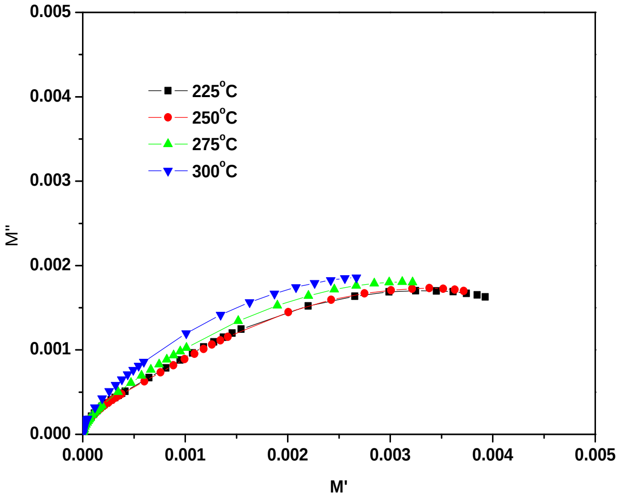

Fig. 5. Complex modulus spectrum of 0.7(BFO)-0.3(PT) at selected temperatures.

Modulus studies

The complex electric modulus can be calculated using the relations: $M^*=M'+jM''=1/\varepsilon^*$ where $M' = \omega C_o Z''$ and $M'' = \omega C_o Z'$ ($\omega = 2\pi f_r$), C_o = geometrical capacitance = $\varepsilon_o A/t$ (ε_o = permittivity in free space, A = area of the electrode surface and t = thickness). The advantage of complex electric modulus formalism **[33]** is that the discriminate electrode polarization from grain boundary conduction process. In polycrystalline materials, impedance formalism give emphasis on grain boundary conduction process, while bulk effects on frequency domain would dominate in the electric modulus formalism. The use of modulus spectroscopy plot is particularly useful for separating components with similar resistance but different capacitance. The other advantage of electric modulus formalism is that the electrode effect is suppressed.

Complex modulus spectrum (M' vs. M'') of 0.7(BFO)-0.3(PT) at selected temperatures is shown in **Fig. 5**. A single semicircle is observed in the complex modulus plot. The intercept on the real axis indicates the real capacitance contributed by the grain effect. Further, it is also confirmed that the grain boundaries are negligible, and even if present, contribution to the overall capacitance of the material is less, and much affect the relaxation process. The modulus spectrum shows a marked change in its shape with rise in temperature suggest the probable change in the capacitance values of the material as a function of temperature **[33]**.

Electrical conductivity

The temperature dependence of ac electrical conductivity (σ_{ac}) of 0.7(BFO)-0.3(PT) at different frequencies are shown in **Fig. 6**. The value of σ_{ac} was calculated using experimental dielectric data by an empirical relation $\sigma_{ac}=\omega\varepsilon_0\varepsilon_r\tan\delta$, where ε_o permittivity in free space and ω angular frequency. The electrical conductivity (σ_{ac}) of the material is thermally activated and obeys the Arrehenius equation: $\sigma_{ac}=\sigma_0\exp(-E_a/K_BT)$; ($E_a$=activation energy, K_B=Boltzmann constant, σ_0=pre exponential factor). It is observed that the ac conductivity of the material increases with rise in temperature and shows the NTCR behavior. The values of E_a of the compound were found to be 0.80eV and 0.57eV at 10 and 50 kHz respectively. The activation energy of ac conductivity was found higher than that of dc conductivity (<1eV). This is due to difference in conduction mechanism (i.e., hopping conduction and extrinsic conduction) in the material **[36-38]**.

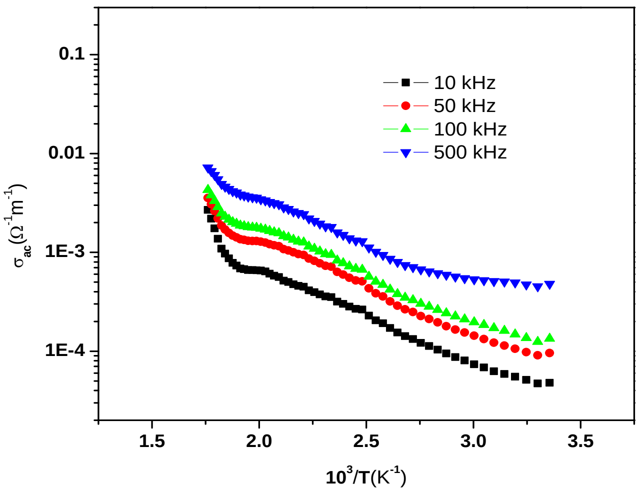

Fig. 6. Variation of ac conductivity (σ_{ac}) with ($10^3/T$) of 0.7(BFO)-0.3(PT) at different frequency.

DC conductivity study

Fig. 7 shows the plot of dc conductivity (σ_{dc}) with $10^3/T$ of 0.7(BFO)-0.3(PT). The bulk conductivity of the material was evaluated from the complex impedance plots at different temperatures. The activation energy is calculated using Arrehenius equation $\sigma_{dc}=\sigma_0\exp(-E_a/K_BT)$ where the symbols have their usual meaning. It is observed that the dc conductivity increases with increase in temperature. The activation energy calculated in the higher temperature region is found to be 0.37 eV. At higher temperatures single ionized oxygen vacancies dominate the conduction process in the materials **[39]**.

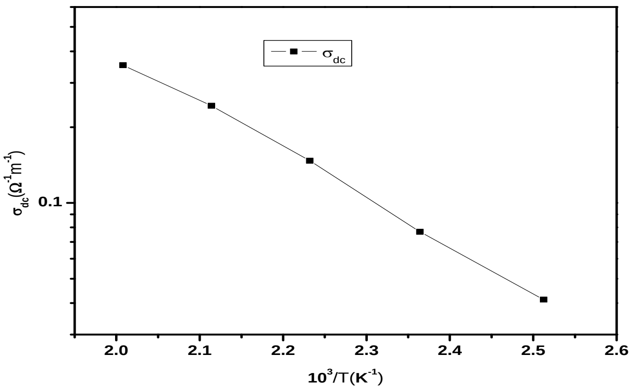

Fig. 7. Variation of σ_{dc} with ($10^3/T$) of 0.7(BFO)-0.3(PT).

Conclusion

The polycrystalline sample of 0.7(BFO)-0.3(PT) was prepared by a high temperature solid state reaction technique. X-ray analysis exhibits the rhombohedral crystal structure of the compound at room temperature. Impedance and modulus studies reveal the significant contribution of grain (bulk) effect only in the material. The compound exhibits the presence of non-Debye of relaxation process. The bulk resistance of the material decreases with rise in temperature and exhibits a NTCR behavior. The variation of ac and dc conductivity of the material as a function of temperature exhibits Arrhenius type of electrical conductivity. The activation energy (calculated from dc conductivity) of the compound is found to be 0.37 eV in the high temperature region.

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