Frequency and temperature dependent impedance study in 50% BaTiO$_3$- 50% La$_{0.7}$Sr$_{0.3}$MnO$_3$ nanocomposite

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ABSTRACT

We report the impedance spectroscopy (IS) behavior of the ferroelectric- ferromagnetic (50% BaTiO$_3$-50% La$_{0.7}$Sr$_{0.3}$MnO$_3$) nano-composite prepared by sol-gel method. Frequency and temperature dependence of the complex impedance and conductivity has been measured over the temperature range 310 K-430 K. A distribution of relaxation times and decentralization of the semicircle has been observed from the Cole–Cole plots of real and imaginary parts of the complex impedance. Non-Debye type relaxation has been observed in the investigated composite system. An equivalent circuit has been constructed to describe the IS. Interestingly, a typical universal dielectric response in the frequency-dependent conductivity at different temperature has been found. The frequency dependent ac conductivity at different temperature indicates that the conduction process is thermally activated. The activation energy has been obtained from the Arrhenius fitting. The obtained dc conductivity showed that the system undergoes a positive temperature coefficient resistance (PTCR) to negative temperature coefficient resistance (NTCR) near 350 K. The results would help to understand deeply the relaxation process in these types of materials. Copyright © 2014 VBRI press.

Keywords: Composite; impedance; ac conductivity; relaxation process.

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Introduction

Impedance spectroscopy (IS) is the powerful technique for the characterization of the electrical behavior of ceramic composites. It appears naturally in complex plane in the form of succession semicircles representing electrical phenomenon involved in the composite due to grain, grain boundaries, electrical interface effect and correlate between the dielectric and electrical characteristics [1-3]. The frequency and temperature dependent IS study on composite materials is commonly employed to (a) deconvolute different contributions in ionic conductors (b) to detect mixed ionic–electronic charge transport, or (c) to characterize insulating materials such as dielectrics and ferroelectrics. It has been observed that in ferroelectric– ferromagnetic composites, the magneto dielectric effect is also largely influenced by the grains and grain boundaries [4, 5]. In recent years we have seen increasing interest focused on the induction of ferromagnetism to nonmagnetic ferroelectric material by intentionally doping transition metal compounds to prepare magnetoelectric materials. Many material systems, such as BTO–NiCuZn [6], BTO– MgCuZn [7], PZT– NiCuZn [8], BTO/La$_{0.7}$(Pb/Ca)$_{0.3}$MnO$_3$ [9] were investigated and found to exhibit interesting changes in conductivity, dielectric and magnetic properties.

The coexistence of the magnetic electric subsystem engenders the material with the "product property" i.e., the composite exhibits responses that are not available on the individual component phases, allowing an additional degree of freedom in the design of actuators, transducers and storage devices [10, 11]. At present there is considerable interest in ferroelectric perovskite $BaTiO_3$ (BTO) because these are promising candidates for the next generation of dynamical random access memory (DRAM) capacitors and tunable microwave devices, owing to their excellent ferroelectric responses and dielectric behavior. On the other hand, composites of BTO with doped rare earth manganites (i.e., $La_{1-x}Sr_xMnO_3$, $La_{1-x}Ca_xMnO_3$: x is the doping concentration, etc.) have been studied because of their colossal magnetoresistance as well as their complex transport properties [12, 13]. Frequency-dependent study of magnetoelectric properties in these materials has shown interesting effects [14]. We have chosen the $BaTiO_3$-$La_{0.7}Sr_{0.3}MnO_3$ (BTO-LSMO) composites for the study of the effect of grain, grain boundary, and interface effects in the relaxation process as well as in frequency-dependent conduction through the study of frequency and temperature dependent complex impedance behavior and conductivity.
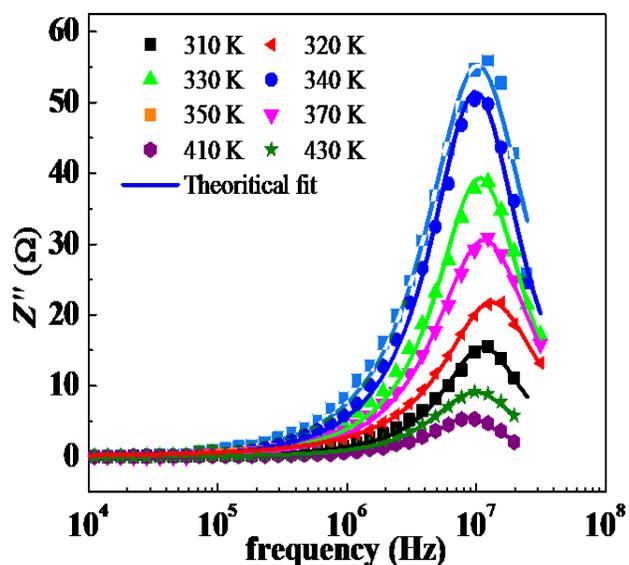

Fig. 1. Variation of imaginary part Z" of the complex impedance with frequency at different temperature.

Experimental

Materials

All the chemicals were used as received without any further purification processes. The barium titanate ($BaTiO_3$, 99%), lanthanum dioxide (La_2O_3, 99%) and strontium nitrate ($Sr(NO_3)_2$, 99%) were purchased from Sigma-Aldrich, USA. The manganese acetate tetrahydrate ($Mn(CH_3COO)_2.4H_2O$, 99.5%) and the concentrated nitric acid (HNO_3, 99.5%) were purchased from Merck Ltd, Mumbai, India.

Synthesis of the composite

The ferroelectric-ferromagnetic nano-composite has been prepared in two steps. At first the precursor $La_{0.7}Sr_{0.3}MnO_3$ nano-powder was prepared by sol-gel method. The starting materials La_2O_3, $Sr(NO_3)_2$ and $Mn(CH_3COO)_2.4H_2O$ were mixed in stoichiometric proportions in nitric acid. This solution was stirred vigorously for homogeneous mixing at 80^0 C for 6h. Powders obtained from dried gels were then calcined in air at 900^0 C for 12h and cooled down to room temperature. BTO- LSMO was prepared next by mixing calculated amount of $BaTiO_3$ and LSMO (each 50 wt %) in ethanol. The solution again stirred gently at the room temperature for uniform mixing. After mixing, the powders were sintered at 900°C for 12h. The sample thus prepared was characterized by powder X-ray diffraction. The pelletized samples were used for the measurements in the frequency range from 42Hz to 5 MHz at different temperature (310-430 K).

Results and discussion

Fig. 1 shows the frequency-dependent variation of the imaginary part (Z'') of the complex impedance (Z^*) at different temperature. Each curve of Z'' vs. frequency plot is characterized by the presence of a peak at particular frequency (ω_{max}) and at a fixed temperature. The shift in peak frequency with decrease in peak broadening has been observed on increasing temperature from 310 K to 350 K and the peak broadening increases with temperature in 370 K- 430 K. Asymmetric peaks suggest that the relaxation process in the material is temperature dependant. Relaxation time (τ) can be calculated using the equation $\omega_{max}\tau = 1$.

All the curves merge into single curve for the frequencies <100 kHz in this temperature region. It has been observed that the maximum (Z''_{max}) value of Z'' increases with temperature upto 350 K and then decreases. This behavior can be attributed to consider the metal-insulator transition of the conducting LSMO phase and ferroelectric-paraelectric phase transition of BTO discussed later. We have studied the impedance spectrum to determine the electrical properties of the materials in terms of the complex impedance (Z^*). It can be expressed by introducing the factor α into the Debye expression [15]

$$Z^* = \frac{R}{1+(j\omega RC)^\alpha} \quad (1)$$

R is resistance and $0 \le \alpha \le 1$. $\alpha = 1$ corresponds the relaxation is perfectly Debye type.

The imaginary part Z'' can be derived from (1) as

$$Z'' = R \frac{(\omega\tau)^\alpha \sin(\alpha\pi/2)}{1+2(\omega\tau)^\alpha \cos(\alpha\pi/2)+(\omega\tau)^{2\alpha}} \quad (2)$$

τ is the relaxation time. The solid lines represent the best fit of Z'' data with Eq. (2) gives the values of α in the range $0.67 < 1$, which reflects that relaxation is non-Debye type [16, 17].
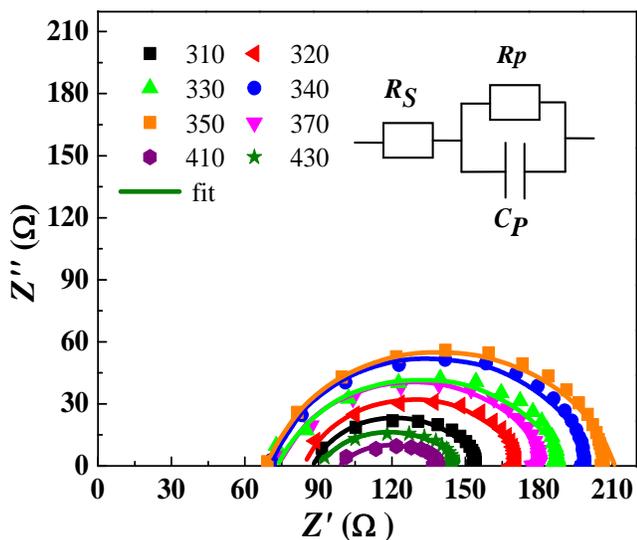

Fig. 2. Cole-Cole plot at different temperature of BTO- LSMO composite. Inset shows the equivalent circuit of the Cole-Cole plot.

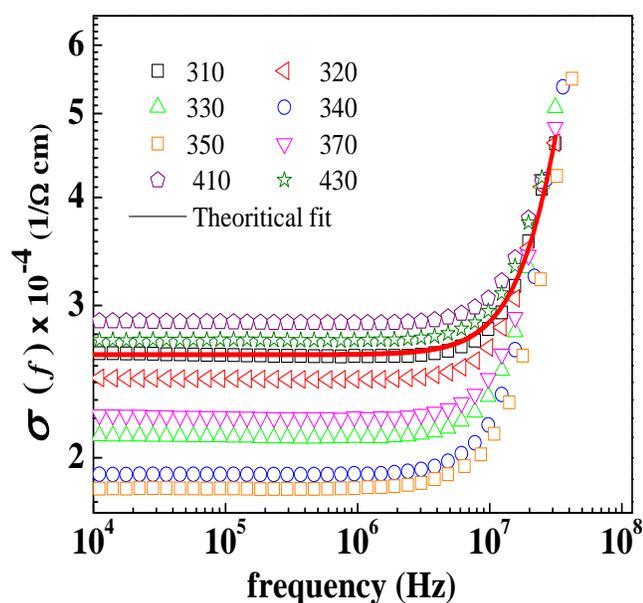**Fig. 3.** Frequency dependent ac conductivity at different temperature of BTO- LSMO composite.

Fig. 2 represents the variations of the real (Z') and imaginary (Z'') parts of complex impedance (Z^*) as function of frequency in the form of Cole–Cole plots at different temperature. Consequently, a distribution of relaxation times and decentralization of the semicircle has been observed [3, 18]. Such behavior indicates polydispersive non-Debye-type relaxation and manifests that there is a distribution of continuous or discrete relaxation time around the mean relaxation time, $\tau_m = 1/\omega_{max}$. In general, composites do not obey the ideal Cole–Cole formalism indicating a single relaxation mechanism. It

can be attributed to many factors such as grain size distribution, grain boundary stress strain, defects and volume fractions of the components. From the **Fig.** 2, it has been observed that the bulk resistance increased as the temperature increased to 350 K and decreased to 410 K. This behavior suggests that the sample shows a PTCR effect upto 350 K and NTCR effect between the temperatures ranges 350-410 K, which implies a thermal activated conductivity of the material. **Fig.** 2 also presents the corresponding equivalent circuits of the Cole-Cole plot (shown in the inset).

Fig. 3 shows variation of ac conductivity with frequency at various temperatures. Frequency independent behavior of $\sigma(\omega)$ in low frequency region is observed however at high frequency region, which is known as hopping region [1] the value of $\sigma(\omega)$ increases. The frequency is called hopping frequency from which the conductivity deviates from the plateau region. In the higher frequency region, $\sigma(\omega)$ increases due to the hopping of charge carrier in finite cluster. It has been observed that the conductivity decreases with increasing temperature below 350 K, which is typical for semiconducting material and increases with that from 350 K to 410 K, which is typical for conducting material and interestingly decreases again above 410 K. This typical behavior of the conductivity can be attributed to the metal-insulator transition of LSMO and ferroelectric-paraelectric phase transition of BTO. The ferromagnetic LSMO shows a metal-insulator transition around 360 K [19]. The change in slope in conductivity around that temperature implies that the change in relation of the composite's conductivity with temperature may relate to metal-insulator phase transition of LSMO phase. The dc conductivity again decreases above 410 K due to the phase transition of BTO at that temperature [20].

A convenient formalism to investigate the frequency behavior of the conductivity at constant temperature is based on the power relation proposed by Jonscher [21].

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \qquad (3)$$

where ω is angular frequency, coefficient A is the temperature dependent constant and n is the power law exponent parameter in the range $0 \leq n \leq 1$, represents the degree of interaction between mobile ions and the environments surroundings and also characterizing the deviation from Debye behavior. Many authors reported that values of the exponent n lies between 0.6 and 1 [22, 23]. In our case the values of the exponent n have been found getter than 1 from the best fit with Eq. (3) (for clarity only one fitting have been shown here). It suggests that the interaction between the mobile ions and defect sites is involved in the conduction mechanism. Recently, Papathanassiou et al. [24] shows that the exponent n can hold values larger than unity e.g. experimentally observed in glassy $0.3[x\text{Li}_2\text{O}/(1-x)\text{Na}_2\text{O}]/0.7\text{B}_2\text{O}_3$ [25], in mixed compounds of $(\text{NH}_4)_3\text{H}(\text{SO4})_{1.42}(\text{SeO}_4)_{0.58}$ [26] and $\text{K}_3\text{H}(\text{SeO}_4)_2$ single crystals [27]. It should be noticed that the simple power law is applicable to the composite for demonstrating the conductivity and the relaxation mechanisms. Obtained dc conductivity, σ_{dc} from the best fit

to Eq. (3) plotted with the inverse of temperature as shown in **Fig. 4.** Interestingly, it has been observed that the dc conductivity decreases with the temperature above 410 K and below 350 K. This phenomenon may be attributed to the phase transition of the BTO from ferroelectric to paraelectric and LSMO from metal to insulator, respectively. Between the transition points 350 K – 410 K, the dc conductivity vs. reciprocal of the temperature response has found to be linear and explained by thermally activated transport of Arrhenius type relation viz.

$$\sigma_{dc} = \sigma_0 \, exp\left(E_a / k_B T\right) \qquad (4)$$

σ_0, is the pre-exponential factor, E_a is the activation energy and k_B is the Boltzman constant. The activation energy, between the metal-insulator and ferroelectric-paraelectric phase transition of LSMO and BTO respectively was found from the best fit to be 0.092 eV of the composite system.
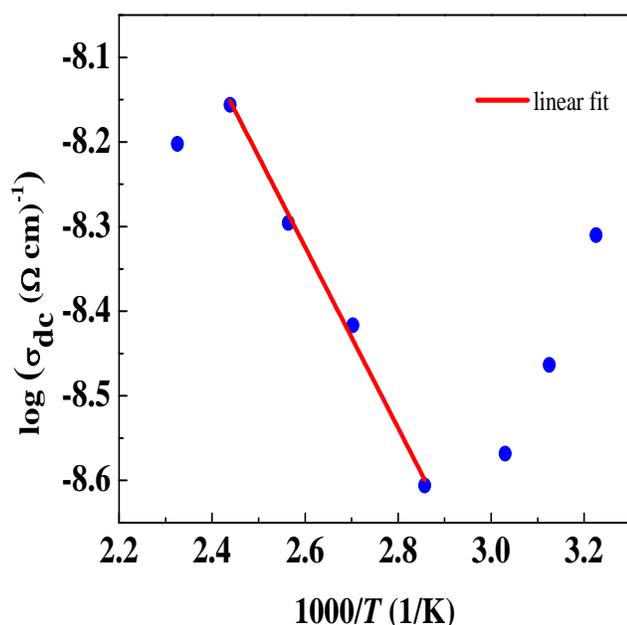

Fig. 4. Temperature dependent dc conductivity of the composite. The dots are experimental data and the solid line is the linear fit.

Conclusion

The electrical parameter Z′, Z″, ac/dc conductivity has been studied as a function of both frequency and temperature in BTO- LSMO nano-composites. Non-Debye relaxation was observed in the investigated system and an equivalent circuit has been constructed. The system shows positive temperature coefficient resistance below the metal-insulator transition temperature of LSMO and negative temperature coefficient resistance above that temperature. The conductivity has been found to decrease above 410 K attributed to the ferroelectric-paraelectric phase transition of BTO. The activation energy has been found to be 0.092 eV from the Arrhenius fitting between the metal-insulator

and ferroelectric-paraelectric phase transition of LSMO and BTO respectively.

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