

Preparation, structural analysis and dielectric properties of $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ perovskite

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Abstract. Rare earth element substituted bismuth ferrites (BiFeO_3) are of enormous importance as magnetoelectric materials. The polycrystalline samples of $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) were prepared by solid-state reaction using standard ceramic method. The single-phase formation of these compounds was confirmed by X-ray diffraction (XRD) studies. The samples with $x = 0, 0.2, 0.4, 0.6$ are found to be orthorhombic while the sample with $x = 0.8$ is triclinic. The dielectric constant (ϵ') and dissipation factor ($\tan \delta$) were measured in the frequency range 100 Hz to 1 MHz at room temperature and as a function of temperature at certain fixed frequencies (1 kHz, 10 kHz, 100 kHz, 1 MHz). All the samples showed dielectric dispersion. The dielectric constant with temperature shows a broad peak; the peak temperature shifts with frequency which reflects the relaxor-type behavior. The peak above 600 K in the measured temperature range corresponds to antiferromagnetic ordering temperature (Néel temperature). The broadness of the peak changes with composition. The ac conductivity as well as ϵ' are found to be maximum for the sample $x = 0.2$ at room temperature.

Keywords. Perovskite; X-ray diffraction; dielectric constant; ac conductivity.

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1. Introduction

In recent years the single-phase magnetoelectric materials have been the object of research due to their technological importance. A large number of single-phase magnetoelectric materials were synthesized by a group of workers at Moscow [1]. Among magnetoelectrics, BiFeO_3 is of particular interest in view of its potential as a good magnetoelectric material. Controversial reports on physical and structural properties of BiFeO_3 have been reviewed by Kubel and Schmid [2]. BiFeO_3 shows ferroelectricity with high Curie temperature of about 1043 K [3,4] and antiferromagnetic ordering below Néel temperature of about 647 K [3,4]. BiFeO_3 shows many anomalies in dielectric behavior with respect to temperature. Ismailzade [5] related these anomalies to a sequence of unknown phase transition leading to successive changes of electric ordering. This paper aims to study the structure and other physical properties such as dielectric properties of La-substituted BiFeO_3 compounds.

2. Experimental

Polycrystalline samples of $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ were prepared by standard solid-state reaction technique. Basic oxides La_2O_3 , Bi_2O_3 and Fe_2O_3 were mixed together in molar proportion and ground for 3 h. These mixtures were presintered at 800°C for 12 h followed by grinding for an hour. The fine homogeneous powders of these compounds were mixed with 2–3 drops of saturated solution of polyvinyl alcohol (PVA) (MW 124000) as a binder and pressed into pellets of diameter 10 mm and thickness 3–4 mm. Pressure of 5 tons was applied using a hydraulic press for 15 min. These pellets were finally sintered at 1000°C for 24 h in air and were later furnace-cooled. The X-ray diffraction (XRD) patterns of final samples were obtained using X-ray powder diffractometer (model PW 3710) with CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$). Two opposite surfaces of the samples in the form of pellet were polished by emery paper and coated with silver paint, for electrical characterization. The dielectric measurements were carried out by using LCR bridge model HP 4284A as a function of frequency in the range 100 Hz to 1 MHz and as a function of temperature at certain fixed frequencies (1 kHz, 10 kHz, 100 kHz, 1 MHz). At the same time, values of resistance were noted at different frequencies. From this, resistivity (ρ) of the samples was calculated at different frequencies. The dc resistivity measurements were carried out by two-probe method.

3. Results and discussion

3.1 Structural analysis

Figures 1a–1e show the XRD patterns of $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ ($x=0, 0.2, 0.4, 0.6, 0.8$) samples, respectively. The lattice parameters were determined by comparing the observed d values with JCPDS data [6]. It was found that the samples with $x=0, 0.2, 0.4, 0.6$ are orthorhombic and the sample with $x=0.8$ is triclinic. The lattice parameters are given in table 1. The lattice parameters are in good agreement with the literature [3,7].

Figure 2a shows the variation of dielectric constant (ϵ') with frequency at room temperature. The value of ϵ' is high at low frequencies and decreases rapidly as frequency increases. Similar behavior has been observed in many other dielectric materials. This is due to the fact that at lower frequencies, dipoles are able to follow the frequency of applied field; as frequency increases dipoles are not able follow the frequency of applied field. The

Table 1. Lattice parameters of $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$.

x	a (\AA)	b (\AA)	c (\AA)	α ($^\circ$)	β ($^\circ$)	γ ($^\circ$)
0	5.591	7.884	5.537	90	90	90
0.2	5.582	7.582	5.557	90	90	90
0.4	5.547	7.868	5.623	90	90	90
0.6	5.568	7.873	5.547	90	90	90
0.8	4.933	4.302	4.162	96.38	90.78	101.206

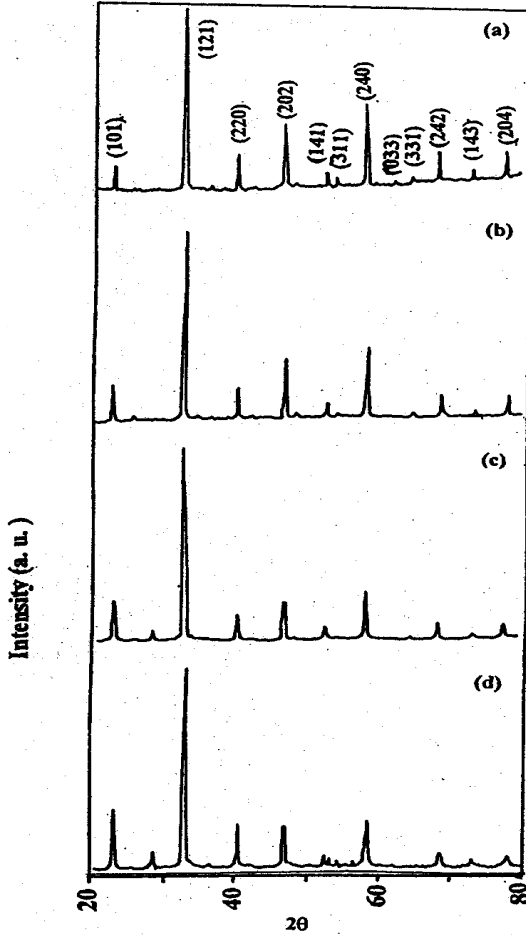


Figure 1. (a)–(e) X-ray diffraction patterns of $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ for $x = 0, 0.2, 0.4, 0.6$ and 0.8 respectively.

dielectric relaxation results in high value of dielectric constant at low frequencies and low value of dielectric constant at higher frequencies. ϵ' decreases rapidly in the range 100 Hz to 100 kHz and thereafter it remains almost constant. LaFeO_3 (i.e. $x = 0$) shows relatively lower value of ϵ' , while for $x = 0.2$ value of ϵ' is relatively higher. Value of ϵ' is found to be enhanced with increase in La concentration in $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ compounds. The enhancement of ϵ' in substituted samples is associated with the electronic structure of Bi^{+3} and A–B bond. The electronic configuration of Bi^{+3} tends to create a ‘cloud’ of electric dipoles polarization (a local ferroelectric phase) around itself due to the local displacement of surrounding ions. Also La substitution causes the weakening of the A–B sub-lattice interaction allowing less resistance to polarization and enhances dielectric constant.

Figure 2b shows the variation of dissipation factor ($\tan \delta$) with frequency for the samples under study. For $x = 0.2$ a peak is observed around 80 kHz frequency. This may be

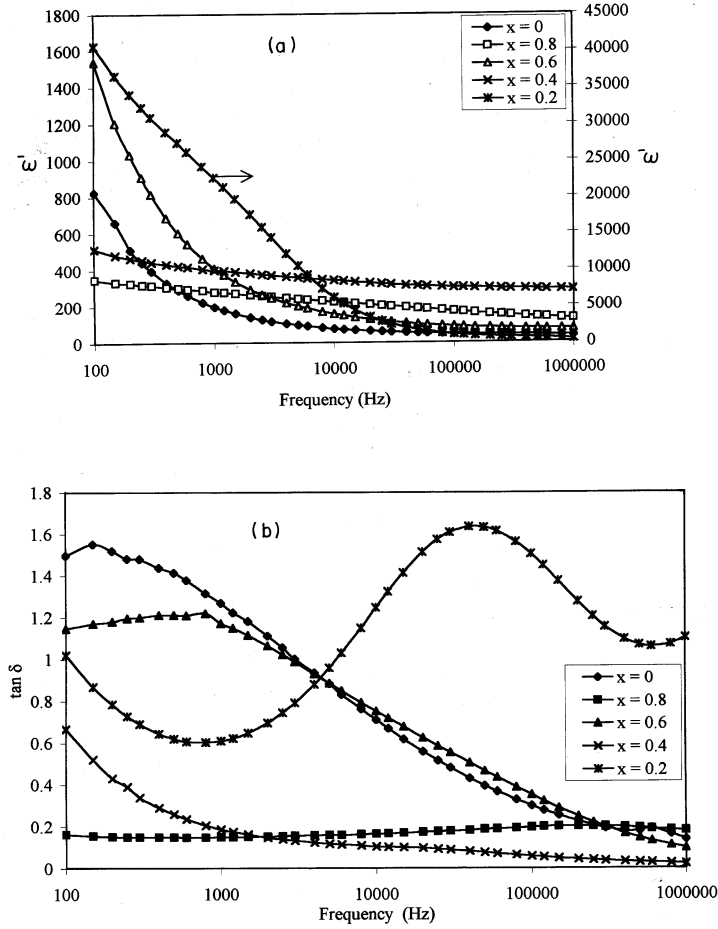


Figure 2. (a) Variation of ϵ' with frequency and (b) variation of dissipation factor ($\tan \delta$) with frequency for $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ for $x = 0, 0.2, 0.4, 0.6$ and 0.8 .

due to grain–grain boundary contribution. In all other samples $\tan \delta$ decreases with increase in frequency. This behavior is consistent with that of the dielectric constant of the corresponding sample.

3.2 Temperature dependence of ϵ' and $\tan \delta$

Figures 3a–3d show the variation of dielectric constant (ϵ') with temperature at certain fixed frequencies for $x = 0, 0.2, 0.6, 0.8$ respectively. These figures show anomalous behavior in the temperature range studied. For $x = 0$ sample, two peaks have been observed (figure 3a). One is around 350 K and the other is around 670 K. The sample with $x=0.2$ exhibits relatively high value even at higher temperature and large dependence on frequency

of ϵ' as observed at room temperature (figure 3b). The peak around 450 K at 1 kHz shows large shift in peak temperature for higher frequencies (10 kHz, 100 kHz, 1 MHz). This is a typical characteristic of relaxor ferroelectrics. For $x = 0.6$ sample a peak is observed at around 650 K for 1 kHz frequency (figure 3c). It shows shift in peak temperature with frequency. The peak at around 650 K for 1 kHz shifts to 615 K for 1 MHz. For $x = 0.8$ sample no anomalous dielectric behavior has been observed (figure 3d). For this sample dielectric constant goes on increasing with temperature. The peaks observed above 600 K in the samples are associated with the antiferromagnetic ordering temperature (Néel temperature) while other anomalies could be associated with unknown phase transition [5]. For sample $x = 0.2$ the value of measured capacitance was found to be negative above antiferromagnetic ordering temperature, and corresponding phase angle (θ) was found to be positive (figure 4), signifying that there is a dominant contribution of inductive component in the measurements. The diffused phase transition observed reflects the relaxor behavior. Broad

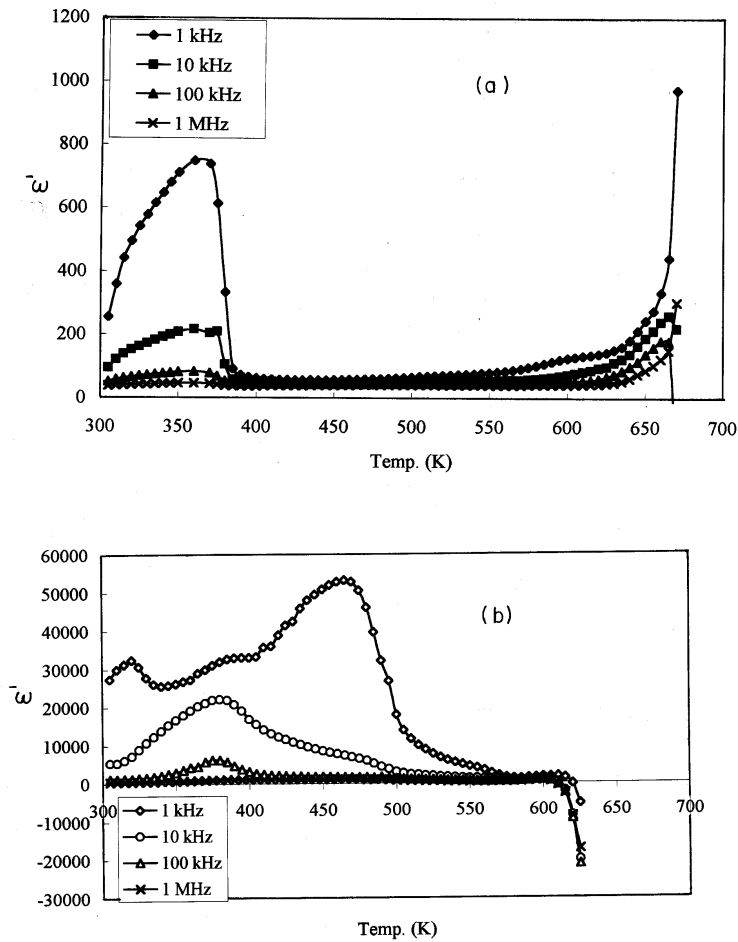


Figure 3a, b.

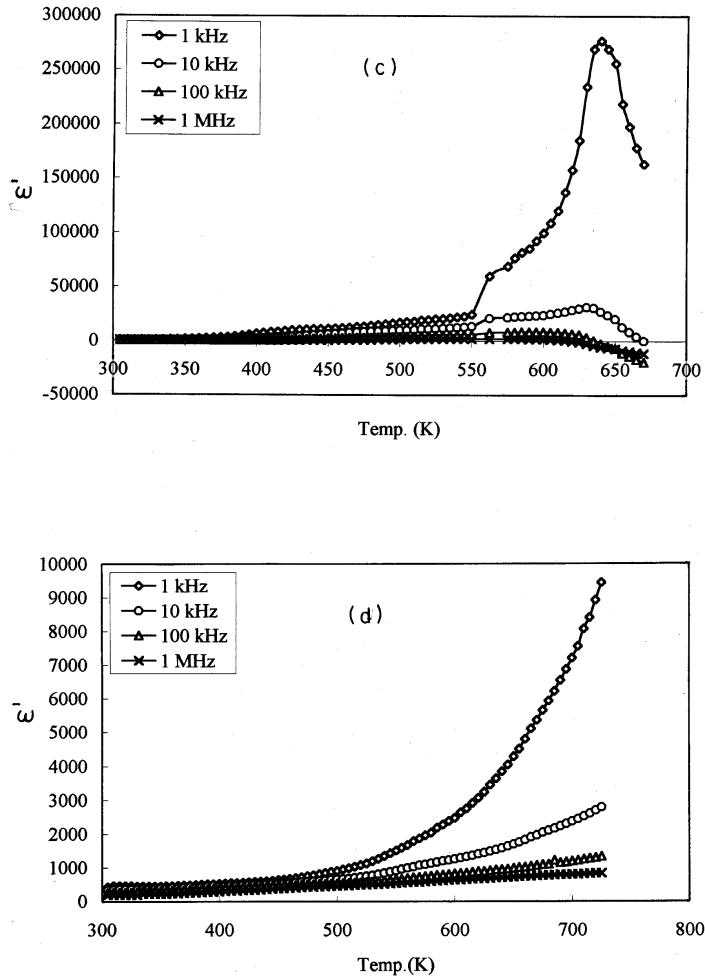


Figure 3. (a)–(d) Variation of ϵ' with temperature for $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ for $x = 0, 0.2, 0.6, 0.8$, respectively.

nature of the peak in ϵ' vs. temperature curves of the sample studied associated with Néel temperature need to be explained on the basis of slow variation of order parameter due to inhomogeneities on account of criss-crossing of magnetic and ferroelectric domains. This is further accentuated by localized nature of the polarizational changes in relaxor-type of ferroelectrics.

Figure 5 shows typical variation of dissipation factor ($\tan \delta$) with temperature for $x=0.6$. A peak behavior in $\tan \delta$ measurements has been observed at around 615 K for 1 MHz frequency, which is similar to ϵ' behavior of the same sample. All other samples show similar behavior.

Figures 6a and 6b show plots of $\log \rho$ vs. $1000/T$ for $x = 0.2$ and 0.8 at certain fixed frequencies along with dc resistivity. These plots suggest that the resistivity remains fairly

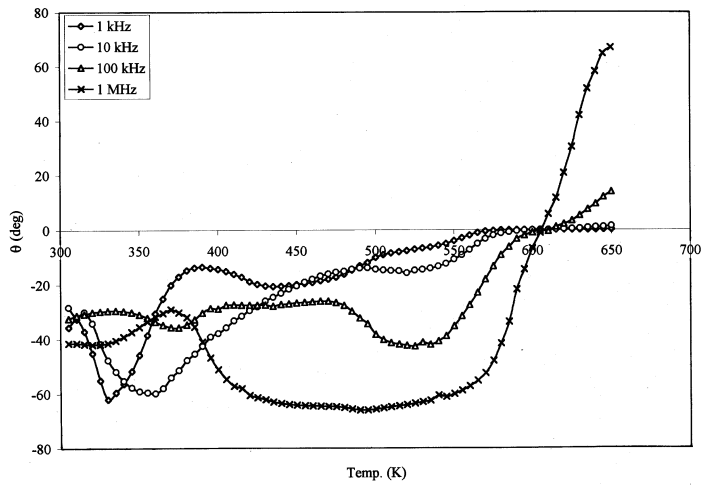


Figure 4. Variation of phase angle (θ) with temperature for $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ ($x = 0.2$) at various frequencies.

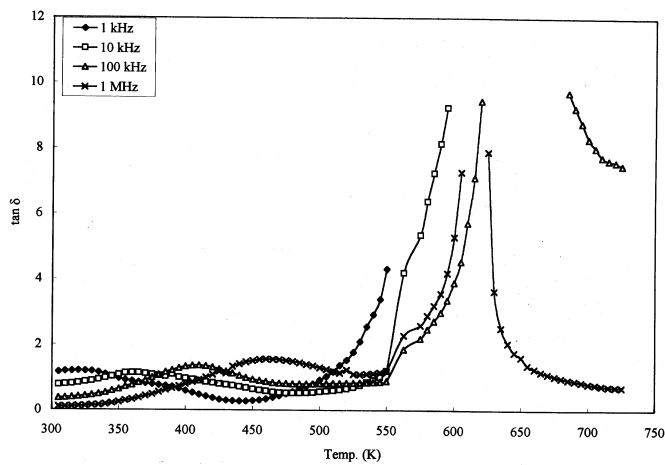


Figure 5. Variation of dissipation factor ($\tan \delta$) with temperature for $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ ($x = 0.6$) at various frequencies.

constant in low temperature region and after a particular temperature resistivity starts decreasing rapidly. The dc and ac resistivity values in low temperature region at 1 kHz, 10 kHz, 100 kHz and 1 MHz are found to be different. At high temperatures these curves coincide with each other. This is attributed to the fact that at low temperature the conduction is due to impurities and defect states while at higher temperature it is intrinsic.

In the band model one does not take into account the electronic correlation which is important for narrow bands. In the narrow bands the mobility of charge carriers is very small.

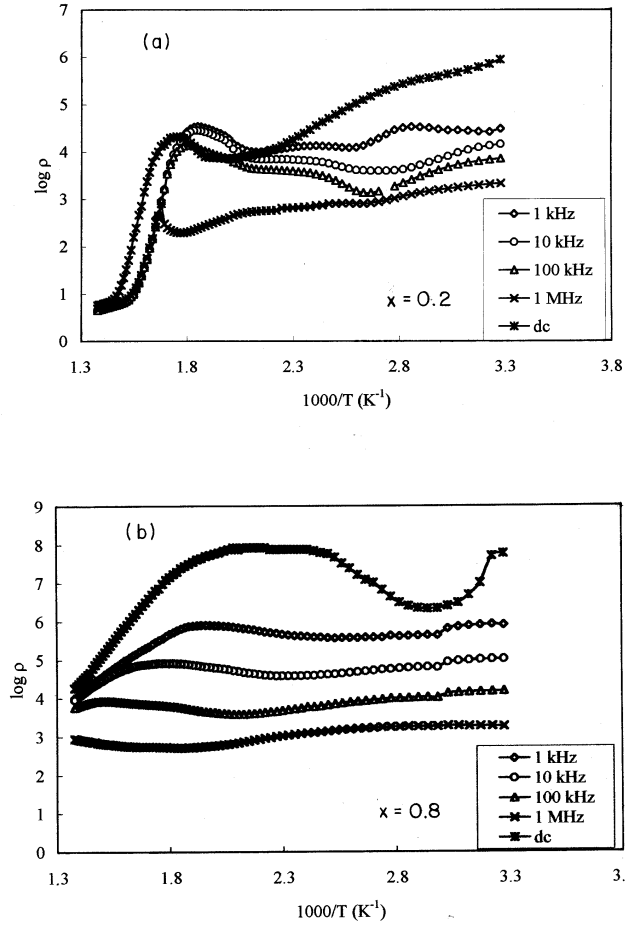


Figure 6. (a)–(b) Plot of $\log \rho$ vs. $1000/T$ for $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ for $x = 0.2$ and 0.8 , respectively.

As the charge particles are moving slowly the time during which they cross the influence of ion is large. Overall, this results in increase in the effective mass of charge carriers. If this fact is taken into account, the entity of charge carriers becomes quasiparticles called polarons, which are categorized as small polarons and large polarons. At low temperature, zero point energy of the lattice enables small polaron to move from one lattice point to another without thermal activation, carrying its polarization with it. The bound polarons are formed out of localized charge carriers at an impurity site in a narrow energy band. At high temperatures the electrical conduction in the hopping regime is independent of frequency but at low temperatures σ depends upon frequency according to the expression [8]

$$(\sigma_{ac} - \sigma_{dc}) = \omega^2 \tau / (1 + \omega^2 \tau^2). \tag{1}$$

In order to find the mechanism of conduction, we have calculated σ at different frequencies at room temperature from dielectric data. It is observed that the conductivity increases with

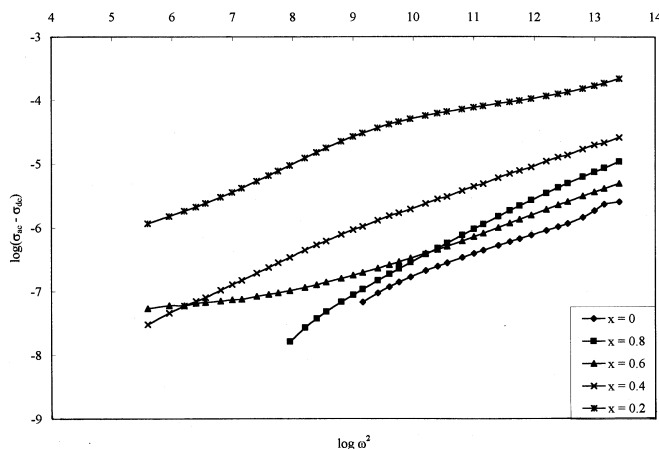


Figure 7. Plot of $\log(\sigma_{ac} - \sigma_{dc})$ vs. $\log \omega^2$ for $\text{Bi}_x\text{La}_{1-x}\text{FeO}_3$ for $x = 0, 0.8, 0.6, 0.4$ and 0.2 .

frequency. Therefore one can suspect hopping conduction by bound small polaron. As the value of τ is expected to be very small, $\omega^2\tau^2 \ll 1$ and so it can be neglected from the denominator of eq. (1). Hence, the plot of $\log(\sigma_{ac} - \sigma_{dc})$ vs. $\log \omega^2$ is expected to be a straight line. Figure 7 shows the plot of $\log(\sigma_{ac} - \sigma_{dc})$ vs. $\log \omega^2$ for $x = 0, 0.2, 0.4, 0.6$ and 0.8 . The curves are found to be nearly linear. This provides a positive confirmation for bound polaron hopping conduction.

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