

# Structural and dielectric properties of $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ ( $0.40 \leq x \leq 0.55$ )

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## Abstract

In order to study the effect of Sr substitution on structural and dielectric properties of  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $0.40 \leq x \leq 0.55$ ) compounds were synthesized by the solid state reaction method. The as-prepared samples were characterized by X-ray diffraction (XRD) and dielectric measurements to correlate structural changes with dielectric properties. The XRD data were further analyzed by the Rietveld refinement. The highest dielectric constant was observed in  $\text{Bi}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$  and  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  systems ( $\sim 10^6$ ) mainly because of orientation polarization. The charge ordering temperature decreases with increasing Sr concentration in  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  systems.

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**Keywords:** B. Rietveld refinement; B. X-ray diffraction (XRD); C. Ac and dc conductivity; C. Dielectric constant

## 1. Introduction

Electroceramics with high dielectric constant can be used for capacitors and memory devices depending upon the required frequency and temperature range. For capacitive and memory devices, in spite of magneto-electric effects, ceramics should have high dielectric constants. In literature, lots of reports have appeared to explain the origin of high dielectric constant in perovskite structured materials [1,2]. The most probable reason for high dielectric constant is its open structure and presence of non stoichiometry defects [3]. In addition to this, the oxygen vacancies also play a crucial role in relaxation and transport phenomenon. Out of these materials, Sr doped perovskites like ( $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ ) have attracted the attention of many researchers because of their high dielectric constant, Colossal magnetoresistance (CMR) and charge ordering phenomenon [4]. In these manganites, different oxidation states of Mn play very important role for high dielectric constants. The different oxidation states of Mn in  $\text{BiMnO}_3$  system depend on the chemical nature of dopants, site

occupancy and its magnitude. It has been observed that higher substitution of  $\text{Sr}^{2+}$  in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  system may lead to the charge ordering [5]. Similar behaviour has also been reported in  $\text{Bi}_4\text{V}_2\text{O}_{11}$  systems [6]. The most important problem associated with  $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$  is low charge ordering temperature which restricts their usage in electronic industry. On the other hand,  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  have shown the high charge ordering temperature ( $T_o \sim 525$  K) as compared to other rare-earth mixed valence manganites. High charge ordering temperature is related to the electronic structure of  $\text{Bi}^{3+}$  which have a highly polarisable  $6s^2$  lone pair [7]. This high  $T_o$  makes this system an interesting candidate for the dielectric studies.

The substituted and non-substituted bismuth based manganites systems have been investigated for their unique magnetic properties. However, very few reports have appeared in the literature related to their dielectric properties [8,9]. Most of these studies are related to  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  systems [10]. However, to the best of our knowledge nobody has reported the study by taking  $\text{Sr}^{2+}$  substituent in different concentrations in these systems. Therefore, we have selected  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x=0.40, 0.45, 0.50$  and  $0.55$ ) systems to understand their dielectric response, ion transport behaviour and relaxation behaviour systematically. The information regarding

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relaxation mechanism and conductivity has been derived from frequency dependent dielectric spectroscopy. Measurement of frequency dependent conductivity and permittivity not only provide information on steady state transport but also reflect at high frequency transient dielectric response resulting from localized displacement of ions [11].

## 2. Experimental details

The polycrystalline samples of  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x=0.40, 0.45, 0.50$  and  $0.55$ ) were prepared by conventional solid state reaction method. The stoichiometric compositions of high purity ( $>99.98\%$ )  $\text{Bi}_2\text{O}_3$ ,  $\text{MnCO}_3$  and  $\text{SrCO}_3$  powders were mixed thoroughly in an agate mortar pestle for 2 h in acetone media to obtain homogeneous powder. The resulting ground mixtures were dried and calcined in air at  $750^\circ\text{C}$  for 12 h. The calcined powders were again ground and palletized into circular discs of diameter 20 mm by applying 10 t of pressure. The as-prepared pellets were given double stage heat treatment. First, the pellets were sintered at  $1050^\circ\text{C}$  for 12 h. The sintered pellets were ground, compacted and resintered at  $1200^\circ\text{C}$ . This was done to ensure complete homogeneity and good sintered density. The as sintered samples were characterized using X-ray diffraction to identify the formed phases. X-ray powder diffraction study was performed at room temperature using PANalytical X'Pert PRO system with Ni-filter. The XRD data were refined by Rietveld refinement using Fullprof setup. During experiment the step size was  $0.013^\circ/\text{min}$ . Dielectric characterization was done by using automated LCR meter (Agilent 4284A precision LCR) in the frequency range of  $20\text{--}10^6$  Hz over temperature range of  $30\text{--}280^\circ\text{C}$ . For dielectric studies, the samples were polished, cleaned and sputtered by gold to ensure good electrical contact with electrode. The generated dielectric data was used to calculate the electric modulus, ac and dc conductivities of as prepared samples.

## 3. Results and discussion

### 3.1. X-ray diffraction

The density of the sintered samples was calculated using mass to volume ratio of the pellets. The relative density of all the samples is higher than 95% of the theoretical density. The XRD patterns of all the samples are shown in Fig. 1(a–d). The XRD data of these samples exhibit single phase with a tetragonal structure having space group  $P4mm$ . The XRD results are consistent with the earlier reported structure of  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  [12,13]. The XRD results are also refined by using Fullproof setup and the parameters are well fitted with  $\chi^2 \leq 2$ . All the refined parameters are tabulated in Table 1. As Sr dopant concentration increases, the lattice parameter along  $a$  and  $b$  direction (basal plane) decreases marginally from 3.91 to 3.89 Å. In contrast to  $a$  and  $b$  lattice parameters,  $c$  parameter decreases from 3.81 to 3.78 Å upto  $x=0.50$

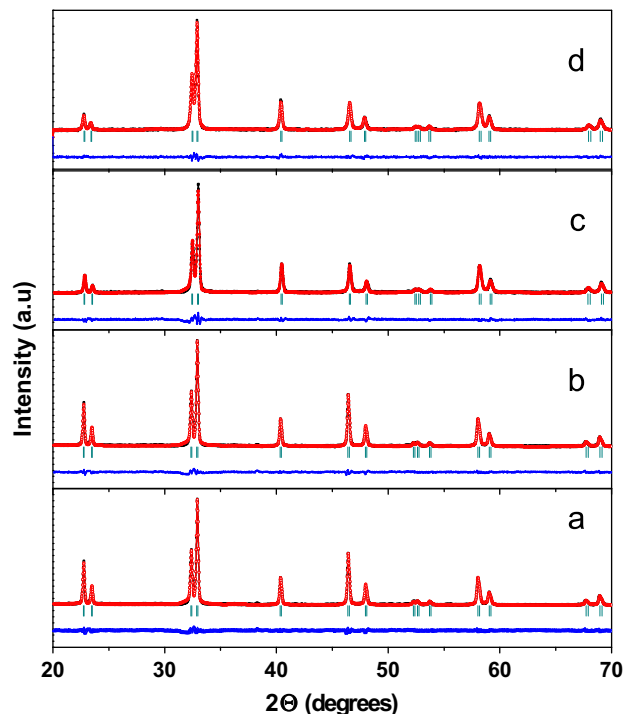


Fig. 1. XRD pattern of  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  (a)  $x=0.40$ , (b)  $x=0.45$ , (c)  $x=0.50$ , (d)  $x=0.55$ .

and after that increases for  $x=0.55$ . Overall, the unit cell volume decreases with the increase in concentration of  $\text{Sr}^{2+}$  as shown in Fig. 2. It is inconsistent with the reported lattice parameter for  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  system [12]. These changes in lattice parameter are unexpected since ionic radii of  $\text{Sr}^{2+}$  (1.18 Å) is greater than  $\text{Bi}^{3+}$  (1.03 Å) cation. Munoz et al. [8] have reported that bismuth  $6s^2$  lone pair can be the origin of this lattice distortion. With the increase of  $\text{Sr}^{2+}$  concentration,  $\text{Bi}^{3+}$  concentration decreases which weakens the local distortion due to the  $\text{Bi}^{3+}$  lone pair that may decrease  $a$  and  $b$  lattice parameters. Therefore,  $\text{Sr}^{2+}$  substitution not only affects the hole carrier density but also the strength due to local distortion in the unit cell. In addition to this, another possible reason for lattice parameter anomalies is the creation of oxygen vacancies as well as the change in oxidation state of  $\text{Mn}^{3+}$  (0.58 Å) to  $\text{Mn}^{4+}$  (0.53 Å) or higher than this to compensate the charge in the overall system. It is well reported in the literature that  $\text{Mn}^{3+}$  gets converted to the higher oxidation state above  $600^\circ\text{C}$  during processing [14].

### 3.2. Dielectric properties

The frequency response of dielectrics to sinusoidal electric fields can be expressed by their complex relative dielectric permittivity as follows:

$$\epsilon_r(w) = \epsilon'_r(w) - i\epsilon''_r(w) \quad (1)$$

where  $i = \sqrt{-1}$  and  $\epsilon_r = \epsilon/\epsilon_0$  ( $\epsilon_0$  is free space permittivity) and  $w$  is angular frequency;  $\epsilon'_r$  is the real component,

Table 1  
Refined structural parameters for  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ .

Composition	Wyckoff positions	Atom	<i>X</i>	<i>y</i>	<i>Z</i>	$\chi^2$
$\text{Bi}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$ ( <i>P4mm</i> ) $a=b=3.915076$ Å, $c=3.815839$ Å	1a	Bi/Sr	0	0	0	1.7
	1b	Mn	0.5	0.5	0.54436	
	1a	OI	0.5	0.5	0.154770	
	2b	OII	0.5	0	0.58350	
$\text{Bi}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ ( <i>P4mm</i> ) $a=b=3.910704$ Å, $c=3.790831$ Å	1a	Bi/Sr	0	0	0	1.6
	1b	Mn	0.5	0.5	0.45509	
	1a	OI	0.5	0.5	0.10435	
	2b	OII	0.5	0	0.54371	
$\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ( <i>P4mm</i> ) $a=b=3.901714$ Å, $c=3.786850$ Å	1a	Bi/Sr	0	0	0	1.8
	1b	Mn	0.5	0.5	0.50378	
	1a	OI	0.5	0.5	0.16705	
	2b	OII	0.5	0	0.60180	
$\text{Bi}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$ ( <i>P4mm</i> ) $a=b=3.895225$ Å, $c=3.792847$ Å	1a	Bi/Sr	0	0	0	1.4
	1b	Mn	0.5	0.5	0.49930	
	1a	OI	0.5	0.5	0.044247	
	2b	OII	0.5	0	0.60753	

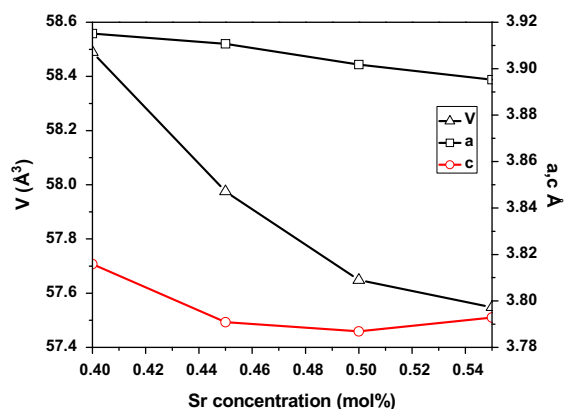


Fig. 2. Variation of lattice constant with respect to Sr concentration.

which is in phase with the applied field and  $\epsilon_r''$  is the imaginary component which is in quadrature with the applied field.

### 3.2.1. Real part of the dielectric constant

The variation of real part of dielectric constant ( $\epsilon_r'$ ) of different samples with respect to frequency at different temperatures are shown in Fig. 3. The dielectric response of these samples does not show any peak related to the losses which clearly indicates that the polarization in this system is dominated by the hopping mechanism [10]. All the dielectric plots can be divided into three parts: lower frequency region ( $< 100$  Hz), intermediate frequency region ( $10^3$ – $10^5$  Hz) and high frequency region, i.e., above  $10^6$  Hz. All the samples show high dielectric constant in lower region. After this, the dielectric constant decreases slightly and becomes constant. In the third part dielectric constant again decreases. The decrement in dielectric constant at high frequency is in steps. The same behaviour is observed in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  systems by other researchers [15,16]. These different steps may arise

due to the electrode, grains and grain boundary contributions. The dielectric behaviour of these samples at low frequencies can be explained on the basis of extrinsic interfacial Maxwell–Wagner model [17]. According to this model the dispersion of  $\epsilon_r'$  at low frequencies is due to interfacial polarization and existence of depletion layers near the sample-electrode contacts. Second, the electrical charge unbalance caused by the divalent  $\text{Sr}^{2+}$  ion substitution for the trivalent  $\text{Bi}^{3+}$  ions is compensated by the creation of the oxygen vacancies as well as transition of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  at the octahedral sites. It could be suggested that due to the ionization of oxygen vacancies, hopping of electrons may contribute to the dielectric relaxation process in these samples. The samples show high values of dielectric constant for frequencies lower than  $10^3$  Hz. This is a clear indication that within a single material two types of dispersion mechanisms are present, one of which dominates at higher frequencies. This behaviour resembles the Debye relaxation and in this region  $\epsilon_r'$  varies as  $(\omega^{m-1})$  [17].  $\text{Bi}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$  shows very small dielectric constant as compared to the other samples. In this particular sample, Sr content is low as compared to other samples, so it may be the reason that low Sr concentration created smaller number of oxygen vacancies as well as low conversion of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  which may lead to less distortion in the lattice as compared to higher  $\text{Sr}^{2+}$  substituted samples. Consequently, it has smaller dielectric constant as compared to  $x=0.45$  and  $x=0.50$  samples. Second, it is possible that higher ordering of oxygen vacancies in these samples is taking place. This type of phenomenon is very common in doped ceramic samples and well reported in literature [6]. Additionally, the low content of oxygen vacancies in  $x=0.40$  sample may be responsible for the low concentration of hopping charge carriers.  $\text{Bi}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$  and  $\text{Bi}_{0.50}\text{Sr}_{0.50}\text{MnO}_3$  show higher values of dielectric constant which is due to creation of higher number of oxygen vacancies as well as

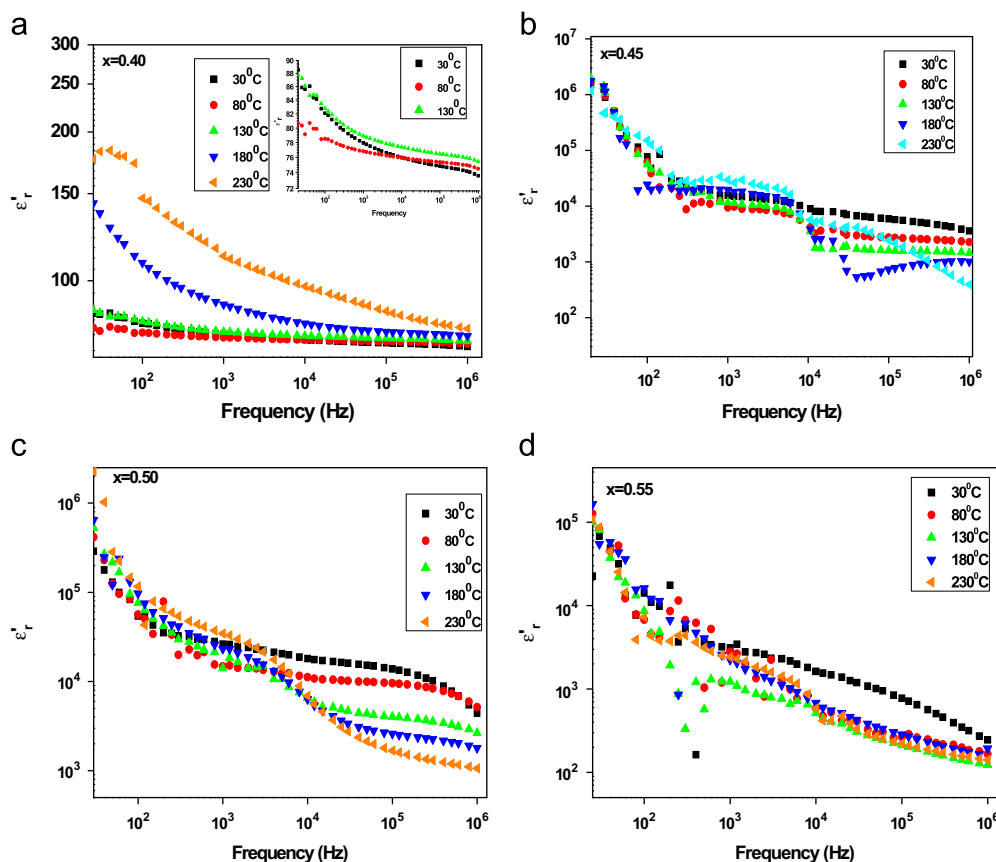


Fig. 3. Variation of  $\epsilon'_r$  with respect to frequency at different temperatures for  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  (a)  $x=0.40$  (b)  $x=0.45$  (c)  $x=0.50$  and (d)  $x=0.55$ .

high conversion of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  in these samples as compared to other samples. Furthermore,  $\text{Bi}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$  again show a decrease in dielectric constant that may be due to the ordering in crystal lattice above  $x=0.50$ . The dielectric constant is not much dependent on the temperature at low frequencies ( $< 10^3$  Hz) except  $x=0.40$ . But at high frequencies ( $10^3$ – $10^6$  Hz), as the temperature increases the dielectric constant decreases. Basically, in the present samples the temperature plays two-fold effect, if orientation polarization is dominated in the system then the temperature randomize it and tend to decrease the dielectric constant. Consequently, the overall dielectric constant is going to decrease in the system. On the other hand, if polarization is predominantly governed by the space polarization then dielectric constant of the system is going to increase with increasing temperature because the rate of interfacial charge accumulation increases. Conclusively, the present samples exhibit the orientational polarization predominantly [18]. Moreover, at low frequencies, the dielectric is mainly because of the movement of free charges which increases with the rise in temperature and further increases the value of dielectric constant. But at the high frequencies and high temperature, dispersion losses increase due to the thermal vibrations and less time is available for the materials to respond for the applied electric field. Variation of real part of dielectric constant  $\epsilon'_r$  with respect to temperature is also shown in Fig. 4 at

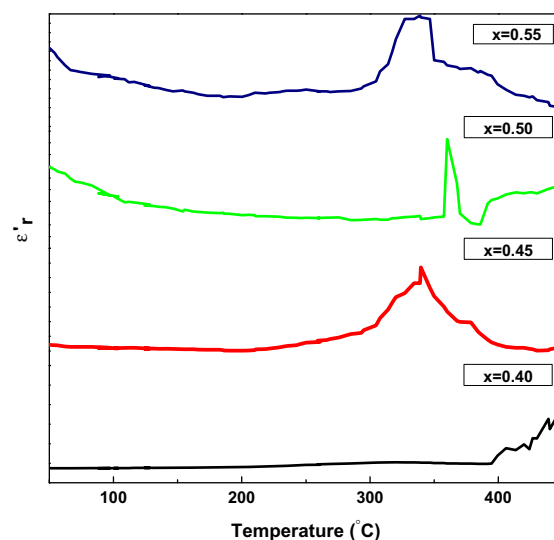


Fig. 4. Variation of  $\epsilon'_r$  with temperature for  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ .

10 kHz. The curves show maxima in the range of 280–350 °C. As the frequency increases, maxima shift to higher values of temperature. This temperature range corresponds to the charge ordering temperature of these compounds [12,13]. This charge ordering can be described as  $\text{Mn}^{3+}/\text{Mn}^{4+}$  separation/ ordering in the ionic systems.  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  has a high charge ordering temperature as

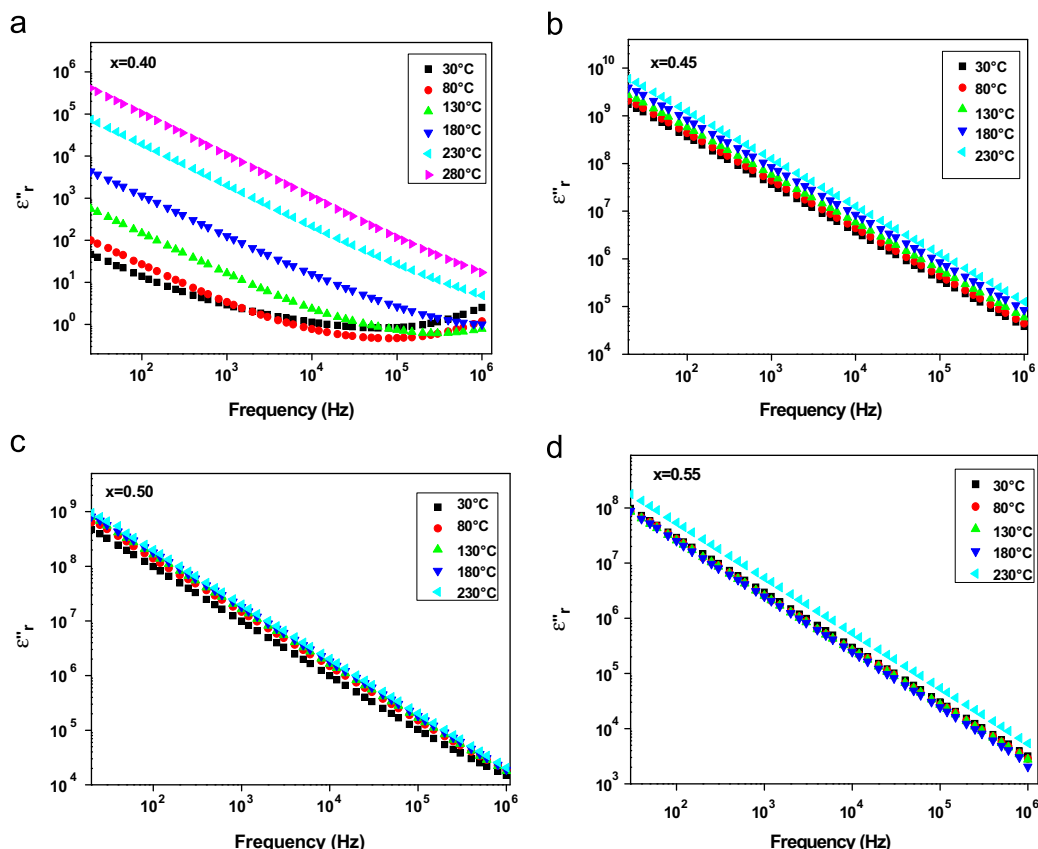


Fig. 5. Variation of  $\epsilon''$  with frequency in  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  (a)  $x=0.40$  (b)  $x=0.45$  (c)  $x=0.50$  and (d)  $x=0.55$ .

compared to other manganites [9]. This high  $T_o$  can be attributed to the electronic structure of  $\text{Bi}^{3+}$ , which has  $6s^2$  lone pairs in its outermost shell and these electrons have strong p-character in these compounds. This lone pair hybridizes with oxygen p-orbitals lowering the mobility of Mn electrons and favours the charge ordering and charge localization. Thus  $T_o$  decreases with increasing content of dopant [8].

### 3.2.2. Imaginary part of dielectric constant

The frequency dependence of imaginary part of dielectric constant ( $\epsilon''$ ) of all the compounds are shown in Fig. 5. It can be seen that in all the samples  $\epsilon''$  shows higher values except for  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x=0.40$ ) that increases as temperature increases and decreases as frequency increases. As a result, these samples exhibit high losses as can be observed from the variation of  $\tan \delta$  versus frequency at different temperatures. In  $x=0.40$ ,  $\epsilon''$  shows minima in the frequency range  $10^4$ – $10^5$  Hz which shifts to higher frequencies as temperature increases. In the case of other samples,  $\epsilon''$  vary from  $10^{10}$  to  $10^4$  in the frequency range of  $20$ – $10^6$  Hz. In the low frequency region, all the samples show higher values of losses and  $\epsilon''(w) > \epsilon'(w)$ . This part of dielectric losses follows  $w^{-1}$  dependence according to the electrodynamics relation  $\epsilon''(w) = \sigma_{dc}/\epsilon_0 w$  [19]. Thus, in this frequency region dc conductivity might dominate. With increasing temperature, conductivity

increases in ionic solids which further increases the losses as can be seen from  $\epsilon''$  versus frequency curve in Fig. 5. For  $x=0.45$ ,  $0.50$  and  $0.55$  the  $\epsilon''$  curves are straight line for complete test frequency range and varies as  $w^{-1}$  which clearly indicates that the conductivity losses for all the samples dominate due to dc conductivity.

### 3.2.3. Dielectric losses

The variation of  $\tan \delta$  with frequency at different temperatures is shown in Fig. 6.  $\tan \delta$  varies in the range of  $10^4$  to  $10^{-2}$  for all the samples in the frequency range of  $20$ – $10^6$  Hz. At lower frequencies ( $< 10^2$  Hz)  $\tan \delta$  have high values. In the case of  $x=0.40$ , as the frequency increases the values of  $\tan \delta$  decreases in the frequency range  $10^2$ – $10^5$  Hz, after that it becomes almost constant in the higher frequency range  $> 10^5$  Hz. The decrease in  $\tan \delta$  corresponds to plateau like behaviour as observed in  $\epsilon''$  versus frequency curve. As the temperature increases the  $\tan \delta$  values also increases.  $\tan \delta$  show a minima in the frequency range  $10^5$ – $10^6$  Hz and minima shifts to higher frequencies with increase in temperature. All these losses are due to the conductivity losses as explained in previous section. In  $x=0.45$ ,  $0.50$  and  $0.55$   $\tan \delta$  curves show two shallow peaks; one at very low frequencies ( $< 100$  Hz) and another at high frequency ( $< 1000$  Hz). The low frequency peak originates due to the interfacial polarization. On the



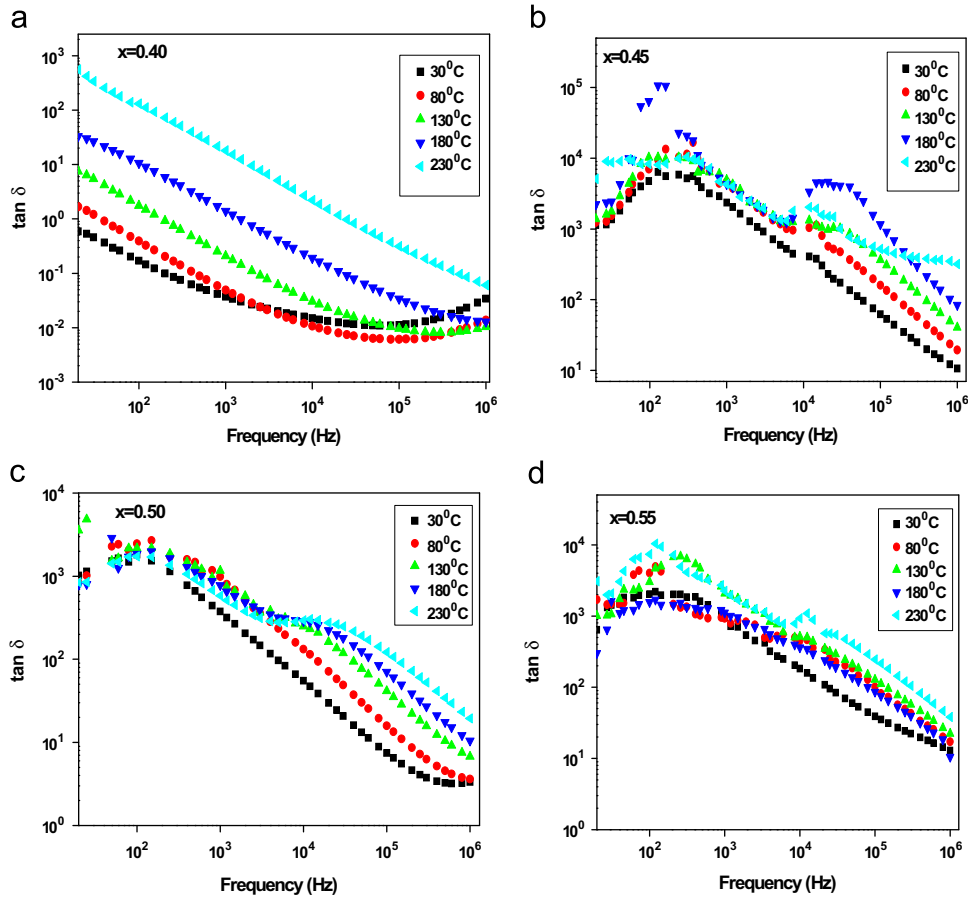


Fig. 6. Variation of  $\tan \delta$  with frequency in  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ : (a)  $x=0.40$ , (b)  $x=0.45$ , (c)  $x=0.50$  and (d)  $x=0.55$ .

other hand, second peak is related to the dc conductivity losses at high frequencies.

### 3.3. Electric modulus

The electric modulus  $M^*(w)$  can be expressed as:

$$M^* = \frac{1}{\epsilon^*} = M'(w) + iM''(w) = M_\infty \left[ 1 - \int_0^\infty e^{-i\omega\tau} \frac{d\phi(t)}{dt} dt \right] \quad (2)$$

where the function  $\phi(t)$  gives the time variation of electric field within dielectric. Real part  $M'(w)$  and imaginary parts  $M''(w)$  of the electric modulus are related to dielectric constant as follows:

$$M'(w) = \frac{\epsilon'(w)}{\epsilon'(w)^2 + \epsilon''(w)^2} \quad \text{and} \quad M''(w) = \frac{\epsilon''(w)}{\epsilon'(w)^2 + \epsilon''(w)^2} \quad (3)$$

As discussed in the results of  $\epsilon'_r$  and  $\epsilon''_r$  with respect to frequency in Figs. 3 and 5, it clearly indicates that  $\epsilon'_r$  and  $\epsilon''_r$  increases with increase in temperature at low frequency region, which may be related to the conduction process in these samples. In order to discuss this phenomenon in detail, the values of dielectric constant is converted into imaginary parts of electric modulus by using Eq. (3) and the as obtained values are given in Fig. 7 for all the samples. From Fig. 7, it is clear that  $M''$  values are very small at lower frequencies indicating the removal of electrode polarization [20]. The values of  $M''$  show decreasing trend with increasing temperature. This may

be due to the increase in the mobility of charge carriers and orientation of the molecular dipoles with the temperature which further increases the conductivity and decreases the electric modulus values. The peak values of  $M''$  depend only on the temperature, which implies that capacitances of grains and grain boundaries depend weakly upon temperature. At higher frequencies sharp peaks are observed for  $x=0.40$  and these peaks shift to higher frequency side with increasing temperature. The low frequency side of the peak represents the range of frequencies in which charge carriers can move over long distances. The high frequency side of the peak represents the range of frequencies in which the charge carriers are spatially confined to their potential wells and thus could make localized motion within the potential well. The frequency region where peak is observed represents the transition from long range to the short range mobility of the carriers. The broadening of the peaks with rise in temperature indicates the increase in non-Debye behaviour [21]. For other samples  $x=0.45, 0.50, 0.55$  the  $M''$  shows very low values up to  $>10^5$  Hz frequency range. This may be due to the high conductivity values of these samples as compared to  $x=0.40$  sample. The frequency ( $f_{\text{max}}$ ) corresponding to maxima of each peak is known as relaxation frequency and gives the most probable conductivity relaxation time for ions. The variation  $\tau$  versus temperature is shown in Fig. 6a. The curve satisfies the Arrhenius behaviour with activation energy 0.59 eV. The rise in

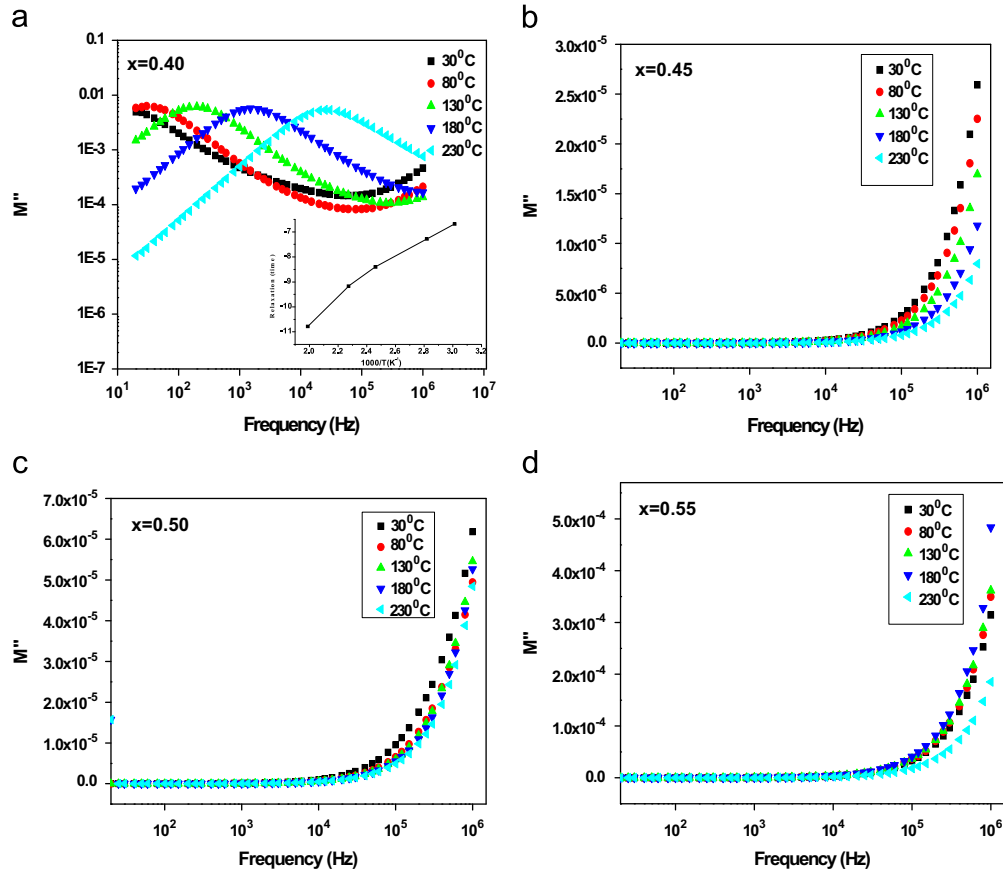


Fig. 7. Variation of electric modulus ( $M''$ ) with frequency in  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ : (a)  $x=0.40$ , (b)  $x=0.45$ , (c)  $x=0.50$  and (d)  $x=0.55$ .

temperature causes a drop in relaxation time due to the increased mobility of ionic carriers.

### 3.4. Electrical conductivity analysis

#### 3.4.1. Frequency dependent conductivity

The ac conductivity has been calculated from real part of dielectric constant and dielectric loss by using the relation

$$\sigma(\omega) = \epsilon_0 \omega \epsilon'' = \epsilon_0 \omega \epsilon' \tan \delta \quad (4)$$

The frequency dependence of ac conductivity ( $\sigma_{ac}$ ) is shown in Fig. 8. The ac conductivity was found to be frequency independent in the low frequency region suggesting that the ionic diffusion is random. As frequency exceeds from hopping frequency, the conductivity increases and follow the universal power law  $\sigma(\omega) \propto \omega^s$  for  $x=0.40$  and  $x=0.50$  [10]. On the other side  $x=0.45$  and  $x=0.55$  samples do not show any variation in conductivity with respect to frequency at different temperatures. With increase in temperature these plateau shifts to high frequency region for  $x=0.40$  and  $x=0.50$  samples. The ac conductivity behaviour is analysed by using the universal power law [10]:

$$\sigma_{ac} = \sigma_{dc} + A\omega^s \quad (5)$$

here  $A = \frac{\sigma_{dc}}{w_h^s}$  where  $A$  is constant for particular temperature,  $\sigma_{dc}$  is dc conductivity and the exponent  $s$  is related to the degree of

correlation among moving ions. In general, the value of  $s$  varies between 0.6 and 1 for ionic conductors. Ac conductivity spectra for different temperatures were fitted using Eq. (5) and the parameters  $s$ ,  $A$  and  $\sigma_{dc}$  were calculated. The as-obtained values of  $s$  and  $A$  have been used to calculate  $w_h$ .  $w_h$  is hopping frequency which is defined as the crossover frequency from dc to the dispersive region of ac conductivity.

For  $x=0.40$ , at low and high frequency region, Eq. (5) gives different results up to 180 °C. For lower frequencies,  $s$  varies between 0.81 and 0.45 in the temperature range of 30–230 °C. This power law frequency dependence indicates that the ac conductivity in the low temperature region corresponds to short range hopping of localized charge carriers through trap sites separated by potential barriers and thus it is hopping type conduction. At higher frequencies, the value of  $s$  varies between 1.75 and 1 in the temperature range of 30–180 °C. In this frequency range  $s > 1$  and the system follows the super linear power law (SLPL) which may account for the resonance like effect between the external electrodes and the sample [22]. Similarly, an abrupt increase is also observed in  $\epsilon''$  versus frequency curve for  $x=0.40$ . For  $x=0.50$ , value of  $s$  varies between 0.5 and 0.9 in the temperature range of 30–280 °C which is again well fitted with the universal power law.

#### 3.4.2. Temperature-dependent conductivity

The variation of  $\sigma_{dc}$  and  $w_h$  versus temperature are shown in Figs. 9 and 10 for all the samples. The conductivity pattern

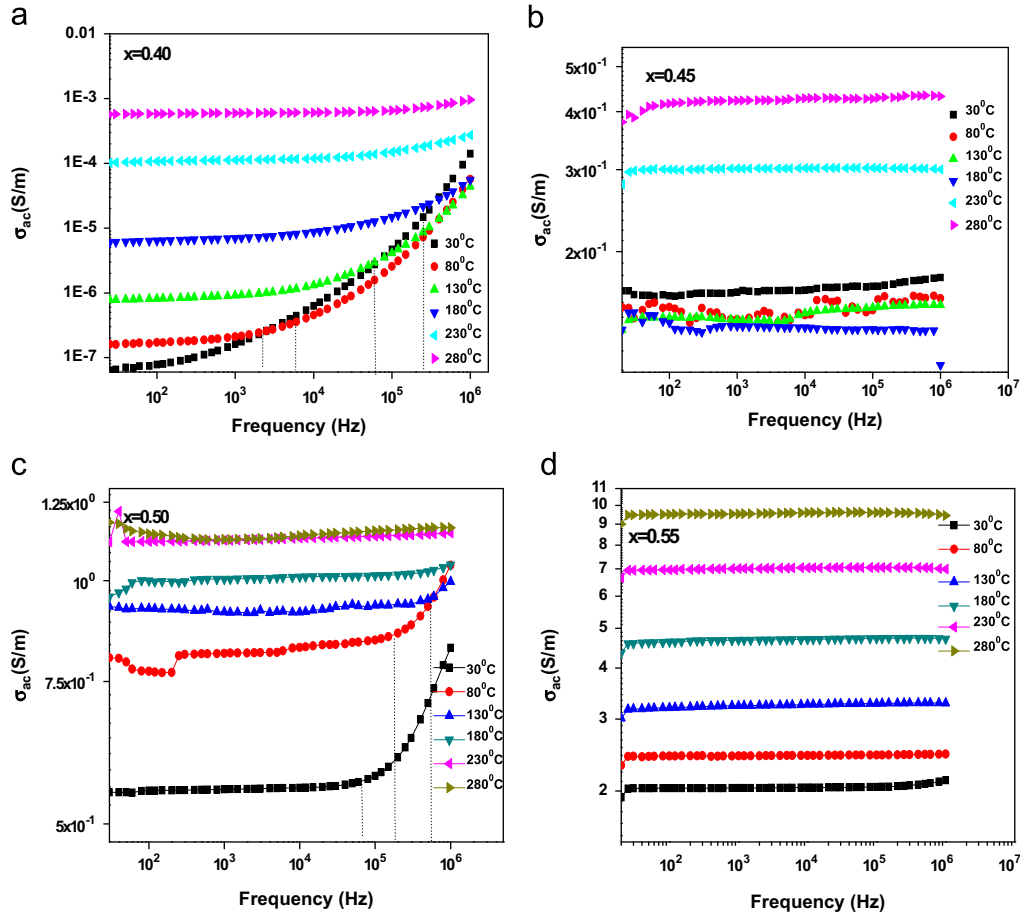


Fig. 8. Variation of conductivity ( $\sigma$ ) with frequency in  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ : (a)  $x=0.40$ , (b)  $x=0.45$ , (c)  $x=0.50$  and (d)  $x=0.55$ .

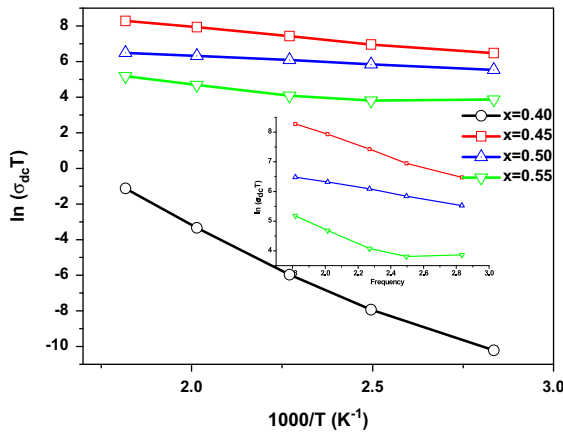


Fig. 9. Arrhenius plot of dc conductivity ( $\sigma_{dc}$ ).

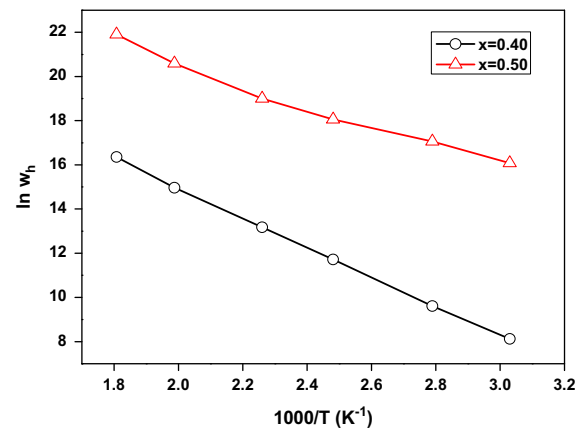


Fig. 10. Arrhenius plot of hopping frequency ( $w_h$ ).

shows an increase in conductivity with temperature. Temperature dependence of conductivity clearly indicates that conduction is a thermally activated process in all the samples. These spectra are fitted with the Arrhenius equation as follows:

$$\sigma_{dc}T = \sigma_0 \exp\left(\frac{-E_\sigma}{kT}\right) \quad (6)$$

$$w_h = w_0 \exp\left(\frac{-E_h}{kT}\right) \quad (7)$$

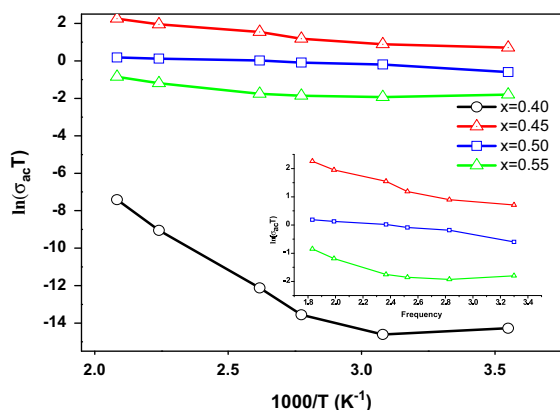
where  $\sigma_0$  is the dc conductivity pre-exponential factor,  $k$  is the Boltzman's constant,  $E_\sigma$  is dc conduction activation energy for mobile ions,  $w_0$  is pre-exponential factor for hopping frequency,  $E_h$  is activation energy for hopping frequency. The activation energies calculated from Eqs. (6) and (7) are shown in Table 2. Based on these results, it can



Table 2

Activation energies of dc, ac and hopping frequency.

Sample composition $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$	$E_{a(\text{dc})}$ (eV)	$E_{a(\text{ac})}$ (eV)	$E_{a(W_h)}$ (eV)
$x=0.40$	0.68	0.62	0.57
$x=0.45$	0.14	0.11	–
$x=0.50$	0.06	0.07	0.40
$x=0.55$	0.08	0.096	–

Fig. 11. Arrhenius plot of ac conductivity ( $\sigma_{ac}$ ) for  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ .

be concluded that the jumps of localized charge carriers from one trap site to another are a thermal driven and random process in these samples.

Ac conductivity versus temperature spectra are shown in Fig. 11. These spectra are also fitted with the Arrhenius equation  $\sigma_{ac} T = \sigma_{0ac} \exp(-E_{\sigma ac}/kT)$  and activation energies calculated for all the samples are tabulated in Table 2. The same values of  $E_{dc}$  and  $E_{ac}$  for all samples may imply the similar origin corresponding to dc and ac conductivity; means similar localized charge carriers are involved in both the conduction phenomenon. Small values of activation energies also indicate that there is mainly electronic conduction in the samples [23]. Even for  $x=0.40$ ,  $E_h$  is also very close to the values of ac and dc activation energies which also confirms the similar origin of ac and dc conductivities in the present sample.

#### 4. Conclusion

The Rietveld refinement confirms the tetragonal crystal symmetry in the present samples. The unit cell volume decreases with the increasing concentration of  $\text{Sr}^{2+}$  in the system. Dielectric constant of all the present samples is in the range of  $10^6$  with high dielectric losses except for  $\text{Bi}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ . The dc conduction in these samples is mainly responsible for these losses. The charge ordering temperature is observed in the range of 280–300 °C. The activation energies and Arrhenius plot behaviour suggest the predominant ionic conduction in  $x=0.40$  sample.

Contrary to this,  $x=0.45$ , 0.50 and 0.55 samples exhibit very low activation energies  $\leq 0.14$  eV.

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