Ac conductivity, dielectric losses, permittivity behavior of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0$, 0.5 and 1) ceramics

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Abstract In this paper, we have investigated ac conductivity, dielectric losses, permittivity of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0$, 0.5, 1) ceramics. It has been observed that increase in barium content decreases activation energy (i.e. conductivity increases) in the higher temperature region (550–770 K). In the lower temperature region system with $x = 0$ shows metallic conductor behavior and system with $x = 1$ shows thermally activated behavior. The ferroelectric peak temperatures are observed at 700, 750 and 723 K for $x = 0$, 0.5 and 1, respectively. This peak temperature can be attributed to the oxygen-vacancy-related dielectric relaxation. With the increase of barium content the dielectric dispersion tend to diminishes. Partial substitution of strontium with barium (for $x = 0.5$) reduces dielectric losses by 50%.

Introduction

Mixed-conducting oxides have a wide range of attractive applications as catalytic materials, electrodes in solid-oxide fuel cells (SOFC), oxygen permeable membranes and oxygen sensors [1]. However detailed knowledge and the understanding of their dielectric and transport properties are very limited. In general, the nature of a perovskite-type (ABO_3) compound is determined by its B-site ions. As for example B-site ions of mixed valence give rise to high-conductivity electrode materials whereas of fixed valence usually produce insulators [2]. According to Teraoka et al. [3–5] cobalt-based perovskite-type oxides acts as a membrane allowing oxygen permeation at elevated temperature without any electrode and an external electric circuit . The properties of the perovskite-type oxides are also sensitive to the oxygen deficiency and type of A-site occupancy [2]. This is because of the charge compensation mechanism in the compounds. Let us consider of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$, when B-ions take a mixed-valance state, charge neutrality is maintained by the formation of oxygen vacancies and a change in the valance state of the B-ions. These oxides may show a high electronic conductivity due to the mixed-valance state and high oxide ion conductivity due to the presence of oxygen vacancies. When the valance state of B-ions is fixed, neutrality is maintained only by the formation of oxygen vacancies. The oxides may be predominantly ionic conductors. This paper aims at reporting for the first time the dielectric nature and ac conductivity of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0$, 0.5, 1) ceramic system. These compositions have potential application as (i) ceramic electrodes in solid oxide fuel cells (SOFC) with reduce polarization losses at the interface and (ii) oxygen separation membranes at elevated temperatures [6, 7].

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Experimental

Sample preparation

The three series of perovskite-type oxides $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0$, 0.5, 1) were prepared by combined-citrate complexing method [8]. The primary powders obtained were calcined in air at 1173 K for 5 h. The powder samples were compressed into discs (size 10 mm diameter and 1.8 mm thickness) under the hydrostatic pressure of 2×10^5 KN/m^2. For ac conductivity measurements and dielectric parameters, discs were sintered at 773 K in air for 5 h and then polished with a fine emery paper to remove surface contaminants.

Measurements with ac impedance spectroscopy

The transport properties of sintered pellets were examined by ac impedance spectroscopy over a frequency range of 100 kHz–1 MHz using an impedance analyzer model HP 4194A. The amplitude of the voltage has been set at 1 V. The data collected includes ac conductivity, dielectric losses, relative permittivity over a temperature range of 300–723 K.

The relative permittivity was calculated using the relation $\varepsilon' = \frac{cd}{\varepsilon_0 A}$, where c = capacitance, d = thickness of pellet (disk), A = area of the surface of the pellet and ε_0 permittivity of free space (=8.85×10^{-12} F/m).

Results and discussion

ac Conductivity

The ac conductivity versus inverse temperature plots of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ compounds with $x = 0$, 0.5, 1 are shown in Fig. 1. These clearly reveal existence of a thermally activated process in the temperature range of 550–730 K and slight decrease of activation energy with the increase of barium content (x). The ac conductivity increases with increasing temperature in the region of high temperatures. It is well described by the Arrhenius relation $\sigma = \sigma_0 \exp(-E_a/K_BT)$, where σ_0 is the pre-exponential factor, E_a is the activation energy, K_B is the Boltzmann constant and T is the absolute temperature. Activation energies (E_a) for $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0, 0.5$ and 1) obtained from Fig. 1 are listed in Table 1. The activation energy, E_a in such system usually consists of two terms—the enthalpy of migration of oxygen ions ΔH_m and the association enthalpy, ΔH_a, resulting from the formation of complex defects [10, 11]. Since value of ΔH_m
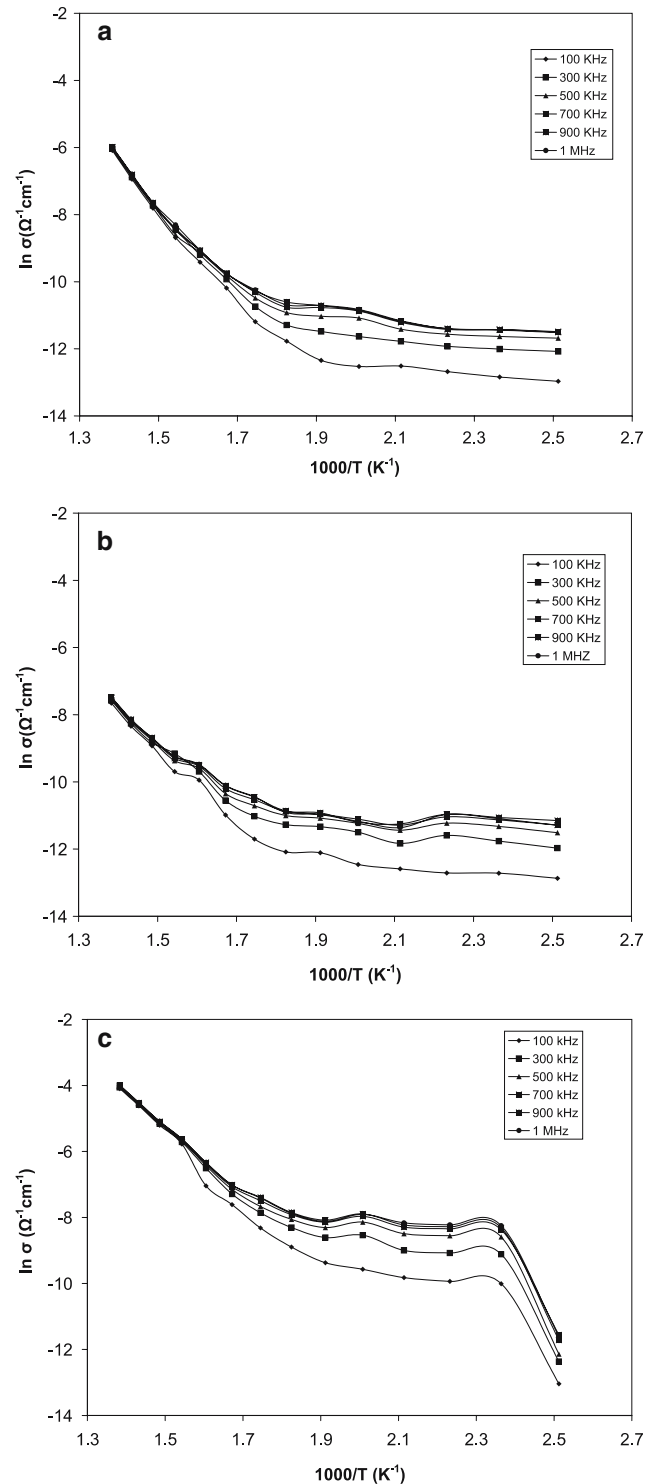

Fig. 1 $\ln\sigma$ versus temperature plot for $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ for (**a**) $x = 0$, (**b**) $x = 0.5$ and (**c**) $x = 1$

depends on the type of crystal structure rather than cation type, its variation with the dopant concentration is small. At the same time the A-site dopant Ba^{2+} cation (radius = 1.61 Å) in the compound is larger

Table 1 Activation energy and dielectric parameters

x	E_a (KJ/mol)	T_c (K)	Dielectric constant at T_c		Dielectric loss (tan δ)	Crystal structure, Lattice parameter (Å)
			600 kHz	1 MHz		
0	48.85	700	790	700	2.826	Cubic: $a = 3.863$ [8]
0.5	38.47	750	900	760	1.490	Cubic: $a = 3.979$ [8]
1	31.33	723	740	690	2.543	Hexagonal: $a = 5.590$, $c = 4.820$ [9]

than the Sr^{2+}(radius = 1.44 Å). Also as the barium content increases the unit cell expands due to its large ionic radius than strontium and hence lattice parameters increases [8]. The oxygen vacancies created tend to disorder at elevated temperatures, maximizing their configurational entropy and then may become highly mobile [6], so decrease in activation energy was expected and hence conductivity increases with the increase in barium content. It may also be possible that the comparatively large values of conductivity for different composition is associated with the coexistence of the different oxidation state of Co and Fe on the octahedral B-sites of the lattice, and that of the bonding energy between the metal oxygen bonds [12]. It is noted that barium substitution gives conductivities a little larger than that of barium free compound. Although, Co-based perovskite-type oxides are excellent oxide ion conductors, their conductivities can be modified considerably with the substitution at A-sites [13]. As oxide ion conduction in Co-based perovskite-type oxides occurs through a vacancy mechanism [13], the oxide ion conductivities would reflect the concentration and/or the mobility of oxide ion vacancies. We can say that there is multiple level hoping conduction mechanism exists as electron exchange may take place between Co–Co, Fe–Fe and Co–Fe of different spin states.

In the temperature range (400–500 K) ac conductivity is almost temperature-independent but strongly frequency-dependent. The observed increase in ac conductivity with frequency (ω) is due to hopping conduction and is proportional to ω^s, where s is a parameter having value less than unity [14]. The temperature dependency of conductivity gradually changes with barium content (x) in low temperature region. At temperature $T < 417$ K, for $x = 0$; it behaves as a metallic conductor and for $x = 1$; conductivity shows a thermally activated type of temperature dependence [15]. The conductivity is affected by two factors—the crystal structure at low temperature and small x ($SrFe_{0.8}Co_{0.2}O_{3-\delta}$ is cubic [8] and $BaFe_{0.8}Co_{0.2}O_{3-\delta}$ is hexagonal [9]).

$\ln(\sigma)$ versus frequency curves at different temperatures are shown in Fig. 2. From these curves it can be

seen that the dependence of conductivity decreases with the increase in temperature. Thus, electronic hopping conduction is dominant at lower temperature and diminishes with the rise in temperature.

Dielectric constant (ε')

In polar dielectric, in most cases the molecules cannot orient themselves in the low-temperature region. When the temperature raises the orientation of dipoles is facilitated, and this increases permittivity. Characteristic sets of curves are obtained if the dependence of the permittivity of strong polarized dielectrics is plotted versus two variable factors—temperature and frequency. The variation of dielectric constant (ε') with temperature at frequencies 600 kHz, 700 kHz, 800 kHz, 900 kHz and 1 MHz for the composition $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0$, 0.5, 1) are shown in Fig. 3. A broad peak around 700, 750 and 723 K for $x = 0$, 0.5 and 1, respectively, can be seen from ε'–T curves. These temperatures correspond to the ferroelectric–paraelectric phase transition in these ceramics. Normally, in ferroelectrics, the dielectric constant initially increases with increasing temperature, reaches a maximum at the transition temperature and thereafter decreases abruptly in accordance with the Curie–Weiss law. The ferroelectric transition temperature in each case is independent of test frequency. The peak does not significantly shift with decreasing frequency. Thus, the dielectric peaks in Fig. 3 might not come from relax or ferroelectric behavior and can be explained in terms of the oxygen-vacancy-related dielectric relaxation [16, 17]. The ε' values of the ceramics decreases slightly from 625 to 610 when the applied frequency increases from 600 kHz to 1 MHz. The typical values of ε' and tan δ are listed in Table 1.

The variation of dielectric constant with log frequency for the composition $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0$, 0.5, 1) are shown in Fig. 4. It can be seen that when the frequency increases the dipole maxima in the temperature trend of ε' are displaced towards higher temperature and become lower (Fig. 4). At higher temperature the dielectric constant (ε') decreases with frequency. An examination of figure reveals the
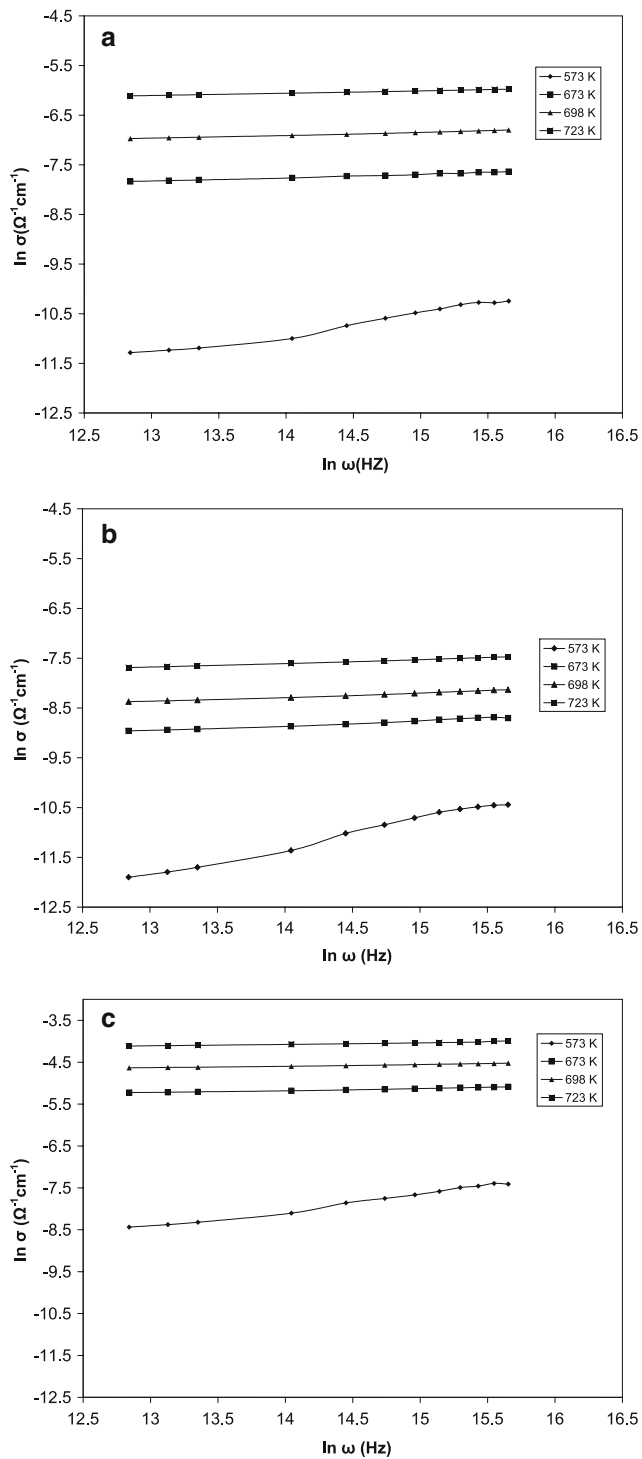
Fig. 2 ac conductivity versus frequency plot of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ system for (**a**) $x = 0$, (**b**) $x = 0.5$ and (**c**) $x = 1$

Fig. 3 Dielectric constant versus temperature plot of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ system for (**a**) $x = 0$, (**b**) $x = 0.5$ and (**c**) $x = 1$

dielectric dispersion at higher temperature (623–723 K) which follows Skanani's pattern [18]. This pattern is shown in Fig. 4. From figure it can be observed that the dielectric constant rapidly decreases at lower frequencies and remain fairly constant at
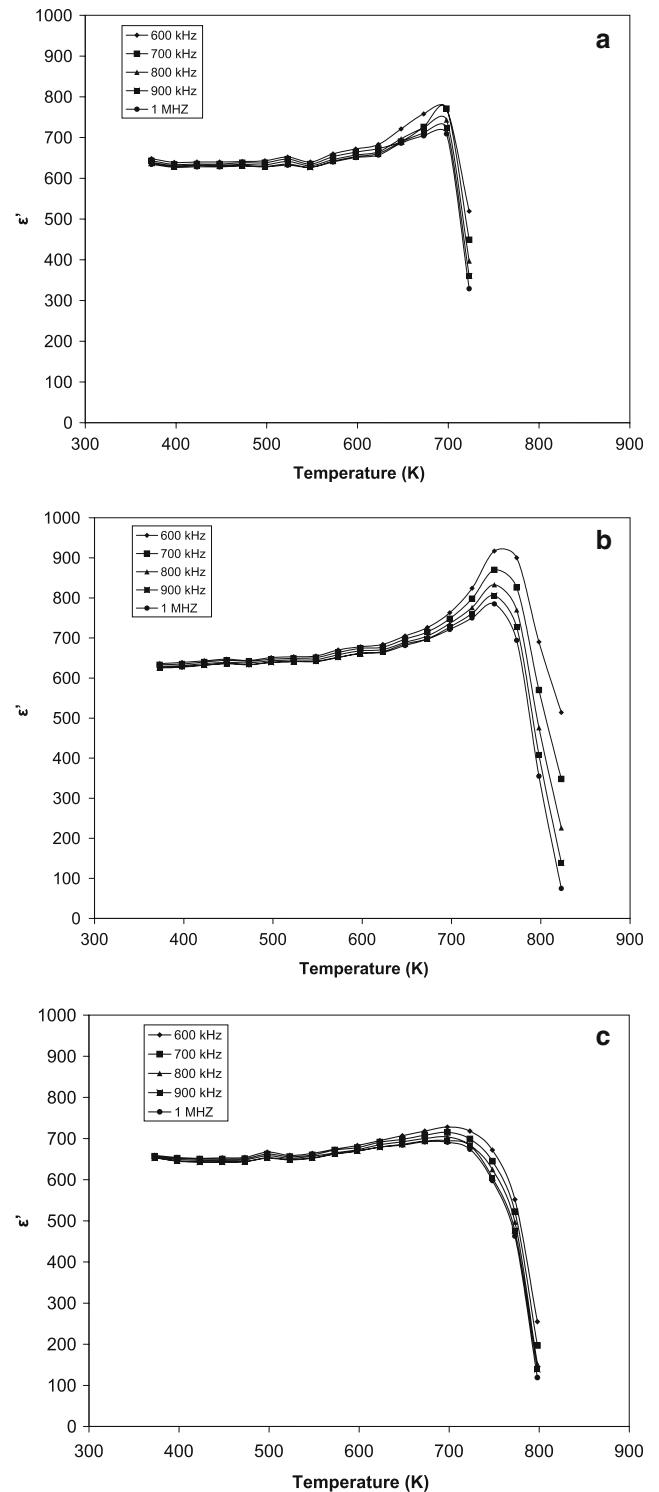
higher frequencies. At lower frequencies, ε' falls rapidly for the composition having higher value of dielectric constant indicating that dispersion is large in compositions with large value of dielectric constant in
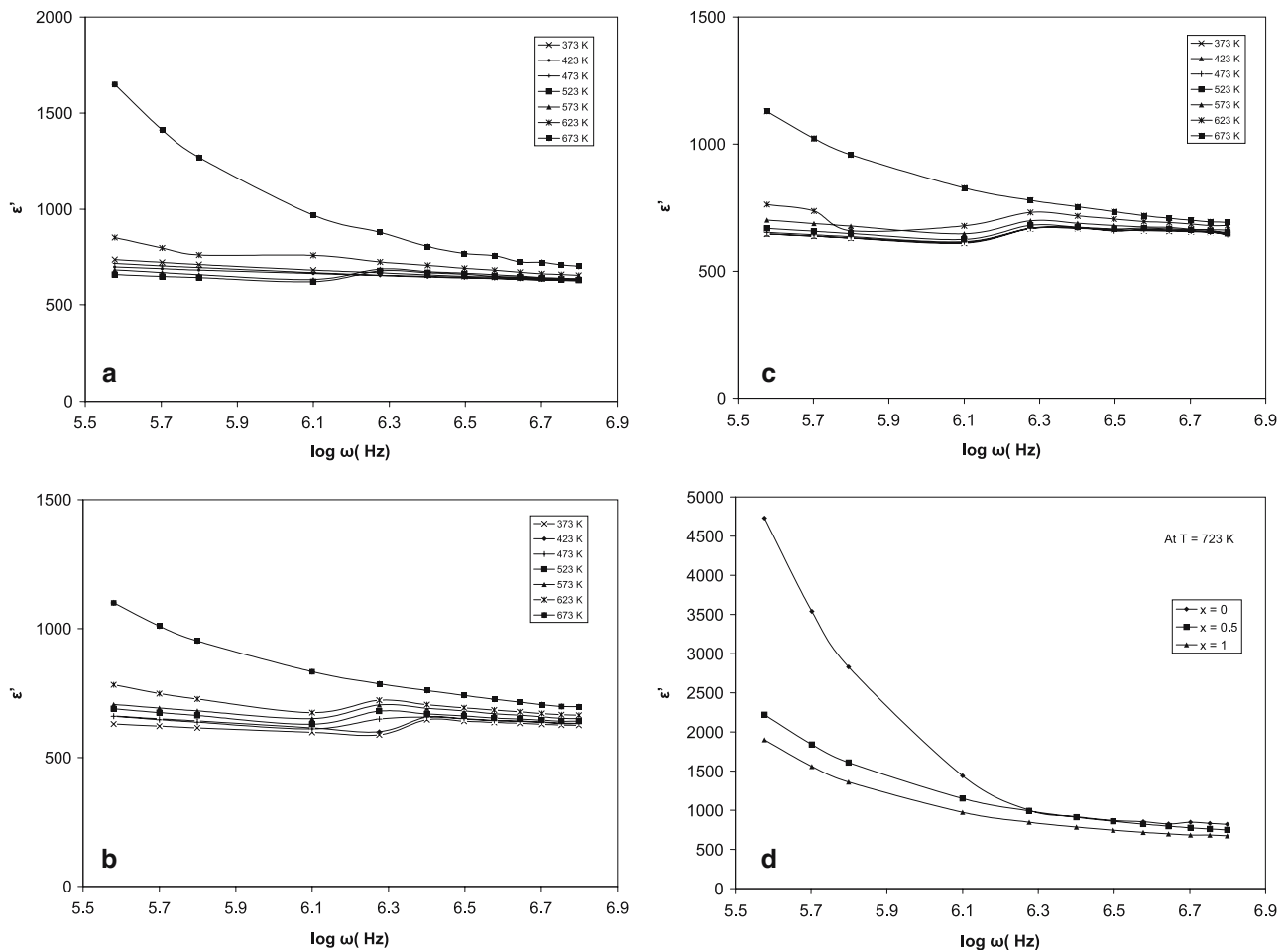
Fig. 4 Dielectric constant versus log frequency plot of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ system (**a**) $x = 0$, (**b**) $x = 0.5$, (**c**) $x = 1$ and (**d**) comparison at temperature 723 K

comparison to those with smaller values of ε'. Hence with the increase of barium content the dielectric dispersion tend to diminishes. The large value of dielectric constant at lower frequencies is due to dislocations and other defects. All samples reveal dispersion due to Maxwell-Wagner [19] type interfacial polarization and in agreement with Koop's phenomenological theory [20]. As the frequency increases from 100 kHz to 1 MHz, the dielectric constants at ferroelectric transition temperature reduced from higher to lower value. It was reported that oxygen-vacancy-induced dielectric polarization becomes more predominant at higher temperatures and this kind of dielectric polarization contribution increases remarkably with temperature due to thermal energy supplied for overcoming diffusion energy barrier [16]. The oxygen-vacancy-induced dielectric relaxation could respond well to low frequency signal but not so well to high frequency signal. In other words, oxygen-vacancy-induced dielectric polarization could not follow high

frequency signal well, resulting in lower dielectric constant at high frequencies.

The high values of dielectric constant observed at lower frequencies are explained on the basis of space charge polarization due to inhomogeneous dielectric structure and resistivity of the samples. The inhomogeneities may be due to complex preparation method of samples and the interfacial polarization arises due to grain boundary between ferroelectric and non-ferroelectric regions. It can be infer that substitution of strontium with barium somehow affecting the dielectric constant as dielectric constant decreases with increase in barium content and hence space charge polarization effect decreases as barium content increase.

In the lower temperature region, it is observed that when the frequency of alternating voltage increases the value of ε' of polar dielectric at first remains invariant but starts with a certain critical frequency when polarization fails to settle itself completely during one half period and begins to drop approaching at very

high frequencies i.e. the values typical of non-polar dielectric [18]. For $Ba_{0.5}Sr_{0.5}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and $Ba-Fe_{0.8}Co_{0.2}O_{3-\delta}$ systems the appearance of small peaks in the dependence of $\varepsilon'(\omega)$ at frequency 400 KHz implies the dielectric relaxation (the relaxation time can be calculated from resonance condition $\omega_c \tau = 1$; $\tau = 2.5\ \mu s$, where ω_c is the relaxation frequency). This can be associated to a polarization mechanism responsible for the dissipation. The origin of this dielectric relaxation phenomenon may be attributed due to the ferroelectric domain wall motion, which contributes to the polarization of ferroelectric materials. In future the detail behavior of this phenomenon will be investigated.

Dielectric loss (tan δ)

Figure 5 shows loss tangent as a function of temperature for $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0, 0.5, 1$) at some
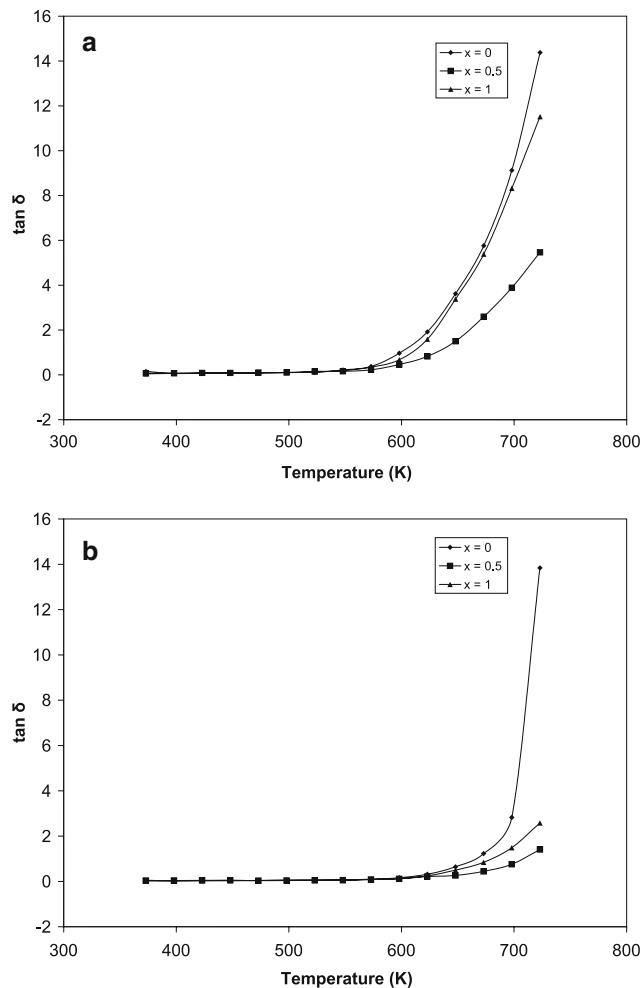

Fig. 5 Dielectric loss versus temperature plot of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ system for $x = 0, 0.5$ and 1 at frequency (**a**) 100 kHz and (**b**) 1 MHz

frequencies 100 kHz and 1 MHz. From these plots it can be seen that the values of tan δ are invariant with the rise in temperature upto 575 and 625 K for frequencies 100 kHz and 1 MHz, respectively. Above 575 K, tan δ begin to increase with the rise in temperature. At higher temperature, the rate of increase of tan δ is higher for lower frequencies due to space charge polarization [18]. For barium free compound (i.e. $x = 0$) the losses are higher than the case of partial substitution of strontium with barium ($x = 0.5$). But for the pure barium compound ($x = 1$), the losses are comparable to barium free compound ($x = 0$). However, the structure of the system are composed of oxygen at octahedral positions and this deviates from the centre of gravity of surrounding ions, thus yielding dipole moment [14]. Accordingly, the variation of tan δ with respect to temperature implies that the losses are of mixed type i.e. dipole losses and losses due to electrical conduction. It is known that the dielectric loss at lower frequency is mainly induced by leakage conduction which would to the decrease of dielectric loss with increasing frequency. Contrary to this, the tan δ value increases slightly with frequency as shown in Fig. 5 for frequency 100 kHz and 1 MHz. The increase in dielectric loss results from that the switches of dipoles in $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (BSCFO) ceramics cannot follow the applied electric field at high frequency, because it takes a short period for dipoles to change their directions in accordance with the applied electric field.

Conclusions

The ac conductivity, permitivity and dielectric losses of $Ba_xSr_{1-x}Fe_{0.8}Co_{0.2}O_{3-\delta}$ ($x = 0, 0.5$ and 1) ceramics were studied in the temperature range (373–723 K) and in the frequency range (100 kHz–1 MHz).

(i) In the higher temperature region, the system behaves like thermally activated system and there is slight decrease in the activation energy with the increase of barium content. In the temperature range (400–550 K), ac conductivity is almost temperature independent but strongly depends on frequency. The electronic hopping conduction is dominant at lower temperature and diminishes with the rise in the temperature. (ii) The ferroelectric transition peaks are observed at 700, 750and 723 K for $x = 0, 0.5$ and 1, respectively. This peak temperature corresponds to oxygen-vacancy-related dielectric relaxation. With the increase of barium content the dielectric dispersion tend to diminishes. At frequency 400 KHz, appearance of small peak in the dependence of $\varepsilon'(\omega)$ for $x = 0.5$ and 1 are observed.

(iii) Partial substitution of strontium with barium reduces dielectric losses by 50% which means $Ba_{0.5}Sr_{0.5}Fe_{0.8}Co_{0.2}O_{3-\delta}$ can be used as dielectric materials with minimum dielectric losses.

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