Studies on a.c. properties of Ca$_{1-x}$Sr$_x$TiO$_3$ perovskites

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Abstract A.c. measurements were preformed on bulk samples of Ca$_{1-x}$Sr$_x$TiO$_3$ (CST) perovskites with $x = 0$, 0.1 and 0.5 as a function of temperature range 300–450 K and frequency range 10^3–10^5 Hz . The experimental results indicate that the a.c. conductivity $\sigma_{a.c.}(\omega)$, dielectric constant ε' and dielectric loss ε'' depend on the temperature and frequency. The a.c. conductivity as a function of frequency is well described by a power law $A\omega^S$ with s the frequency exponent. The obtained values of $s > 1$ decrease with increasing temperature. The present results are compared to the principal theories that describe the universal dielectric response (UDR) behavior.

Introduction

Several studies on Perovskite type oxides of general formula ABO$_3$ [1] have shown that the interesting properties of these oxides in material sciences, physics and earth science with special emphasis on their electrical and optical properties [2–6] and for their ability to immobilize high-level radioactive waste [7]. It is known that the ternary system formed by the compounds barium titanate, calcium titanate and strontium titanate is of great interest in the field of dielectrics. Ca$_{1-x}$Sr$_x$TiO$_3$ (CST) system where ($x = 0$, 0.1 and 0.5) is a more complex form of perovskite family with general formula (A′A″)BX, where the A′, A″, B and X atoms contact each other according to the very definition of ionic radii. In this form of perovskite there are more than one type of ion on a particular crystallographic site with site sharing ions.

The measurement of a.c. conductivity $\sigma_{a.c.}$ generally shows frequency dispersion i.e dependence of $\sigma_{a.c.}(\omega)$ on the angular frequency ω. The study of this dispersive behavior offers a powerful experimental method to gain insight into the details of ionic motion in ionically conducting materials. It is well established that the electrical behavior of complex ionically conducting materials as a function of frequency shows two regions of behavior named the universal dielectric response (UDR) [8–11] and nearly constant loss (NCL) in which the dielectric loss ε'' is nearly constant [12–14]. The dependence of the a.c. conductivity $\sigma_{a.c.}(\omega)$ on the frequency is found to obey the form:

$$\sigma_{a.c.}(\omega) \ = \ A \ \omega^S \tag{1}$$

where: $\sigma(0)$ is termed as the d.c. conductivity, ω the angular frequency, A constant and s the frequency exponent. Such behavior was first reported by Jonscher [15, 16] for a wide variety of materials and defined as the (UDR). A wide variety of theoretical approaches have been used to clarify the (UDR) behavior, in general involving hopping of carrier ions with appropriate relaxation of surrounding ions occurs in the crystalline or glassy materials. In the (NCL) model, at high frequency and low temperature the frequency exponent s tends to the value of 1. (Actually, it is often

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found to go slightly higher to a value ~ 1.03–1.05). A value of $s = 1$ corresponds to ε'' equal constant, independent of frequency and varies only slowly with temperature i.e. it is not activated. This behavior can be observed down to cryogenic temperatures [12, 13].

In this work, the temperature and frequency dependence of a.c. conductivity and dielectric properties were measured for bulk Ca_{1-x} $Sr_x TiO_3$ perovskite materials where $x = 0$, 0.1 and 0.5, through the temperature range 300–450 K and frequency range 10^3–10^5 Hz.

Experimental details

Three bulk samples of the $Ca_{1-x}Sr_x TiO_3$ system with nominal compositions $x = 0$, 0.1 and 0.5 were prepared in the form of disc with 1.3 cm in diameter and uniform thickness. Details for sample synthesis can be found in previous work [17]. This samples were covered on the opposite surfaces with thin layer of silver paste film to obtain a good contact and were mounted between two copper electrodes in special holder. The sample holder was inserted in a small furnace and the temperature was measured to better than ±1 °C with calibrated chromel–alumel thermo-couple which was set up near the sample. The d.c. conductivity $\sigma(0)$ measurements were carried out in the same manner mentioned before [17]. A program-mable automatic RLC bridge (PM 6304 Philips) was used to measure the impedance Z, the capacitance C_p and the loss tangent $\tan \delta$ directly. All values of the capacitance C_p which taken from the screen of the bridge were parallel with the resistance R.

The total conductivity was calculated from the equation:

$$\sigma_t(\omega) = L/Z\,a \tag{2}$$

where L is the sample thickness and a the sample cross-sectional area, a.c. conductivity was calculated using the relation:

$$\sigma_{a.c.}(\omega) = \sigma_t(\omega) - \sigma(0) \tag{3}$$

where $\sigma(0)$ is termed as the d.c. conductivity, The dielectric constant was calculated using the relation:

$$\varepsilon' = C_p\,L\,/\,a\,\varepsilon_o \tag{4}$$

where ε_o is the free space permittivity. The dielectric loss ε'' was calculated from the relation:

$$\varepsilon'' = \varepsilon'\,\tan\,\delta \tag{5}$$

where $\delta = 90\text{-}\Phi$, Φ is the phase angle which has been measured using the same bridge. The values of the impedance Z, the capacitance C_p and the loss tangent $\tan \delta$ were measured in the frequency range 10^3–10^5 Hz and temperature range 300–450 K. These data were converted to a.c. conductivity $\sigma_{a.c.}(\omega)$ in $(m\Omega)^{-1}$, dielectric constant ε' and dielectric loss ε'' using the above equations.

Results and discussion

X-ray diffraction patterns obtained for the Ca_{1-x} $Sr_x TiO_3$ with $x = 0$, 0.1 and 0.5 shows that there is no traces of other compounds and the line widths indi-cated that the products were homogeneous, thus all the samples are in good quality with the perovskite structure.

Frequency and temperature dependence
of a.c. conductivity

The relation between the a.c. conductivity $\sigma_{a.c.}(\omega)$ and the frequency at different constant temperature values for the system under investigation are plotted as ln $\sigma_{a.c.}(\omega)$ versus ln ω. Figure 1 shows the frequency dependence of a.c. conductivity $\sigma_{a.c.}(\omega)$ for the com-position $Ca_{0.9}Sr_{0.1}TiO_3$ as an example. Similar behav-ior of a.c. conductivity has been observed for other two compositions ($x = 0$ and 0.5). It can be observed from
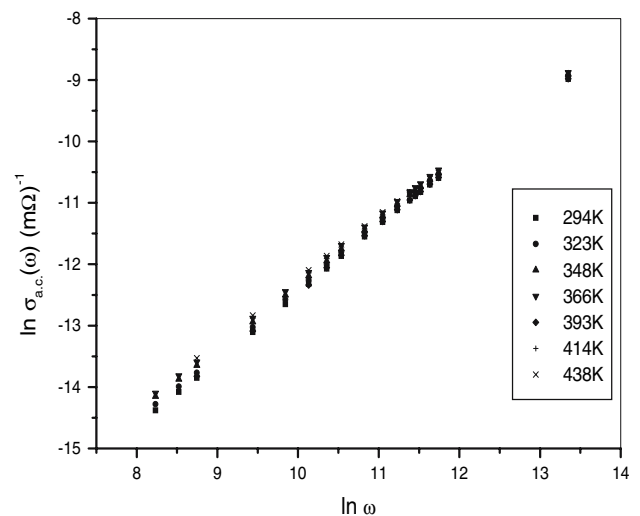

Fig. 1 Frequency dependence of $\sigma_{a.c.}$ for $Ca_{0.9}Sr_{0.1}$ TiO_3 at different temperatures

the figure that $\sigma_{a.c.}(\omega)$ increases linearly with frequency. The frequency exponent s is calculated from the slopes of $\ln \sigma_{a.c.}(\omega)$ versus $\ln \omega$ graphs for each composition through the measured frequency and temperature ranges. The temperature dependence of the frequency exponent s (shown in Fig. 2) gives information on the specific mechanism involved. It can be seen from Fig. 2 that the exponent s decreases with increasing temperature. This behavior of a.c. conductivity is analogous to that observed in ionic glasses [15]. It is reported that the a.c. conductivity of highly disordered materials including amorphous semiconductors and ionic conducting glasses is obeying Eq. 1. This equation is known as the universal dynamic response (UDR) which has been described by Jonscher [15]. This behavior was noted originally for amorphous semiconductors and glasses [14]. In most cases, s is found to be between 0.6 and 1 for ionic conducting materials [18]. The value of $s = 1$ is regarded theoretically as the limiting value. The experimental values of s obtained for all samples are illustrated in Fig. 2. The observed values of the exponent s are somehow frequency dependent. It decreases with increasing temperature from 1.14 to 0.9 for the composition at $x = 0.1$ as an example. This can be attributed to hoping conduction of mobile charge carrier (ions) over barrier between two sides, which is similar to that observed in amorphous semiconductors and glasses [13, 18]. The case of $s > 1$ has been reported in a few samples of crystalline, semiconductors and glasses at relatively low temperatures [13, 19]. The motion of mobile charge carriers from site to site with quantum mechanic tunneling between asymmetric double-well potentials was proposed for that case [20]. The change of s with the temperature corresponds to a thermally activated phenomenon. The high value of s can be explained as
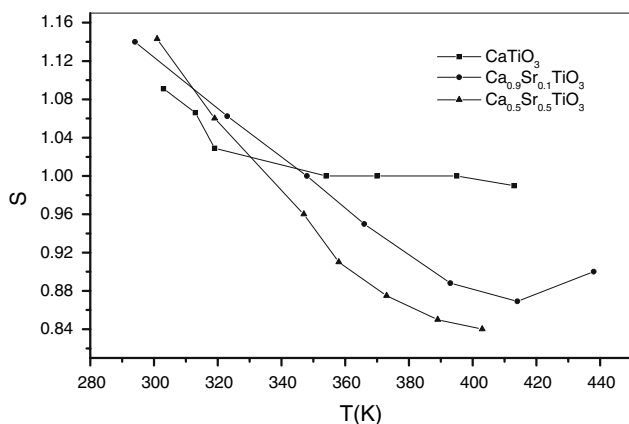
follows. The doping of Ca^{+2} in $SrTiO_3$ leads to the replacement of Ca^{+2} in its site by Sr^{+2} which are of the same charge. Some of Ca^{+2} may be located at Ti^{+4} sites, and the next neighbor oxygen can be vacant V_o and forming a Ca^{+2}–V_o neutral center which relax the hopping of conduction ions. Thus the addition of Sr^{+2} leads to decrease the number of Ca^{+2}–V_o forming neutral centers, and consequently the a.c. conductivity $\sigma_{a.c.}$ increases [21].

The temperature dependence of $\sigma_{a.c.}(\omega)$, at some representative frequencies for the $Ca_{1-x}Sr_xTiO_3$ system was measured in the range of 300–450 K. The results obtained are shown in Fig. 3a, b and c where $\ln \sigma_{a.c.}(\omega)$ plotted as a function of $1000/T$. It is clear from these figures that the a.c. conductivity shows a less temperature dependence with increasing frequency, as usually observed in many other materials [22].

The common feature which characterizes the curves in this figure, is the presence of minimum near the end of the figures with addition of Sr to replace Ca in the system under test. This behavior may be attributed to that the sample undergo certain type of transition. Similar behavior is observed in other materials [22]. It is clear that the increase of Sr content in the considered system up to 0.5 leads to increase the a.c. conductivity $\sigma_{a.c.}(\omega)$ by one order of magnitude. As an example the value of $\sigma_{a.c.}(\omega)$ at 5 kHz is equal to 6.999×10^{-6} $(m\Omega)^{-1}$ for $CaTiO_3$ and equal to 6.2×10^{-5} $(m\Omega)^{-1}$ for $Ca_{0.5}Sr_{0.5}TiO_3$.

Frequency and temperature of the dielectric constant and the dielectric loss.

Figure 4a, b and c shows the frequency dependence of dielectric constant ε' at different temperature for the compositions under investigations. The dielectric constant ε' shows an increase with increasing the frequency up to 1.5×10^4 Hz then it becomes nearly less frequency dependent for all measured temperatures. The same behavior was observed for other materials [22].It is clear that ε' increases firstly with temperature and then becomes weak temperature dependence for all values of frequency. The effect of increasing frequency on ε' is overwhelmed by polarization and thus increase in the value of ε' of the system under consideration is observed. The increases of Sr content in the system leads to increasing in the dielectric constant ε'. This may be because the $CaTiO_3$ concentration decreases with increasing Sr content.

Figure 5a, b and c shows the frequency dependence of dielectric loss ε'' at different temperatures for the three samples. It is clear from the figure that, ε'' increases with frequency in the range 2–4 kHz then it
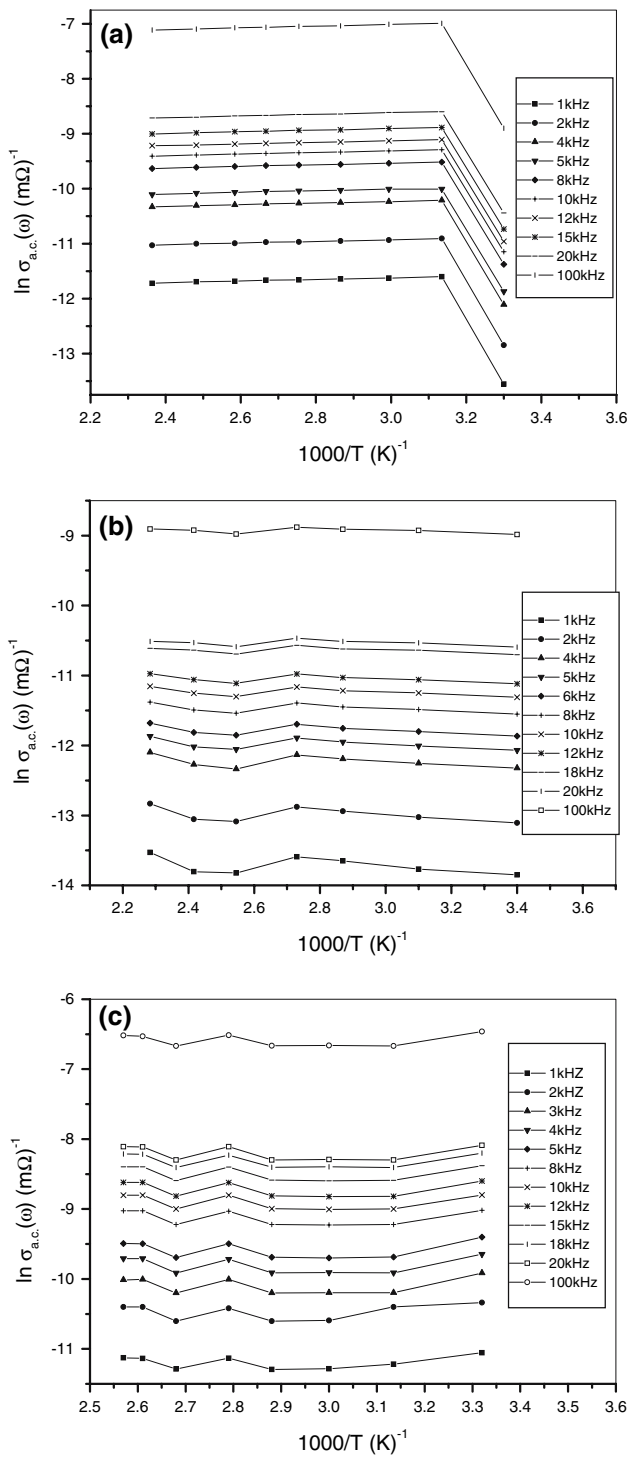

Fig. 2 Temperature dependence of the frequency exponent S for CST

Fig. 3 Temperature dependence of $\sigma_{a.c.}$ (ω) for CST. (**a**) CaTiO$_3$ (**b**) Ca$_{0.9}$Sr$_{0.1}$TiO$_3$ (**c**) Ca$_{0.5}$Sr$_{0.5}$TiO$_3$

Fig. 4 Frequency dependence of dielectric constant at different temperatures for (**a**) CaTiO$_3$ (**b**) Ca$_{0.9}$Sr$_{0.1}$TiO$_3$ (**c**) Ca$_{0.5}$Sr$_{0.5}$ TiO$_3$

decreases with increasing frequency up to 100 kHz. While the dielectric loss ε'' increases with increasing the temperature. This behavior is observed for all measured temperatures. The increase of ε'' with temperature can be explained by Stevels [23] who
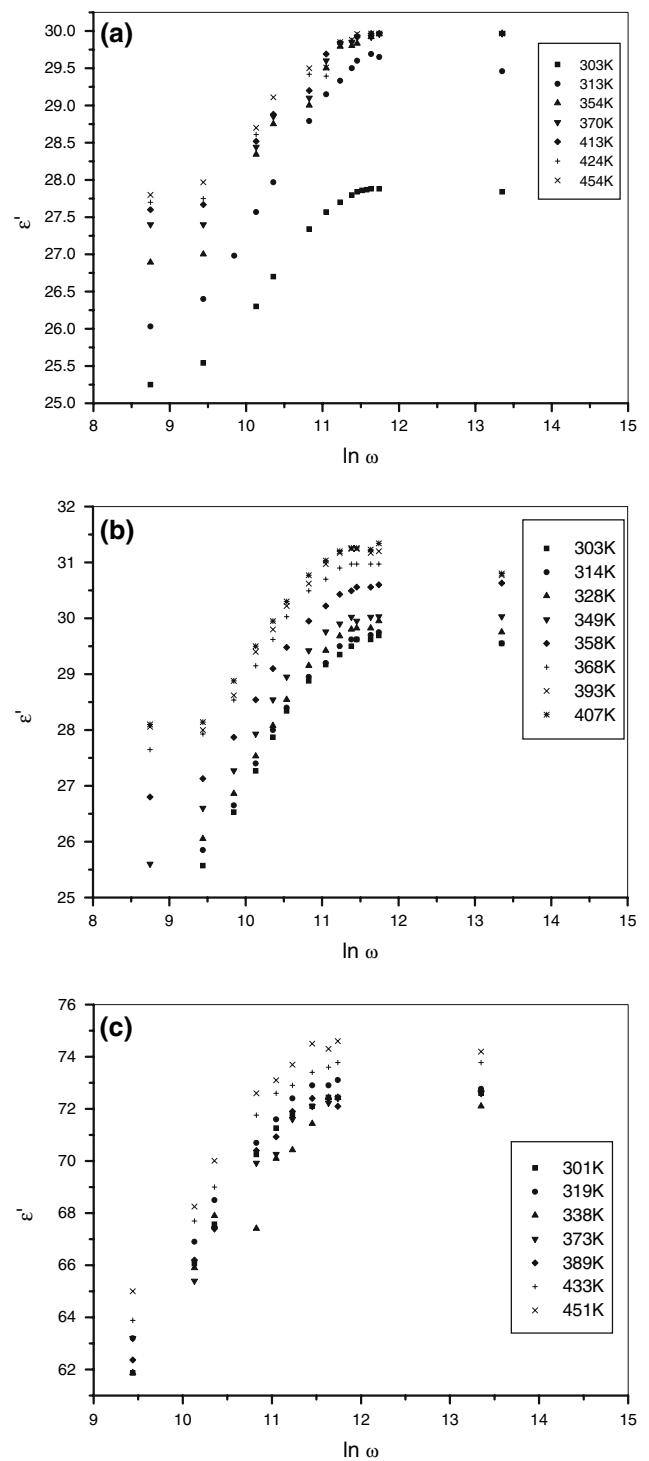
divided the relaxation phenomenon into three parts, conduction losses, dipole losses and vibrational losses. At low temperatures conduction losses have minimum value since it is proportional to σ/ω. As the temperature
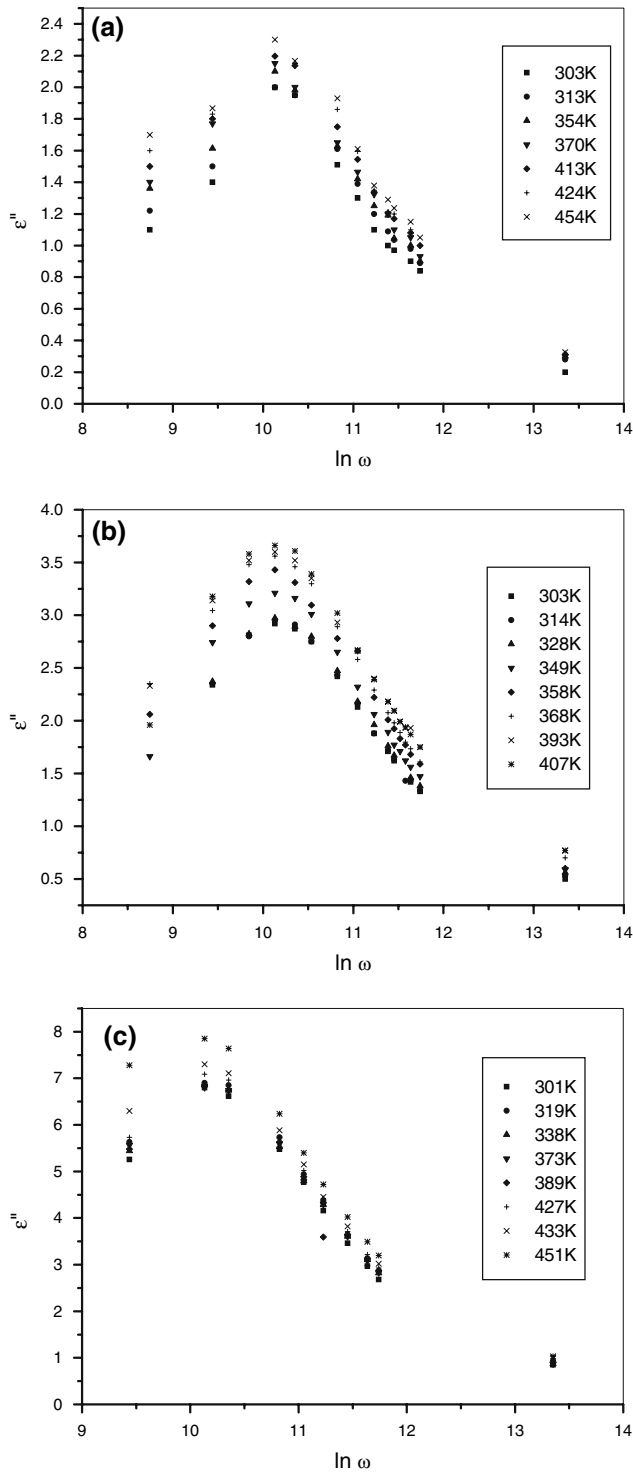
Fig. 5 Frequency dependence of dielectric loss at different temperatures for (**a**) $CaTiO_3$ (**b**) $Ca_{0.9}Sr_{0.1}TiO_3$ (**c**) $Ca_{0.5}Sr_{0.5}TiO_3$

increases σ increases and so the conduction losses increase. This increase the value of ε'' with increasing temperature.

Conclusion

Results of a.c. measurements performed on bulk samples of $Ca_{1-x}Sr_xTiO_3$ perovskites has been given in this work. The dependence of a.c. conductivity on angular frequency is found to follow the Jonscher's universal dielectric response (UDR). The decreases of s with increasing temperature is similar to that observed in amorphous semiconductors, glasses and crystalline materials. However an appreciable difference in the temperature dependence of s is observed. The dielectric constant and the dielectric loss were found to be frequency and temperature dependent through the measuring ranges. The increases of Sr content in the investigated system leads to increase the a.c. conductivity, the dielectric constant and the dielectric loss.

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