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Effect of lanthanum doping on electrical and electromechanical properties of $Ba_{1-x}La_xTiO_3$

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Abstract. **The effect of lanthanum doping is studied on ferroelectric properties of $Ba_{1-x}La_xTiO_3$ with $x = 0{\cdot}0005$, $0{\cdot}001$, $0{\cdot}003$ prepared through solid state sintering route. Dielectric and impedance spectroscopic studies have been carried out. The tetragonal distortion of the unit cell decreased and ferroelectric transition temperature, T_c increased with the increase of lanthanum content.**

Combined impedance and admittance spectroscopy was used to analyse impedance data. The electromechanical parameters were calculated from the resonant and anti-resonant frequencies from vector admittance plots. The electromechanical coefficients for $Ba_{1-x}La_xTiO_3$ with $x = 0{\cdot}003$ were found to be much larger than that of pure barium titanate.

Keywords. **Ferroelectric; resonant frequency; anti-resonant frequency; vector admittance plots.**

1. Introduction

The study of electrical properties of $BaTiO_3$ had been and still is a very important research topic because of its technical importance and the difficulty of explaining the behaviour thoroughly. The electrical resistance and ferroelectric transition temperature can be controlled effectively by doping in either barium or titanium site with proper donor impurity ions (Tennery and Cook 1961; Murakami *et al* 1973; Hewang 1984; Arlt *et al* 1985). Barium titanate and its related compounds have been widely used in the manufacture of ceramic multi layer capacitors and PTC resistors. Since its discovery, $BaTiO_3$ has been used as a high permittivity capacitor material because of its high dielectric constant (Fagen 1993). Variation in chemical composition or thermal treatment in these ceramics led to quite drastic changes in physical properties while retaining substantially piezoelectric properties (Desu Seshu 1990).

By adding oxide group softeners, hardeners and stabilizers one can modify these materials. Softeners (donors) reduce the coercive field strength, elastic modulus and the aging effects and increase the permittivity and dielectric constant and mechanical losses. Doping of hardeners (acceptors) gives higher conductivity, reduces dielectric constant and increases mechanical quality factor and aging effect (Desu Seshu 1990). The permittivity of $BaTiO_3$ is usually reported at fixed frequency. Such data gives information that is relevant to practical applications of $BaTiO_3$ while a great deal of information can be obtained by studying the electrical properties at various frequencies. Interesting changes can be observed with partial substitution of A site ion with suitable impurities. Multiple ion occupation of A and/or B sites in ABO_3 compounds is expected to bring in changes in Curie temperature and other physical properties. This kind of substitution can affect the lattice parameters, tetragonal distortion (c/a), polarization, ferroelectric transition and electro mechanical conversion characteristics of the samples. The aim of present investigation is to apply the variable-frequency techniques of impedance/admittance spectroscopy to lanthanum doped $BaTiO_3$ to probe some of the above aspects.

2. Experimental

The specimens were prepared from commercially available $BaCO_3$, TiO_2 and La_2O_3 through conventional solid state sintering route. The powders in stoichiometric ratios were ground well in agate motor in acetone medium and then calcined at 1100°C for 2 h. The specimens were pressed with 2% polyvinyl alcohol as binder under a pressure of 5 MPa into disks of convenient size and then sintered at 1300°C in air in a microprocessor-controlled furnace.

X-ray diffractogram of calcined powders of the samples were taken using CuKα radiation (figures 1a–c). Formation of the single-phase material was confirmed by indexing all recorded peaks on the basis of a tetragonal cell.

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The lattice parameters *a* and *c* were calculated and tetragonal distortion (*c*/*a* ratio) decreased with the increase in lanthanum content. The relevant parameters are summarized in table 1.

Contacts were made on both sides of the sample, using conductive silver paint. Electrical measurements were performed under unclamped condition (freely suspended). The electrodes used were not spring loaded. The dielectric constant was measured as a function of temperature from room temperature, 30–150°C. Impedance measurements were performed from room temperature to 300°C in the frequency range 500 Hz–12 MHz using Auto lab with PGSTAT 30 and FRA2 module and HP 4192A low frequency impedance analyser. The hysteresis behaviour of the sample was studied from room temperature to 150°C using a P–E loop tracer Imagetronics Model No. FEPE-1·0.

3. Results and discussion

XRD patterns of lanthanum doped barium titanate ceramics (figure 1) show the formation of single-phase materials. Since *c*/*a* ratio indicates the tetragonal distortion (Park *et al* 1997), in the present compounds lanthanum incorporation decreases this distortion (for pure barium titanate this has been found to be 1·011 (Uchino *et al* 1989)).

Figure 2 presents the variation of dielectric constant as a function of temperature for all the three samples. Increase in the lanthanum content increases the room temperature dielectric constant of the samples. The values of dielectric constant increased little up to 80°C and with the further increase in temperature the value of dielectric constant increased rapidly attaining a peak at a particular temperature (transition temperature) depending on the lanthanum content. Increase in lanthanum content increases the peak value of the dielectric constant and the temperature of the peak. The data was fit to Curie Weiss law and Curie constants of the samples were calculated. The values of Curie constant and ferroelectric transition temperatures increased with the increase of lanthanum content. Some of these results are presented in table 2. DSC data supports the transition temperatures obtained from dielectric studies.

The four fundamental formalisms viz. impedance (Z), admittance (Y), permittivity (e), electric modulus (M), offer wide scope for graphical analysis (Macdonald 1987). Usually it is necessary to consider at least two complex planes in order to extract the maximum amount of information. Complex impedance (Z' vs Z'') and complex admittance (Y' vs Y'') plots are used in the present study as complex impedance/admittance formalism helps in eliminating stray frequency effects and in determining inter particle interactions like grain, grain boundary effects etc.

The variation of imaginary part of impedance (Z'') as a function of real part (Z') gives cole–cole plots. The shapes of the cole–cole plots obtained in the present study are dependent on temperature and are shown in figures 3a–c. At lower temperatures the shape of cole–cole plot is a straight line with a large slope indicating the insulating behaviour of the sample. With the increase in temperature the slope of the lines decreases and they curve towards real axis and at temperatures above 250°C the curve becomes almost semi-circular indicating increase in conductivity of the sample. All these curves start at the origin and hence there is no series resistance

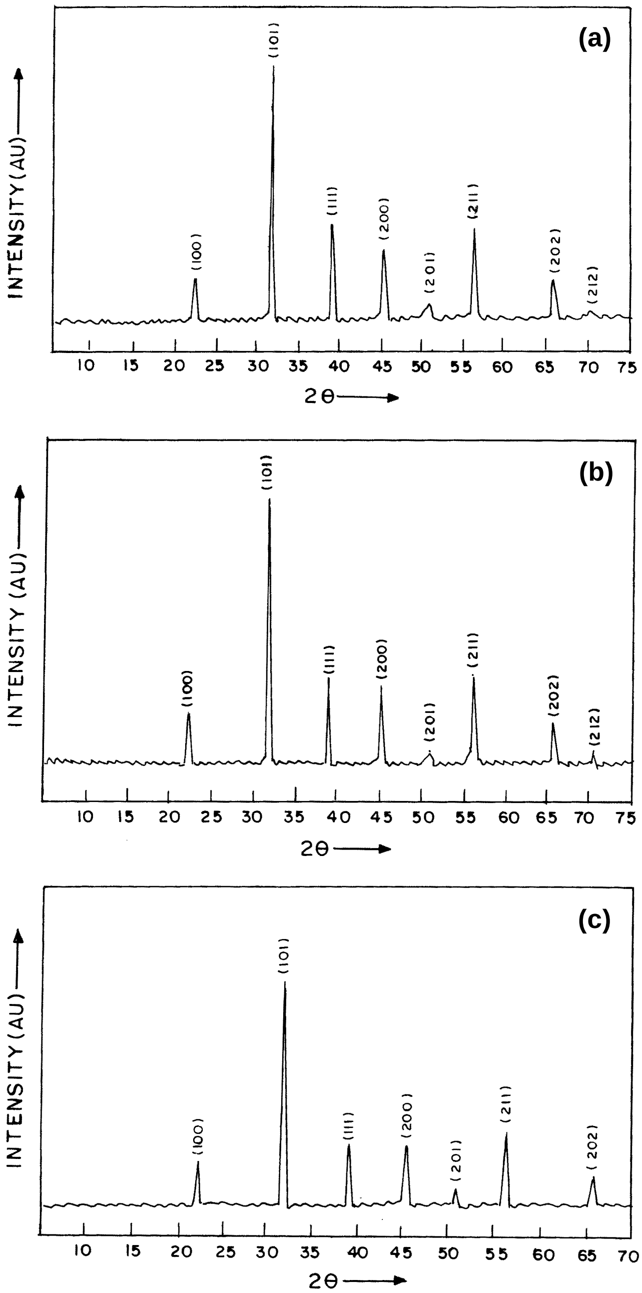

Figure 1. XRD pattern of the $Ba_{1-x}La_xTiO_3$ with **a**. x = 0·0005, **b**. x = 0·001 and **c**. x = 0·003.

Table 1. Pertinent density and XRD data of lanthanum doped $BaTiO_3$.

Compound	Density (g/cm^3)	*a* (Å)	*c* (Å)	*c*/*a* (tetragonal distortion)
$Ba_{0·9995}La_{0·0005}TiO_3$	5·98	4·001 ± 0·001	4·009 ± 0·001	1·002 ± 0·001
$Ba_{0·999}La_{0·001}TiO_3$	6·03	4·012	4·019	1·001
$Ba_{0·997}La_{0·003}TiO_3$	6·01	4·008	4·007	0·999

Table 2. Dielectric constant and resistivity of lanthanum doped $BaTiO_3$.

Compound	T_c ± (1°C)	Dielectric constant at *RT*	Dielectric constant at T_c	Curie constant	Resistivity at Ω-cm D.c.	Resistivity at Ω-cm A.c. (1 kHz)	Activation energy 50°C and 180°C (eV)
$Ba_{0·9995}La_{0·0005}TiO_3$	119°C	307	1176	$2·23 \times 10^4$ °C	$2·66 \times 10^{12}$	$4·32 \times 10^6$	0·646
$Ba_{0·999}La_{0·001}TiO_3$	122°C	414	1624	$3·34 \times 10^4$ °C	$2·03 \times 10^{11}$	$3·02 \times 10^6$	0·631
$Ba_{0·997}La_{0·003}TiO_3$	132°C	998	3325	$3·39 \times 10^4$ °C	$1·20 \times 10^{11}$	$1·60 \times 10^6$	0·253

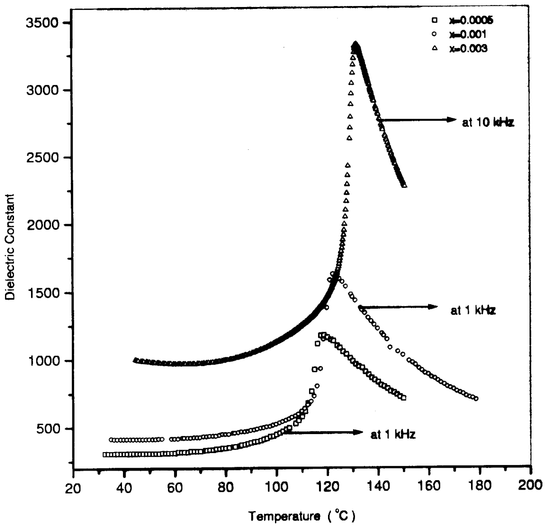

Figure 2. Dielectric constant as a function of temperature for different La doping of $Ba_{1-x}La_xTiO_3$ at different frequencies.

that can be ascribed to the LCR circuit representation of the samples (figure 4). It should be mentioned here that the piezoelectric ceramics could be represented as tank circuits (Proc. of IRE 1961). The radius of these semicircles gives the exact relaxation time of the lumped parameters that are associated with the samples. The semi circles have their centres located away from the real impedance axis, indicating the presence of relaxation species with distribution of relaxation times in the sample. Impedance measurements undertaken in these samples within the frequency range of 500 Hz–12 MHz show a peak in imaginary part of impedance (Z'') when plotted as a function of frequency at higher temperatures (> 250°C) indicating the presence of relaxation of charged entities in the samples. The variation of imaginary part of admittance with the frequency shows a resonant and anti-resonant behaviour of the $Ba_{1-x}La_xTiO_3$ sample with $x = 0·003$ (figure 5).

Figure 6 shows the vector admittance circles at different temperatures for $x = 0·003$ system. With conduction type dielectric loss, the locus of the vector admittance curve describes a vertical straight line. Maximum motional impedance occurs at series resonant frequency, f_s. The parallel resonant frequency, f_p is the point near minimum admittance, at which the total admittance has the same phase angle as at f_s. The maximum and minimum of total admittance occur at f_m and f_n respectively (figure 7). These parameters describe electromechanical-coupling characteristics of the samples and the factors, which limit the piezoelectric characteristics. The limiting electromechanical characteristics are (Mason 1964): (i) dynamic strength of the ceramic, (ii) reduction in efficiency due to dielectric losses, (iii) reduction in efficiency due to internal mechanical losses, (iv) depolarization of the ceramic due to electric field, and (v) depolarization of the ceramic due to temperature rise.

The admittance, in the frequency range over which vector admittance circle lie in the positive quadrant is capacitive and the admittance is inductive over the other frequency range. This is in accordance with general principle that many ferroelectric ceramics have decreasing capacitance with increasing frequency and at very high frequencies inductive effects dominate.

Unloaded piezoelectric material can be represented near resonance by an equivalent circuit (figure 4) (Mason 1964; Katiyar *et al* 1994). The frequency response of admittance of such a circuit on a complex impedance plane and its resonant frequencies along with other parameters are shown in figure 7. Piezoelectric coupling

Table 3. Electromechanical coupling parameters of $Ba_{1-x}La_xTiO_3$ with $x = 0{\cdot}003$.

Temperature	f_r (kHz)	f_a (kHz)	f_s (kHz)	f_p (kHz)	K	K_p	K_{31}	K_{33}
RT	5130	6261	5571	10901	0·85	0·57	0·33	0·88
65	5081	6021	5501	7941	0·72	0·53	0·31	0·75
85	4981	5921	5381	9741	0·83	0·54	0·32	0·73
100	3460	4080	3740	5120	0·68	0·53	0·30	0·71
110	3080	4000	3500	4900	0·69	0·63	0·38	0·73
120	3180	4080	3600	6280	0·81	0·62	0·37	0·84

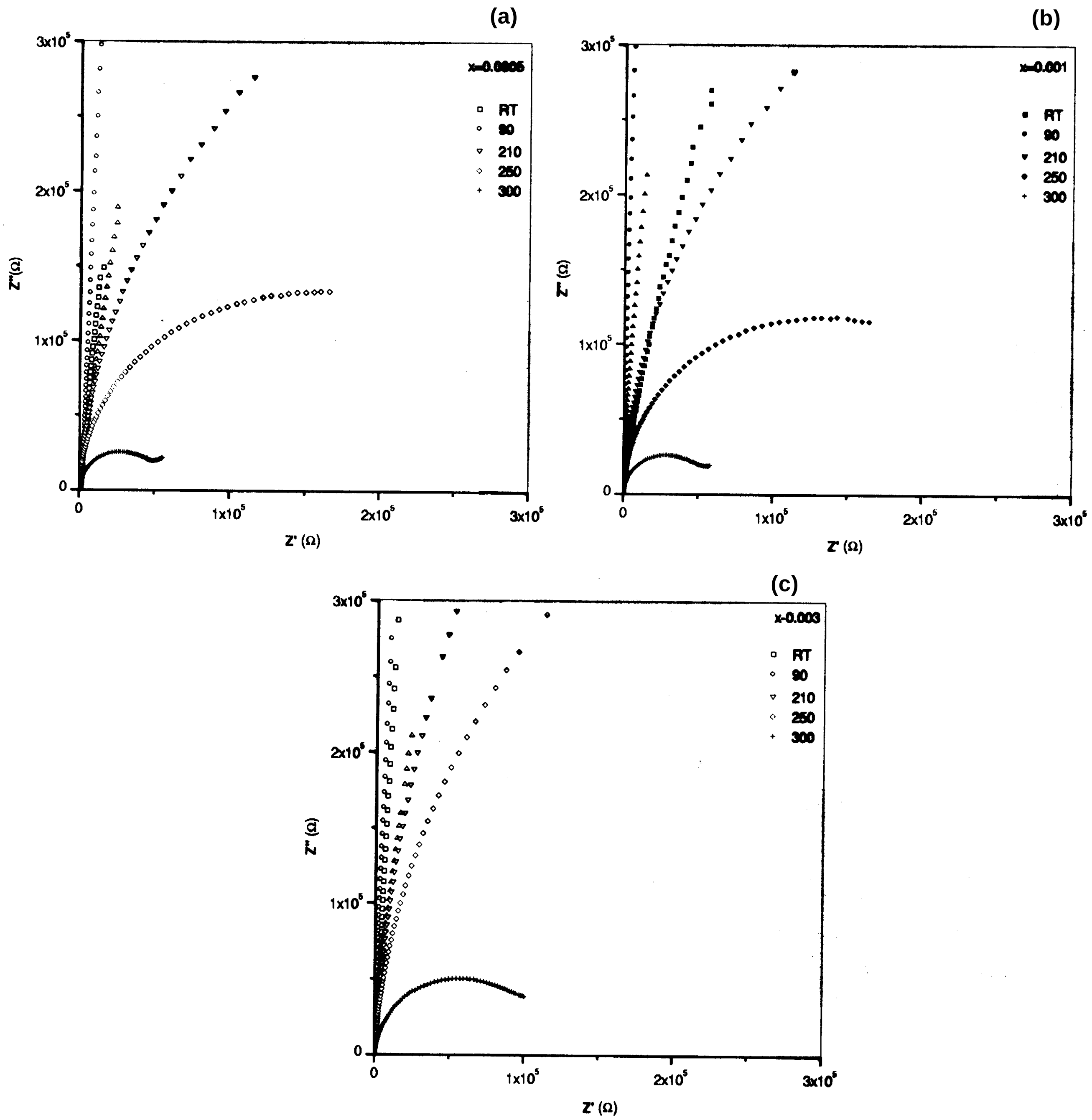

Figure 3. Complex impedance plot (Z') vs (Z'') at different temperatures for $Ba_{1-x}La_xTiO_3$ with (**a**) $x = 0{\cdot}0005$, (**b**) $x = 0{\cdot}001$ and (**c**) $x = 0{\cdot}003$.

factor may be defined as the ratio of mutual energy to that of elastic and dielectric energy densities neglecting thermal and magnetic terms.

Piezoelectric coupling factor, K characterizes a piezoelectric ceramic material for power transudation. The elastic, dielectric and piezoelectric constants and bandwidth of a filter or transducer are dependent on appropriate coupling factor. Ceramic disks, which are most convenient shapes to fabricate, support radial mode of vibration, and are inherently free from spurious responses (Holland 1969).

In piezoelectric materials the radial modes of thin disks are particularly important because they are free from the interference effects. According to IRE standards (1961), the planar coupling coefficients are related to f_s, the series resonant frequency, f_p and parallel resonant frequency.

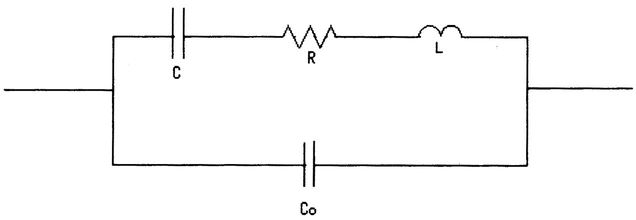

Figure 4. Equivalent circuit of a piezoelectric ceramic.

The values of dynamic electromechanical coupling factor K, K_p, K_{31}, K_{33} were calculated using the method proposed by Holland (1969) and Katiyar *et al* (1994). The values of K, K_p, K_{31} and K_{33} are given in table 3. It is well known that the electromechanical coupling coefficients K, K_p, K_{31} and K_{33} are very much dependent on synthesis of the sample and also on the doping. It was reported earlier (Rehrig *et al* 1999) that the doping of barium titanate (single crystal) with zirconium in place of titanium enhances K_{33}. For pure barium titanate (single crystal), K_{33} is 0·56 (Berlincourt and Jaffe 1958), while for zirconium doped barium titanate it is 0·74 (Rehrig *et al* 1999). In the present investigation it is found that the coupling coefficients K_p, K_{31} and K_{33} get enhanced by almost 50%. This enhancement is large when compared to coefficients obtained for most of the piezoelectric materials. The value of K_p at room temperature is found to be slightly more than that of PZT. The value of K_p at room temperature for PZT with Zr/Ti atomic ratio = 52/48 is 0·529 which is higher compared to other Zr/Ti atomic ratios (Berlincourt

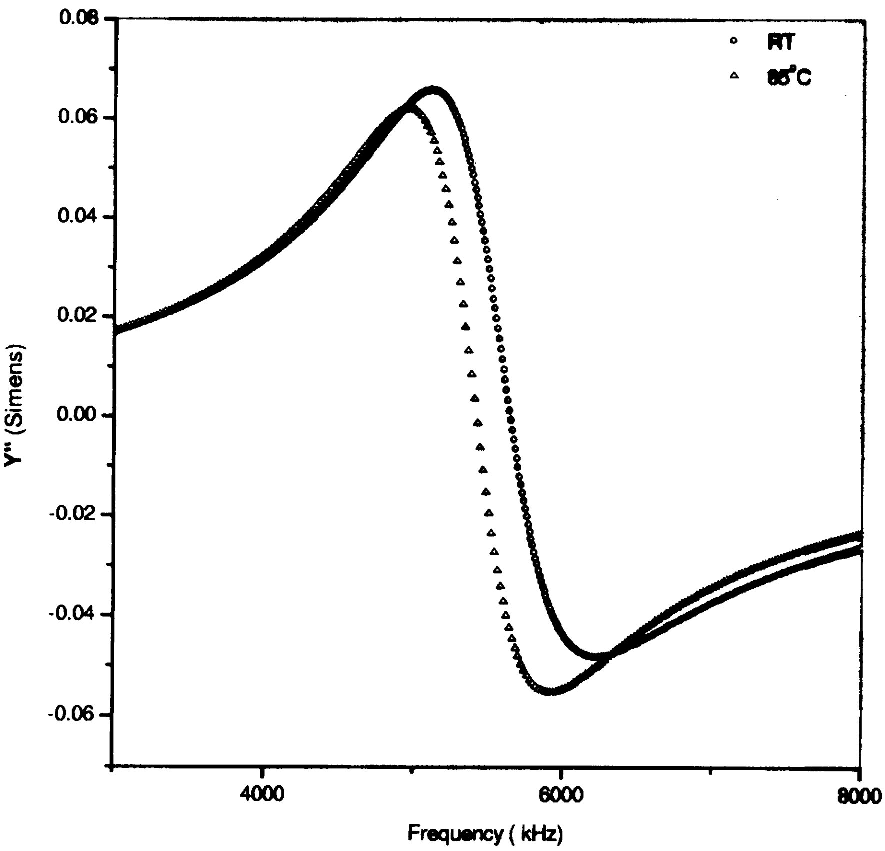

Figure 5. Imaginary part of admittance (Y'') as a function of frequency at the temperatures indicated for $Ba_{1-x}La_xTiO_3$ with $x = 0{\cdot}003$.

et al 1960). It appears from the present investigation that the electromechanical coefficients are not affected much by variation of temperature except in the transition region. However, in respect of K_{33} the variation appears to be more. Hence, it may be concluded that the substitution of lanthanum in place of barium in barium titanate enhances electromechanical coupling coefficients K_{31} and K_{33} through which the piezoelectric coefficient d_{31}, d_{33} and also the piezoelectric voltage coefficient g_{31} are enhanced. Hence this material can be used as a transducer. The advantage of this compound is that it is lead free and hence the degradation of the compound can be avoided.

Figures 8a–c present the variation of d.c. conductivity as a function of inverse of temperature. D.c. conductivity decreases in these samples with increasing lanthanum content. The decrease is about two orders. Increase in density with the increase in lanthanum content and a decrease in tetragonal distortion may be correlated with the decrease in the conductivity. We observe only one slope change for $x = 0{\cdot}001$ and $x = 0{\cdot}0005$ systems and the activation energy for d.c. conduction is around 0·6 eV in these samples indicating hopping mechanism of electron charge conduction. A small kink is observed at the ferroelectric transition temperature of the present samples. The change in slope may be attributed to the release of space charges, which get accumulated at the grain boundaries. The corresponding activation energies calculated are given in table 2. For $x = 0{\cdot}003$ system, with the increase in temperature the conductivity increased up to 111°C and with further increase in temperature up to 128°C conductivity decreased and increased with further increase in temperature.

4. Conclusions

Above results and discussions indicate formation of single phase $Ba_{1-x}La_xTiO_3$ for $x = 0{\cdot}0005$, 0·001, 0·003. Lanthanum doping in $BaTiO_3$ led to slight change in the lattice. Dielectric constant and ferroelectric transition tem-

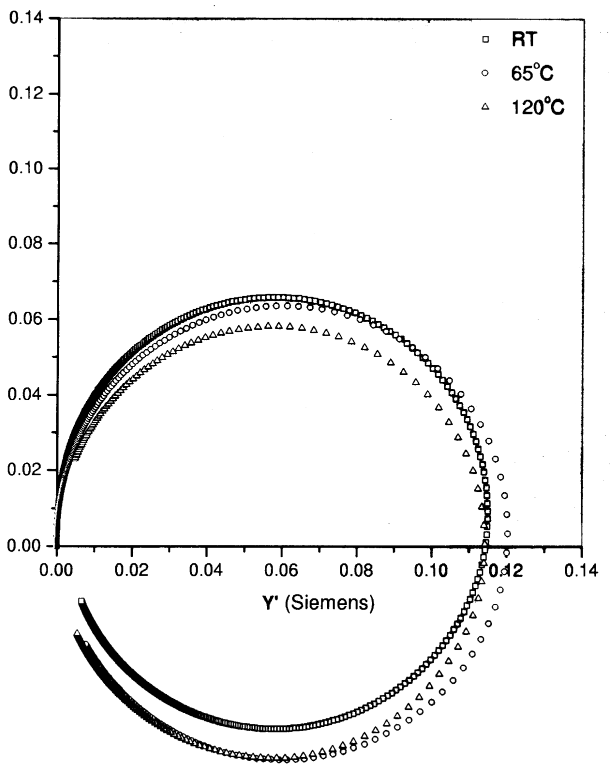

Figure 6. Complex admittance circles (Y' vs Y'') for $Ba_{1-x}La_xTiO_3$ with $x = 0{\cdot}003$.

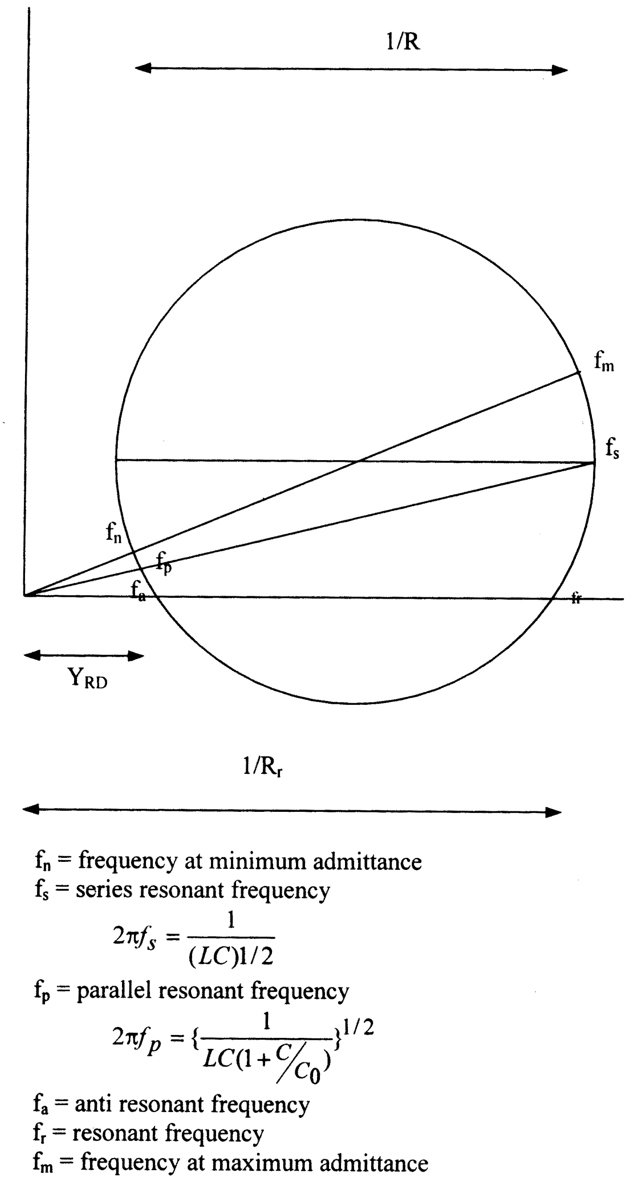

Figure 7. Complex admittance diagram indicating various frequencies involved in resonance and anti-resonance.

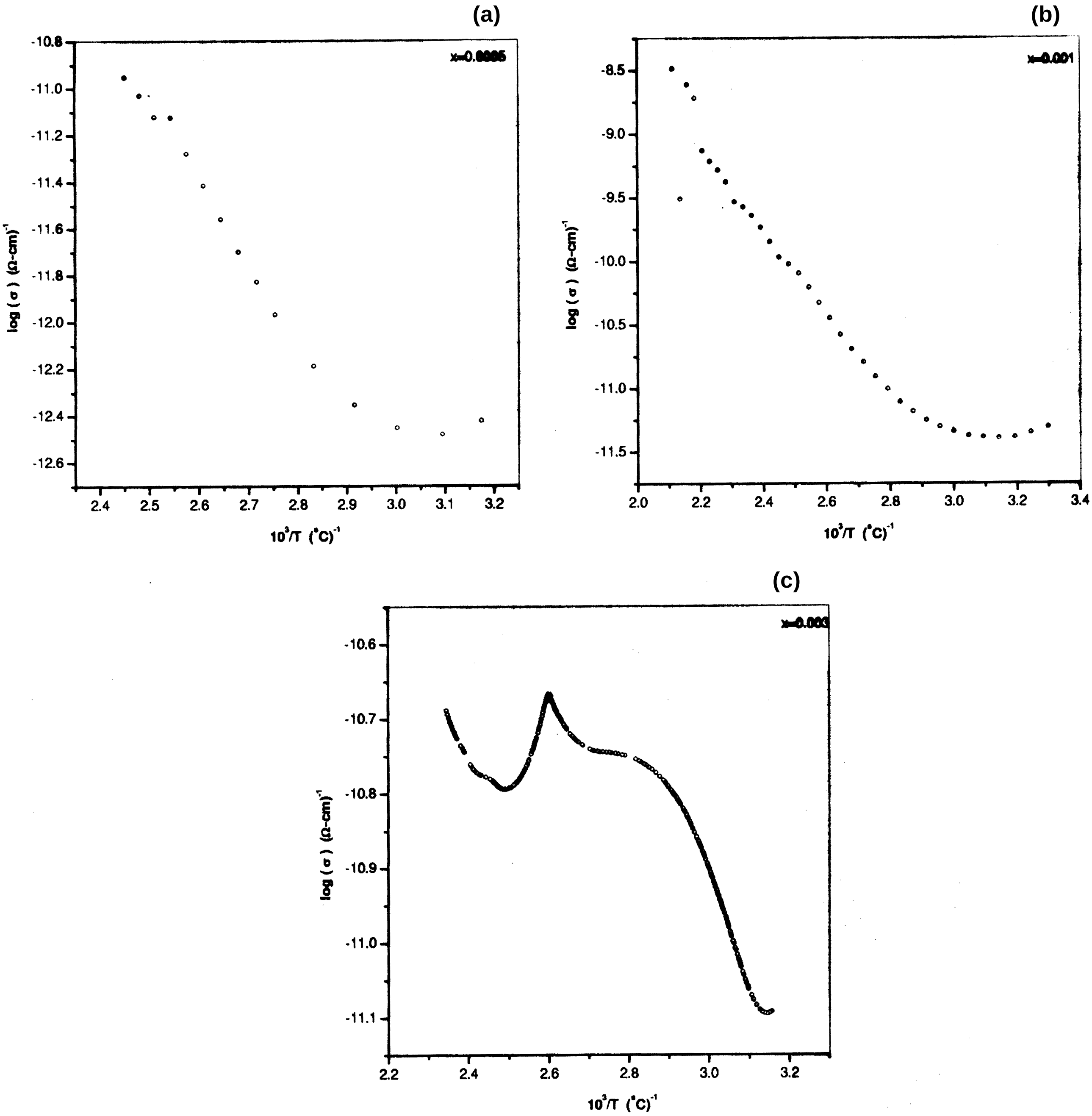

Figure 8. D.c. conductivity variation as a function of inverse of temperature for $Ba_{1-x}La_xTiO_3$.

peratures increased with increase of La content. The sample with $x = 0{\cdot}003$ possess maximum dielectric constant and is characterized for electromechanical coupling. Frequency variation of admittance of these samples showed resonance and anti-resonance behaviour. Complex admittance plots are circles and the radius of the circles showed variation with temperature. A new compound with higher electromechanical coupling coefficients has been synthesized and it may find application as a transducer.

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