

Evidence of two ferroelectric PTCR components in valence-compensated ceramic system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$

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Abstract. The electrical behaviour of valence-compensated ceramic system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ has been studied as a function of temperature (300–600 K) and composition ($x \leq 0.20$), using the method of impedance spectroscopy. The necessary equivalent circuit models that represent the data best have been obtained using impedance and modulus formalisms and grain and grain boundary contributions have been separated out. The compositions $x = 0.20$ and 0.10 show a negative temperature coefficient of resistance (NTCR) behaviour whereas a very small variation of the grain and grain boundary resistance with temperature is observed for $x = 0.05$. A positive temperature coefficient of resistance (PTCR) behaviour having two ferroelectric components is observed for $x = 0.01$. These results reveal limitations in current theories of the PTCR effect.

Keywords. PTCR; valence-compensated ceramic; impedance analysis.

1. Introduction

Titanates, with the general formula ABO_3 ($A = \text{Ca}, \text{Sr}, \text{Ba}$ and Pb), and having perovskite structure, are useful materials because they have applications in a wide variety of electronic devices (Jaffe *et al* 1971; Lines and Glass 1977; Goodman 1986; Moulson and Herbert 1990). With suitable substitutions of A' and B' at A and B sites, such that charge neutrality is maintained, the so-called valence-compensated solid solutions, having the general formula $\text{A}_{1-x}\text{A}'_x\text{B}_{1-x}\text{B}'_x\text{O}_3$ are obtained. These materials show interesting properties which can be controlled by the type of substitution and processing (Moulson and Herbert 1990). For the last few years we have been investigating the possibility of solid solutions formation, between perovskites having widely different electrical behaviour, with a view to identify the promising electronic ceramics for further development (Bahadur and Parkash 1983; Kumar *et al* 1985; Parkash *et al* 1987, 1989a, b, 1990; Upadhyay *et al* 1996). BaTiO_3 is a very popular and extremely useful perovskite that undergoes a ferroelectric to paraelectric phase transition at 120°C where its structure goes from tetragonal to cubic and is usually an electrical insulator. Suitably doped and/or processed BaTiO_3 ceramic becomes semiconducting and has been used to fabricate technologically important devices such as barrier layer capacitors, positive temperature coefficient of resistance (PTCR) thermistors, electro-optic materials etc (Lines and Glass 1977; Moulson and Herbert 1990). Lanthanum cobaltate, LaCoO_3 , is also a perovskite with potential applications as a catalyst for automotive exhaust gases, as an oxygen-electrode catalyst for zinc-air alkaline solution

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batteries used for urban transport and as a cathode material for high temperature solid electrolytic fuel cells (Tedmon *et al* 1969; Meadowcroft 1970; Voórhoeve *et al* 1977; Yamamoto *et al* 1987). The solid solutions $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ have been prepared between BaTiO_3 and LaCoO_3 for $x \leq 0.50$ (Kumar *et al* 1990). La^{3+} ions occupy the Ba^{2+} sites whereas Co^{3+} go to Ti^{4+} sites yielding a valence-compensated material. All these are single phase materials where the structure is cubic for $x > 0.01$ and tetragonal for $x = 0.01$ (Kumar *et al* 1990).

In this paper we report the study of the electrical behaviour of the system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ using the immittance analysis of the impedance data. This study is important as it is known that lanthanum-doped BaTiO_3 shows a positive temperature coefficient of resistance (PTCR) behaviour (Lines and Glass 1977; Basu and Maiti 1986; Moulson and Herbert 1990) and here we are dealing with a valence-compensated lanthanum and cobalt doped BaTiO_3 . The preliminary results have already been reported earlier (Katare *et al* 1996).

2. Experimental

The ceramic system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.20, 0.10, 0.05$ and 0.01) were prepared by conventional solid-state ceramic method. The details of sample preparation and X-ray diffraction studies have been published earlier (Kumar *et al* 1990). Sintered samples in the form of cylindrical pellets with dia 12 mm and thickness about 2 mm and coated with silver paint followed by suitable heat treatment were installed in a sample holder having spring-loaded parallel plate arrangement (Kumar *et al* 1990). Impedance measurements were carried out with the help of HP 4192 A impedance analyzer in the frequency range 100 Hz–2 MHz and temperature range 300–500 K.

3. Complex immittance analysis

The overall dielectric properties of a ceramic system would arise due to contributions from intra-grain, inter-grain and electrode processes (Hodge *et al* 1976; Hooper 1977; Macdonald 1987). The intra-grain and inter-grain processes depend upon the constituents and the processing parameters. Therefore, to understand the effect of additives and the processing parameters, the intra-grain (i.e. grain, g), inter-grain (i.e. grain-boundary, gb) and electrode contributions must be separated out. The method of complex impedance analysis has emerged as a very powerful tool for this. In this method the imaginary part, Z'' , of the experimentally measured impedance,

$$Z^* = Z' - jZ'',$$

of the material is plotted as a function of real part, Z' , at various frequencies. The appearance of three clear semi-circular arcs in this plot indicates the presence of three polarization processes in the system. Since the grain, gb and electrodes have, in general, different response times, these three arcs are usually attributed to the g , gb and electrode processes, the grain response being at the high frequency side and electrode response at low frequencies (Macdonald 1987). A parallel RC circuit has one time constant and hence can be conveniently used as a model to represent one polarization process. A Z'' vs Z' plot for such a RC model contains a semi circular arc in the positive quadrant

(Macdonald 1987; Jonscher 1983; Katare 1990) with its intercept on the Z' -axis at $Z' = R$. The maximum value of Z'' is $R/2$ and occurs at $\omega = 1/RC$ where ω is the angular frequency of measurement. Thus the three arcs appearing in the Z'' vs Z' plot can be simulated by the help of an equivalent circuit model, comprising three parallel RC combinations $R_1 C_1$, $R_2 C_2$ and $R_3 C_3$ connected in series. If $R_1 C_1 < R_2 C_2 < R_3 C_3$ holds, R_1 , R_2 and R_3 can be assumed to correspond to grain, gb and electrode resistance. The values of R_1 , R_2 and R_3 i.e. the grain, gb and electrode resistance are obtained using the intercepts. The values of C s are obtained by finding the frequencies ω_1 , ω_2 and ω_3 where $\omega_1 R_1 C_1 = 1$, $\omega_2 R_2 C_2 = 1$ and $\omega_3 R_3 C_3 = 1$ i.e. where the Z'' vs Z' plot shows a maximum. These tentative values obtained graphically are further refined by using complex non-linear least squares procedure (CNLS) (Macdonald 1987; Pandey 1992, 1993) (A CNLS programme 'IMPSPEC. BAS' developed in BASIC by authors is available and can be supplied on request). This model is not unique but to facilitate

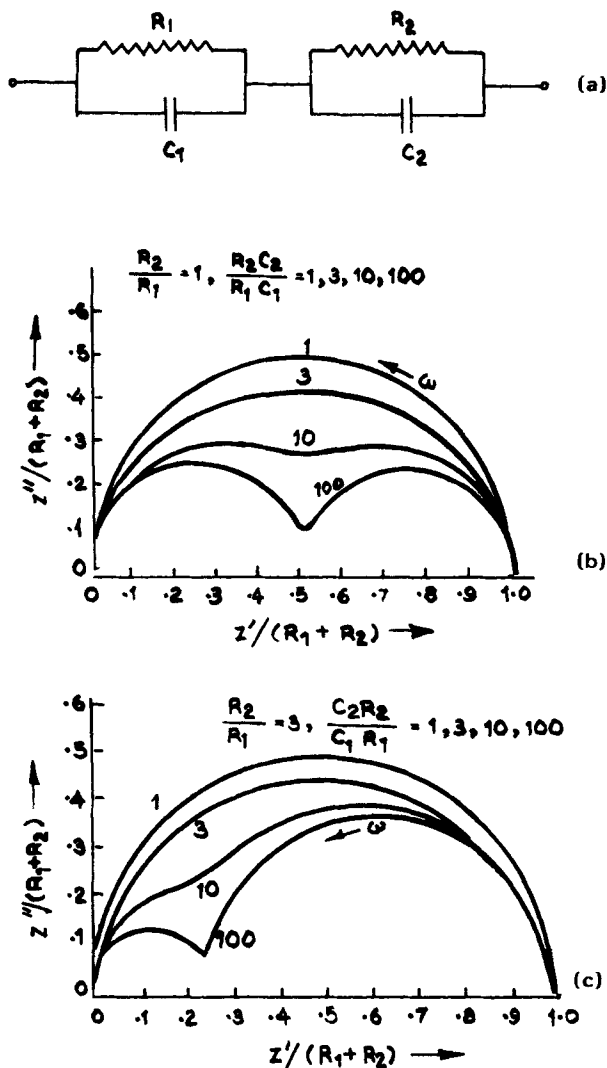


Figure 1. a-c.

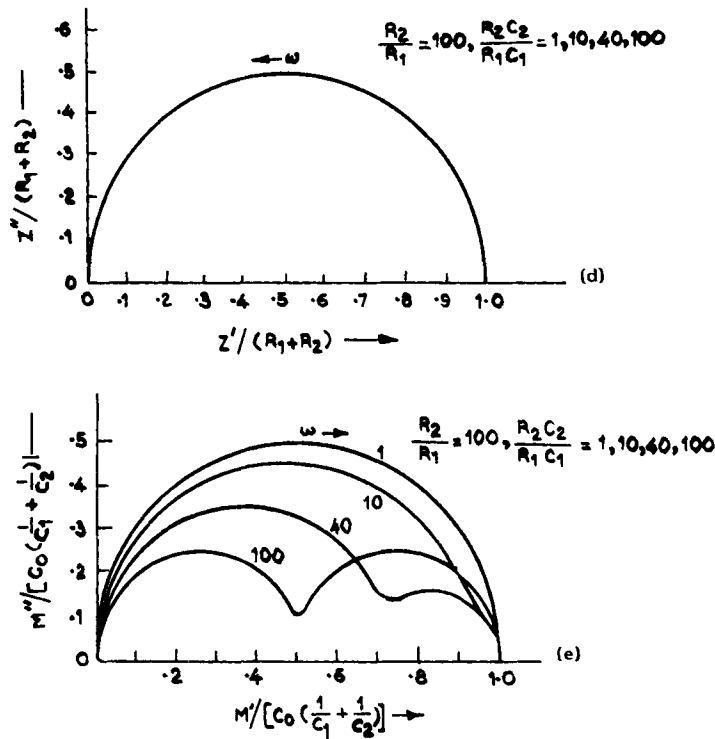


Figure 1. (a) Model comprising two parallel RC circuits connected in series, (b) normalized $Z''/(R_1 + R_2)$ vs $Z'/(R_1 + R_2)$ plots for various values of $R_2C_2/(R_1C_1)$ and $R_2/R_1 = 1$, (c) $R_2/R_1 = 3$, (d) $R_2/R_1 = 100$ and (e) normalized $M''/[C_0(1/C_1 + 1/C_2)]$ vs $M'/[C_0(1/C_1 + 1/C_2)]$ plot for various values of $R_2C_2/(R_1C_1)$ and $R_2/R_1 = 1$.

a proper interpretation of the data it is always preferable to choose simple models. The choice of an appropriate model is greatly facilitated by comparing the experimental plots with those simulated for different models. A method for choosing an appropriate equivalent circuit model has been described in detail by Macdonald (1987) and Pandey *et al* (1995). The simulated plots for a model comprising two parallel RC circuits connected in series are given in figure 1 (a–e) for a ready reference. If these two RC combinations are further connected to a series resistance R , the shape of the Z'' vs Z' plot would remain the same except that it would get shifted by R i.e. the high frequency intercept would be at $Z' = R$.

The dielectric behaviour of a system can be expressed in terms of the so-called inter-related immittance functions: impedance $Z^* = Z' - j Z''$, admittance $Y^* = 1/Z^* = Y' + jY''$, relative permittivity $\epsilon^* = (j\omega CoZ^*)^{-1} = \epsilon' - j\epsilon''$ and modulus $M^* = (\epsilon^*)^{-1} = j\omega CoZ^* = M' + jM''$, where $j = \sqrt{-1}$ and $\omega = 2\pi f$. Here f is the frequency of the ac excitation and Co the capacitance of the empty cell used to house the sample. For magnetic materials the modulus can be defined in terms of the magnetic permeability (von Hippel 1954; Katare 1997). Since these immittance functions have inverse relations, they can be conveniently used to highlight certain information that is being suppressed in a particular representation. For example, for the situation where two polarization processes are present it has been shown that if the time constants R_1C_1

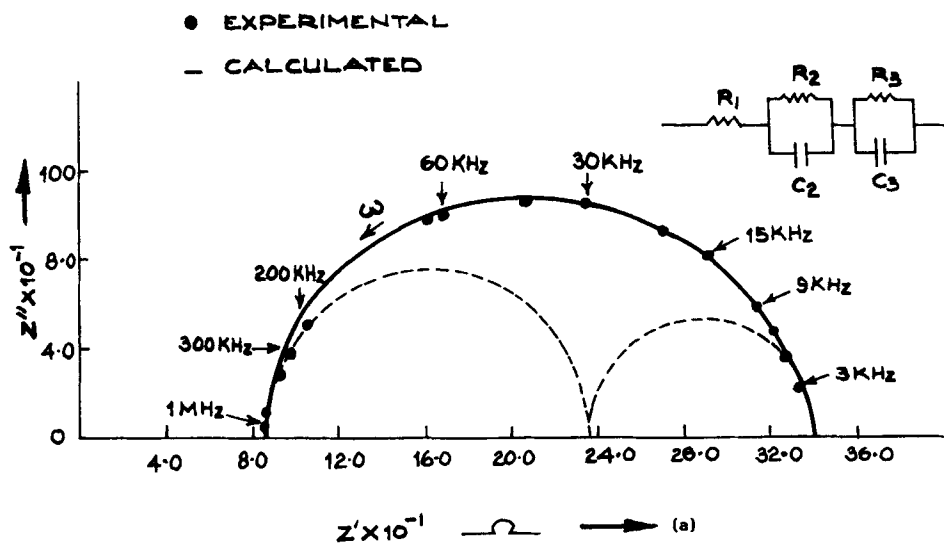
and R_2C_2 corresponding to the two processes are widely separated and R_2 is much different from R_1 , an almost single semi circular arc would appear in the Z'' vs Z' plot (see figure 1d). This would indicate the presence of one process only. But a M'' vs M' plot for the same situation contains two distinct arcs (see figure 1e), indicating the presence of two processes. It has been, thus, concluded that appearance of a single clear semicircular arc in Z'' vs Z' plot does not necessarily mean the presence of single polarization process. Therefore, if the experimental Z'' vs Z' plot contains a single semicircular arc, plots using other formalisms also must be looked at. Our experience has been that usually Z^* and M^* formalisms suffice (Pandey *et al* 1995).

4. Results

A typical Z'' vs Z' plot for the system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x = 0.20$ is given in figure 2a and the corresponding spectroscopic plots are shown in figure 2b. The Z'' vs Z' plot of figure 2a is not a clear semicircular arc and has intercepts on the Z' -axis at both the frequency ends. Comparison of this plot with the simulated plots of figure 1 (b–e) indicates that an equivalent circuit model that may represent the data well would contain two parallel RC combinations say R_2C_2 and R_3C_3 , connected in series, further connected to a series resistance R_1 where $R_3C_3 \parallel R_2C_2 \approx 2$, $R_3 \approx R_2$, $R_1 \approx 85\ \Omega$ and $R_1 + R_2 + R_3 \approx 340\ \Omega$. The accurate values of the components R_1 , R_2 etc were obtained using the CNLS program (Pandey 1992, 1993) and are given in table 1. The continuous line of figure 2a corresponds to the values of Z' and Z'' calculated using these best fit values. Figure 2b shows the corresponding spectroscopic plot. The fits are very good. It was found that the impedance data for $x = 0.20$ for other temperatures could be well represented by the same model. The values for R_1 , R_2 , C_2 etc are given in table 1 for other temperatures also. Since we are interested in grain and gb contributions, R_3 and C_3 values, that are attributed to the electrodes, are not given.

The typical impedance data for the composition $x = 0.10$ is shown in figure 3a. It contains a big depressed arc at high frequency side and a small arc at the low frequency side. A glance at figures 1 a–e indicates that the big depressed arc of figure 3a may arise due to two processes whose time constants have a ratio approximately equal to 3 and the corresponding resistances are almost equal. A simple model that could represent this behaviour well and would directly correspond to the grain, gb and electrode contributions would comprise three parallel RC circuits, with time constants R_1C_1 , R_2C_2 and R_3C_3 , connected in series. Tentative independent arcs, corresponding to such a situation, are shown by dotted curves in figure 3a. Assuming that $R_1C_1 < R_2C_2 < R_3C_3$ i.e. R_1C_1 corresponds to the grain, R_2C_2 to the gb and R_3C_3 to the electrodes, the values of R_1 , C_1 , R_2 , C_2 , etc were obtained from the intercepts as $R_1 \approx 13.2 \times 10^2\ \Omega$, $R_2 \approx 17 \times 10^2\ \Omega$, $R_3 \approx 6 \times 10^2\ \Omega$, $R_2C_2/R_1C_1 \approx 3$, $R_3C_3/R_2C_2 \approx 30$. The exact values of these obtained using the CNLS program are given in table 1. The Z' and Z'' values obtained using the best fit parameters are shown by continuous lines in figures 3a and b. The M values are shown in figure 4. It is clear that the fits are very good.

The data for the composition $x = 0.05$ and $x = 0.01$ were also analyzed in the same way. The best fit values of R_1C_1 etc are given in table 1 for different temperatures. Since we are interested in the grain and gb behaviour, the values of R_1 , C_1 and R_2 , C_2 only i.e. those for grain and gb , are given in table 1.



$\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.20$), Temp = 200°C

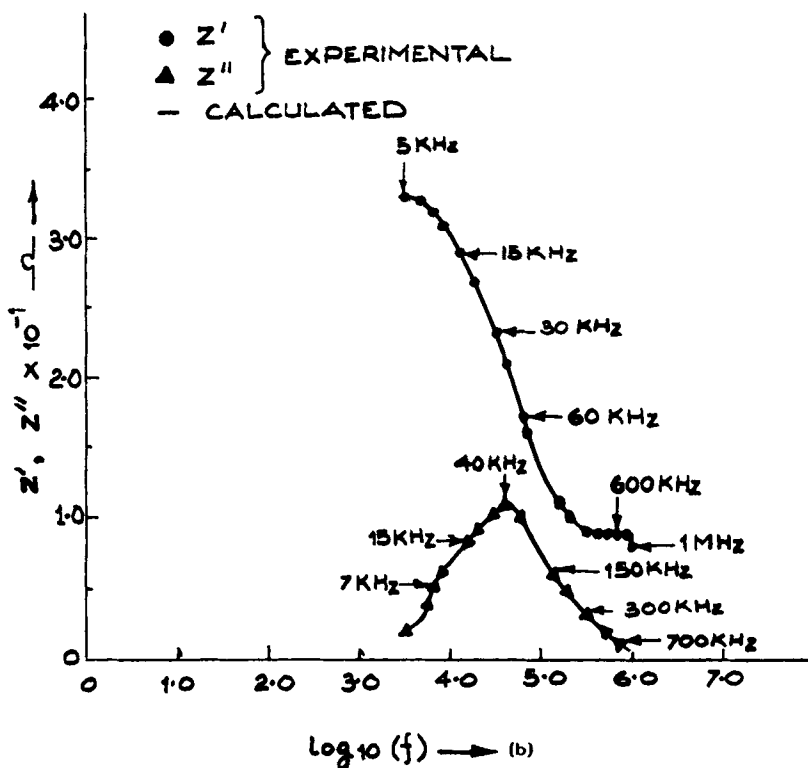


Figure 2. (a) Z'' vs Z' and (b) Z' and Z'' vs $\log_{10}(f)$ plots for the ceramic $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.20$) at temperature 200°C (●, ▲, experimental values; —, values calculated using CNLS fitting for the model shown in the corner; ----, tentative curves indicating the independent contributions of R_1 , R_2 , C_2 and R_3 , C_3).

Table 1. Values of R_1 and C_1 (grain) and R_2 and C_2 (grain boundary) obtained using CNLS fitting for $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ at various temperatures and compositions x .

x	Temperature (K)	$R_1(\Omega)$	$C_1(\text{F})$	$R_2(\Omega)$	$C_2(\text{F})$
0.01	313	156 ± 7	$(6.19 \pm 0.22) \times 10^{-9}$	$(2.38 \pm 0.04) \times 10^3$	$(5.18 \pm 0.07) \times 10^{-9}$
	373	86 ± 17	$(6.84 \pm 0.64) \times 10^{-9}$	$(0.59 \pm 0.07) \times 10^3$	$(9.00 \pm 0.07) \times 10^{-9}$
	423	134 ± 9	$(8.33 \pm 0.41) \times 10^{-9}$	$(2.69 \pm 0.15) \times 10^3$	$(10.12 \pm 0.02) \times 10^{-9}$
	473	1605 ± 184	$(4.03 \pm 0.21) \times 10^{-9}$	$(49.71 \pm 2.82) \times 10^3$	$(1.07 \pm 0.03) \times 10^{-9}$
	523	5245 ± 322	$(0.88 \pm 0.03) \times 10^{-9}$	$(38.76 \pm 0.59) \times 10^3$	$(0.61 \pm 0.01) \times 10^{-9}$
0.05	313	1137 ± 81	$(2.82 \pm 0.08) \times 10^{-9}$	$(17.34 \pm 0.62) \times 10^3$	$(1.85 \pm 0.03) \times 10^{-9}$
	323	1274 ± 87	$(2.51 \pm 0.07) \times 10^{-9}$	$(17.74 \pm 0.59) \times 10^3$	$(1.74 \pm 0.02) \times 10^{-9}$
	373	1443 ± 66	$(1.34 \pm 0.03) \times 10^{-9}$	$(13.59 \pm 0.27) \times 10^3$	$(1.47 \pm 0.02) \times 10^{-9}$
	423	1668 ± 60	$(1.07 \pm 0.02) \times 10^{-9}$	$(11.58 \pm 0.26) \times 10^3$	$(1.74 \pm 0.03) \times 10^{-9}$
	473	1825 ± 52	$(6.82 \pm 0.11) \times 10^{-10}$	$(12.79 \pm 0.32) \times 10^3$	$(1.31 \pm 0.02) \times 10^{-9}$
	523	1380 ± 44	$(4.82 \pm 0.09) \times 10^{-10}$	$(12.59 \pm 0.21) \times 10^3$	$(7.04 \pm 0.08) \times 10^{-10}$
0.10	309	3295 ± 86	$(5.11 \pm 0.07) \times 10^{-10}$	$(30.61 \pm 0.69) \times 10^3$	$(6.79 \pm 0.07) \times 10^{-10}$
	333	3295 ± 77	$(4.43 \pm 0.06) \times 10^{-10}$	$(37.71 \pm 0.89) \times 10^3$	$(5.47 \pm 0.05) \times 10^{-10}$
	373	2176 ± 63	$(3.70 \pm 0.06) \times 10^{-10}$	$(29.30 \pm 0.61) \times 10^3$	$(3.82 \pm 0.03) \times 10^{-10}$
	423	1867 ± 65	$(2.98 \pm 0.05) \times 10^{-10}$	$(17.35 \pm 0.13) \times 10^3$	$(3.12 \pm 0.04) \times 10^{-10}$
	473	1508 ± 86	$(2.49 \pm 0.06) \times 10^{-10}$	$(6.72 \pm 0.08) \times 10^3$	$(3.35 \pm 0.10) \times 10^{-10}$
	523	1308 ± 109	$(1.80 \pm 0.06) \times 10^{-10}$	$(1.67 \pm 0.11) \times 10^3$	$(5.88 \pm 0.71) \times 10^{-10}$
0.20	309	402 ± 25	--	2005 ± 22	$(1.28 \pm 0.03) \times 10^{-10}$
	373	366 ± 12	--	186 ± 9	$(1.14 \pm 0.15) \times 10^{-9}$
	423	178 ± 4	--	103 ± 19	$(1.72 \pm 0.19) \times 10^{-8}$
	473	88 ± 3	--	149 ± 6	$(1.79 \pm 0.33) \times 10^{-8}$

The behaviour of R_1 and R_2 as a function of temperature is shown in figures 5 and 6 for all the compositions. It is seen that for $x = 0.20$ and 0.10 both R_1 and R_2 decrease as temperature rises whereas they change very little for $x = 0.05$ and show a steep rise at $T \approx 400$ K for $x = 0.01$. This temperature is close to the ferroelectric to para electric Curie temperature of BaTiO_3 . The plots of C_1 and C_2 as a function of temperature for $x = 0.01$, shown in figure 7b indicates that C_1 and C_2 show a peak at about 400 K. This temperature is exactly the same where R_1 and R_2 for $x = 0.01$ start rising (see figure 7a). Since the tetragonality of BaTiO_3 has not been destroyed in the solid solution $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x = 0.01$, it could be inferred that the temperature where C_1 and C_2 peak is the Curie temperature for ferroelectric to paraelectric phase transition for the two regions represented by $R_1 C_1$ and $R_2 C_2$ i.e. grain and grain-boundaries. It is further inferred that both the grain and *gb* show a PTCR behaviour.

5. Discussion

The PTCR effect in polycrystalline ceramics is believed to be grain-boundary phenomenon and is explained in terms of theories proposed by Heywang and others (Heywang 1961, 1971; Lines and Glass 1977; Daniels *et al* 1978; Lewis and Catlow 1985; Jonker 1987). In its essence, the model assumes that in the donor-doped BaTiO_3

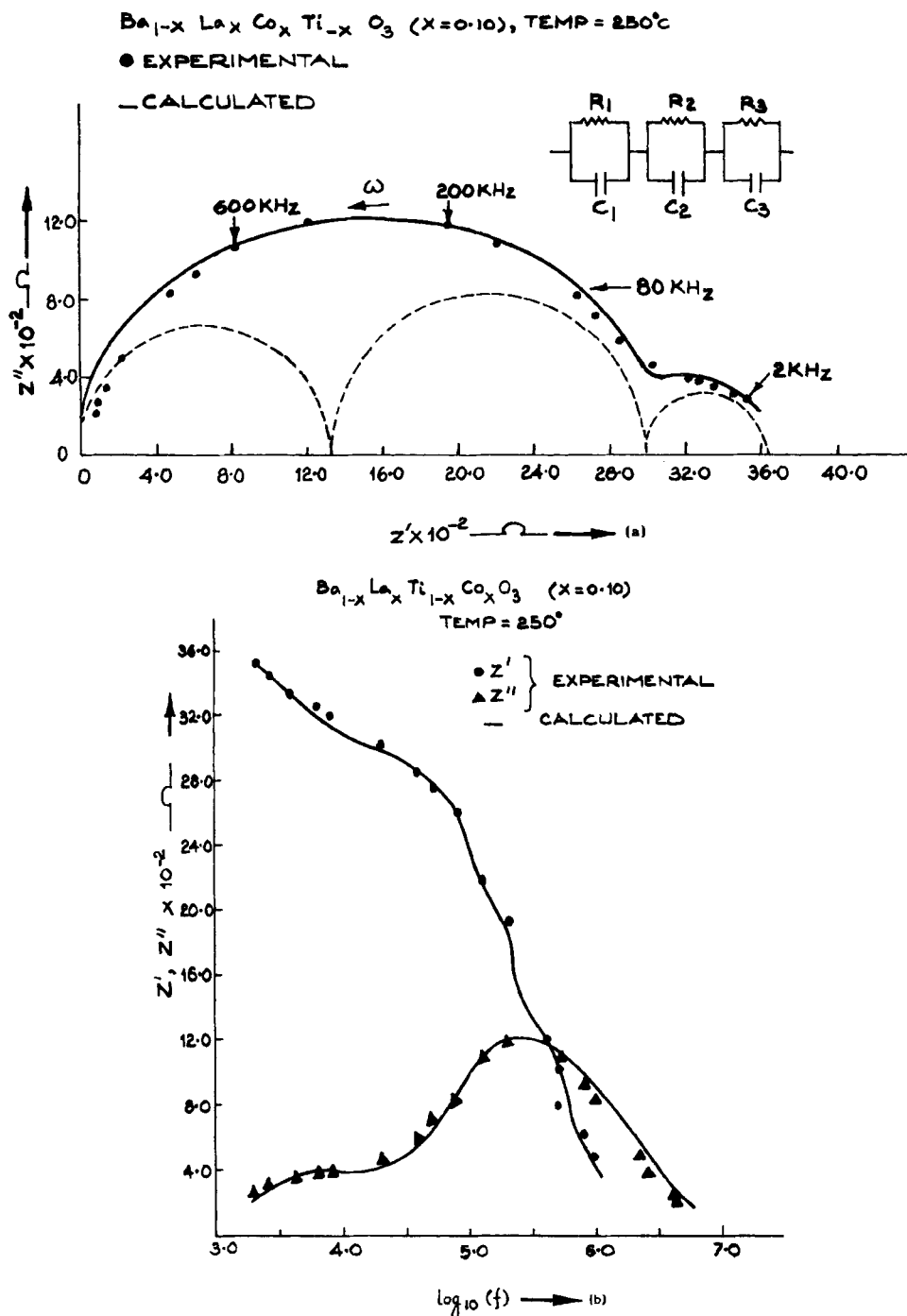


Figure 3. (a) Z'' vs Z' and (b) Z' and Z'' vs $\log_{10}(f)$ plots for the system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.10$) at temperature 250°C. (●, ▲, experimental values, —, values calculated using CNLS fitting for the model shown in the corner; ----, tentative arcs indicating the independent contribution of R_1C_1 , R_2C_2 and R_3C_3).

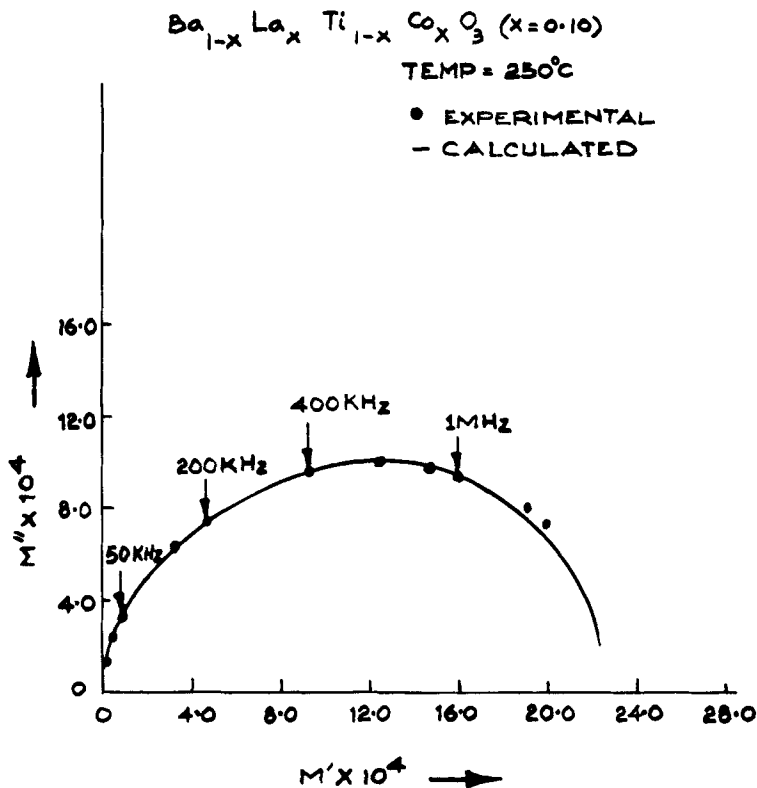


Figure 4. M'' vs M' plot for $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.10$) at temperature 250°C . (●, experimental values; —, values calculated using CNLS fitting for the model shown in figure 3a).

the electron acceptor states in the grain-boundary together with nearby ionized donor states give rise to an electrical double layer, extending up to some distance into the grains. Conduction band electrons coming up to the *gb* then experience a potential barrier whose height depends inversely upon the dielectric constant. In the region near the Curie temperature where the dielectric constant diverges, barrier height decreases and the resistivity drops. Below the Curie temperature, since the material is ferroelectric, the electrical double layer is partially cancelled and the *gb* resistance may get short circuited due to the charges residing at the domain surfaces opening up at the *gb*. This would result in a low resistance below the ferroelectric Curie temperature. After the ferroelectric to paraelectric transition temperature the dielectric constant drops down and the barrier height increases very fast rendering the *gb* highly resistive.

There are number of observations which can be explained in terms of the above argument. However, there have been reports of PTCR behaviour due to Schottky barrier in reduced BaTiO_3 single crystals (MacChesney and Potter 1965; Lines and Glass 1977). Recently Sinclair and West (1989) have observed, through combined impedance and modulus plots, the presence of two PTCR components in doped BaTiO_3 . In order to explain this in light of the existing theory of the PTCR phenomenon, they had to postulate a microstructural model which considers the presence of

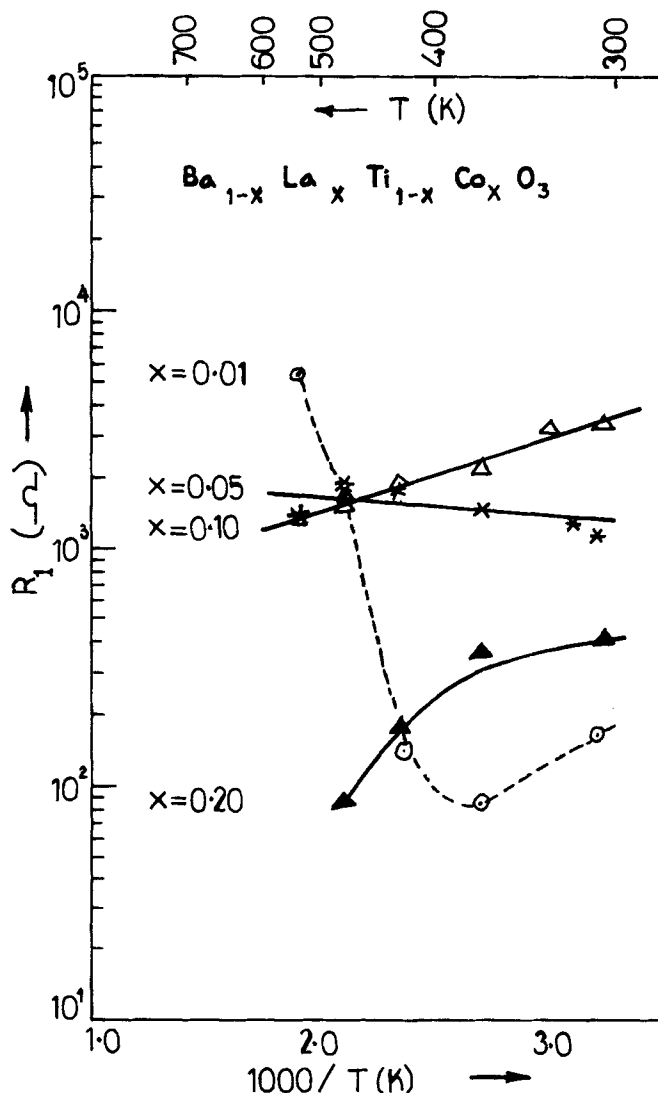


Figure 5. R_1 vs $1000/T$ plots for the ceramic $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x = 0.01, 0.05, 0.10$ and 0.20 .

a ferroelectric-resistive surface layer surrounding each grain where the interior of the grain was conducting. However they could not present any evidence in support of this. They also mention, without giving any details, observations of two ferroelectric PTCR components, in some of their samples. In view of these, they further concluded that the current theories of the PTCR effect must be revised to explain the variety of phenomena revealed by in-depth ac analysis.

The results reported in this paper viz. presence of two ferroelectric PTCR components in the system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.01$) also cannot be directly explained in terms of the current theories (outlined briefly in the preceding paragraphs) as they do not predict two components. However, an attempt to explain the observations can be made as is discussed in what follows. In the system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.01$)

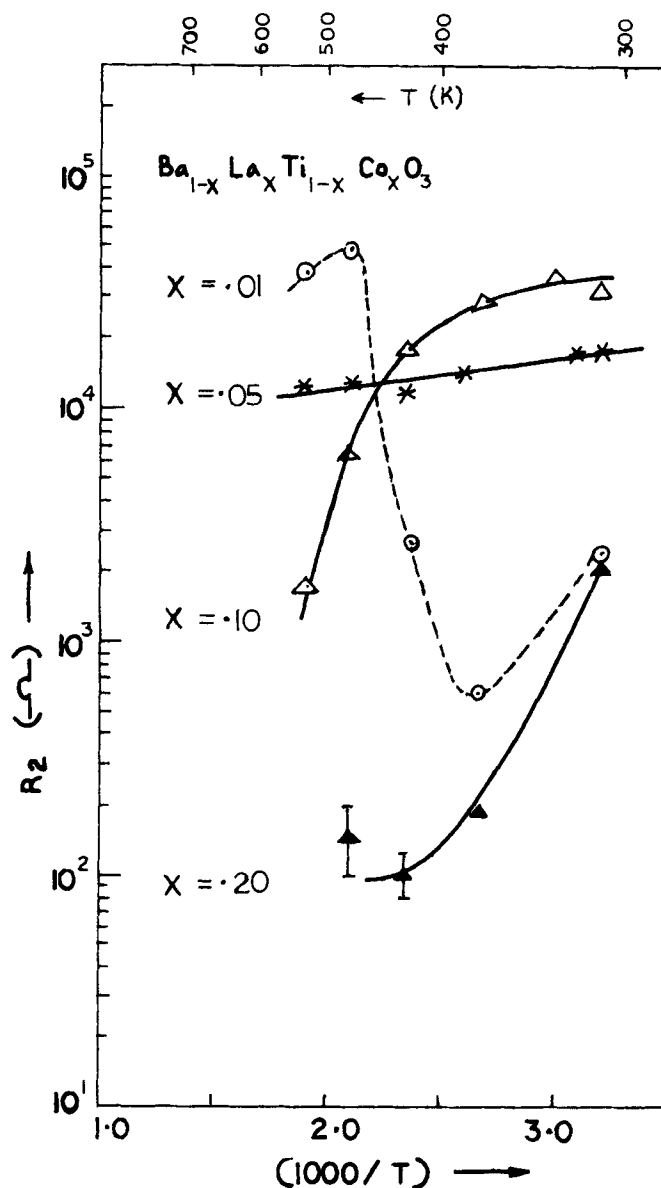


Figure 6. R_2 vs $1000/T$ plots for the system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x = 0.01, 0.05, 0.10$ and 0.20 .

La^{3+} ions occupy the Ba^{2+} sites and Co^{3+} occupy the sites normally occupied by Ti^{4+} . Thus this system is valence compensated. Since the distribution of La^{3+} and Co^{3+} ions is statistical, the probability that the effective valence compensation would occur uniformly throughout the same granular unit may be small. It is very likely that La^{3+} ions sitting at Ba^{2+} sites and Co^{3+} at Ti^{4+} sites are far away from each other. La^{3+} ions substituting the Ba^{2+} ions would give rise to donor levels whereas Co^{3+} ions going to Ti^{4+} sites would give acceptor states. Thus a grain may comprise separate regions having donor and acceptor levels. It means that there is a global charge compensation

but not regional. Since our samples were sintered in open atmosphere, the grain boundaries may have extra oxygen. It is known that adsorbed oxygen in BaTiO_3 tends to create acceptor levels (Moulson and Herbert 1990). Thus the gb would be richer in acceptor levels than the intra-grain regions having acceptor levels. Now we can apply the Heywang model. The intra-grain acceptor levels would give rise to electrical double layer (Schottky barrier) within the grain. The gb acceptor states too would create electrical double layer near the grain-boundary. Some of the conduction band electrons travelling up to the gb would experience the intra-grain potential and the others would experience the gb potential barrier. These potential barriers are inversely related to the dielectric constant. After the ferroelectric to paraelectric transition temperature, these potential barriers would rise very fast yielding the two PTCR components, one due to the intra-grain barrier and the other due to inter-grain (gb) barrier. The response time

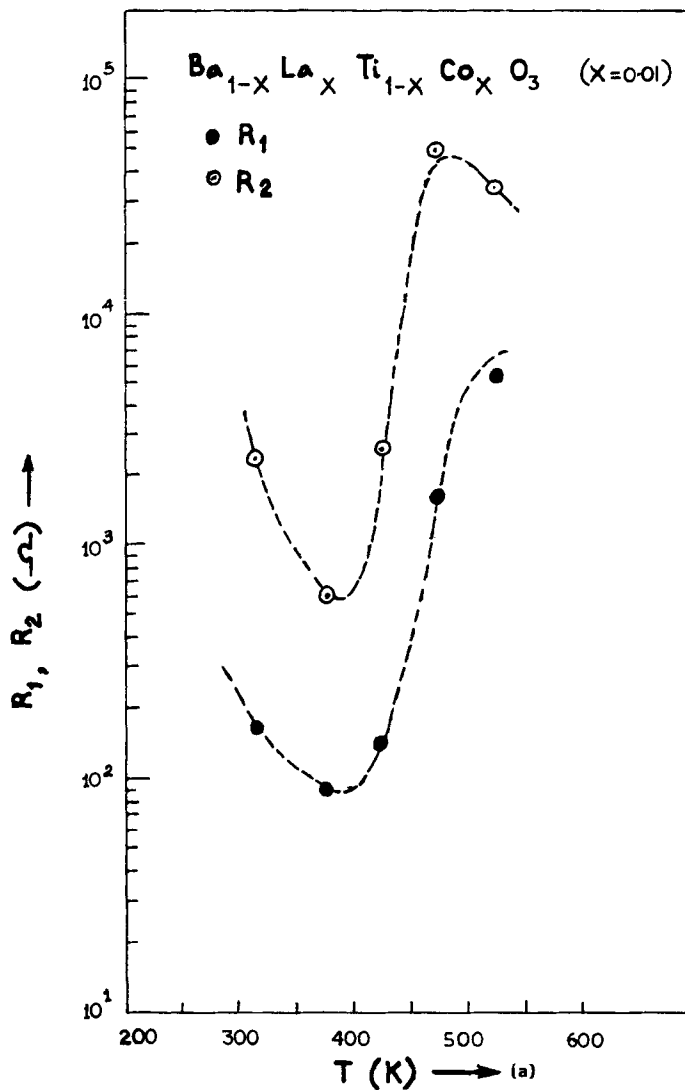


Figure 7a.

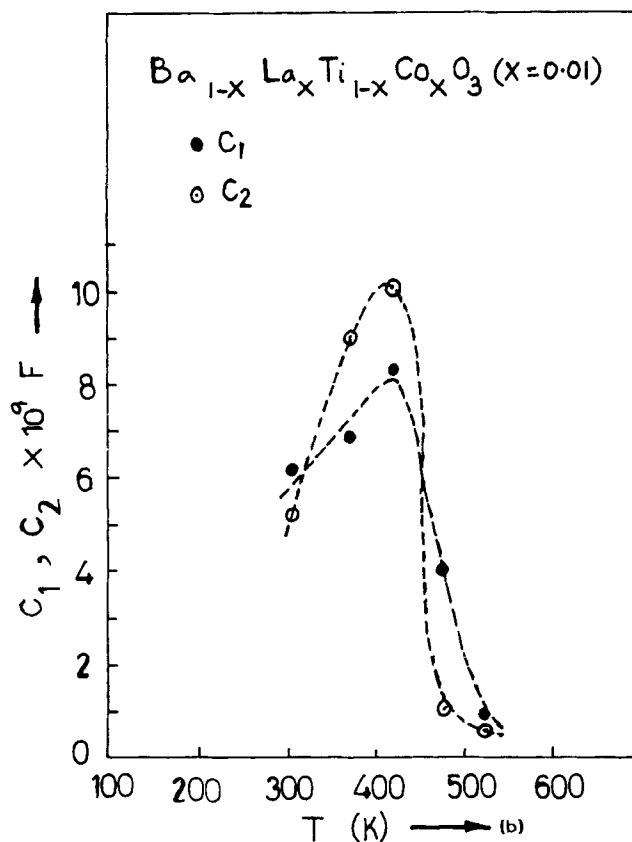


Figure 7. Plots of (a) R_1 and R_2 and (b) C_1 and C_2 vs temperature for $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x=0.01$.

for the charge transfer inside the grain would be shorter as compared to that in *gb*. Since the ac impedance analysis is capable of probing into such process, the two PTCR components are being revealed.

It should be mentioned that if our line of reasoning is correct all BaTiO_3 -based ceramics having this type of heterovalent valence-compensation would show two ferroelectric PTCR components. A detailed and quantitative study on these lines is in progress and will be published elsewhere. We believe that this is probably the first report of PTCR effect in valence-compensated solid solution. It is also worth mentioning now that the composition $x=0.20$ and $x=0.10$ have NTCR and do not show a PTCR behaviour. It is not surprising since the structure for these values of x is cubic and therefore no divergence of dielectric constant can take place. The composition $x=0.05$ shows very little variation in grain and *gb* resistance. The structure for $x=0.05$ is cubic so we cannot expect ferroelectricity. However, since $x=0.01$ has a tetragonal structure, it can be assumed that $x=0.05$ is a border-line case and traces of tetragonality there are not detectable by X-rays. A very little variation in grain and *gb* resistances with temperature, then, would mean that the number of charge carriers in the interface states is almost equal to that required to compensate for the polarization divergence, eliminating the formation of depletion layers (Lines and Glass 1977).

6. Conclusions

- (i) The valence-compensated ceramic system $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.20, 0.10, 0.05$ and 0.01) has been studied using complex impedance analysis. The grain and grain-boundary resistances for the compositions $x = 0.20$ and 0.10 show a NTCR behaviour whereas for $x = 0.05$ very little variation of resistance with temperature is observed.
- (ii) The composition $x = 0.01$ shows a PTCR behaviour with two ferroelectric components. This has been qualitatively explained in terms of the possible acceptor states that would exist inside the grains due to a statistical distribution of Co^{3+} ions going to Ti^{4+} sites along with the acceptor states arising at the grain boundaries due to oxygen. La^{3+} ions going to Ba^{2+} sites act as donors. Due to the statistical nature of the La^{3+} going to Ba^{2+} and Co^{3+} going to Ti^{4+} , only a global, but not regional, charge compensation would be achieved. This would lead to intra-grain and grain-boundary depletion layers and potential barriers. As the response times for the intra-grain and grain-boundary charge transfers would be, in general, different, the ac impedance analysis successfully reveals the two components. We believe that PTCR with two components will be observed in other similar solid solutions of BaTiO_3 , involving heterovalent valence compensation.
- (iii) The existing theories of PTCR effect concentrate on the grain-boundary behaviour and are inadequate for explaining the variety of phenomena observed. This agrees with a similar conclusion recently drawn by Sinclair and West (1989).

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