Dielectric anomaly and low frequency dispersion in ferroelectric materials at high temperatures

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A dielectric anomaly related to the observed departure from the Curie–Weiss law in several Aferroelectric materials has been characterized in this work in ferroelectric $BaTiO_3$. The electrical properties of the material were investigated using the a.c. analysis technique. From the analysis of the permittivity versus frequency curves collected at various temperatures, we discuss the anomalous behaviour as a result of a low frequency dispersion phenomenon due to the characteristics of the conduction processes at the material inhomogeneities.

1. Introduction

The departure from the Curie–Weiss law because of a strong increment of permittivity or capacitance at high temperatures, above the Curie point in ferroelectric materials, is a dielectric anomaly which has been observed in several works [1–4]. Some authors have supposed that this anomaly should be related to additional polarization phenomena, perhaps involving a grain-boundary impedance. R. Flores–Ramírez *et al.* [4] observed this phenomenon in ferroelectric $BaTiO_3$, and its analysis was carried out in terms of the conduction processes at grains and grain boundaries.

In this work we present results of a similar study on this material using the a.c. analysis technique to look for more detailed information. We found a strong relation between the anomaly and a dielectric dispersion phenomenon over lower frequencies than those related to the dipole rotation [5, 6]. The a.c. analysis technique has been widely used for the study of many dielectric solids and permits the separation of the grain electrical properties from those corresponding to the grain boundaries, by representing the material through a circuit combination of resistance–capacitance (R–C) networks in parallel, connected in series [4, 7, 8].

2. Experimental procedure

$BaTiO_3$ was elaborated, starting from $BaCO_3$ and TiO_2 powders of high purity. These reagents were mixed in an automatic agate mill for 1 h, dried and calcined at 1000 °C for 1 h. The mixture was then remilled for 1 h and polyvinyl alcohol solution was used as the binder. The redried powder was pressed at 120 MPa into discs of 13 mm in diameter and ~1.9 mm in thickness. Then the discs were sintered at 1350 °C for 2 h.

For dielectric property measurements, silver electrodes were fired on both surfaces of the sintered discs. The temperature dependence of permittivity was carried out by using an LCR meter (PM 6303 Philips Germany) at 1 kHz from 25 °C up to ~410 °C. The a.c. measurements were performed in an impedance analyser (HP 4192A) over the frequency range ~20–5×10^5 Hz and temperature range ~250–450 °C. Both kinds of measurements were automatically controlled by a computer. The work takes also into account the results observed in other $BaTiO_3$ samples elaborated by the same route.

3. Results and discussion

In Fig. 1 the temperature dependence of permittivity of the ferroelectric $BaTiO_3$ measured at the fixed frequency of 1 kHz is given. This shows a ferroelectric–paraelectric phase transition at about 128 °C, in good agreement with the literature. Moreover, there is a large departure from the Curie–Weiss law close to 350 °C characterized by an abrupt increment of permittivity as the temperature increases.

As we have mentioned above, a study of the material properties was carried out by using the a.c. analysis technique in order to investigate the origin of this anomalous behaviour. In general, the a.c. measurements can be expressed in terms of the complex admittance ($Y = Y' + jY''$), complex impedance ($Z = Z' - jZ''$) and complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) with the following transformation relationships

$$Y(\omega) = [Z(\omega)]^{-1} \quad (1)$$

and

$$Y(\omega) - Kj\omega\varepsilon_0\varepsilon \quad (2)$$

where ω is the angular frequency ($\omega = 2\pi f$), ε_0 the permittivity of free space and K a geometrical factor,

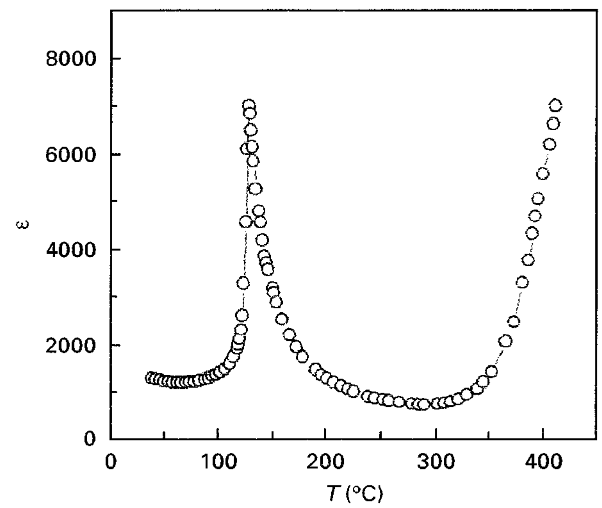

Figure 1 Temperature dependence of permittivity of $BaTiO_3$ measured at 1 kHz.

i.e. the ratio between the surface area and the thickness of the specimen.

The systematic procedure was to plot the complex impedance plane Z'' versus Z' to elucidate the appropriate equivalent circuit model for the material. In Fig. 2a–d we show these plots for some temperatures, each point in each figure corresponding to a different frequency. From all the observed results we can choose as a good approximation the series combination of two lumped circuits, R_g–C_g connected in parallel and R_{gb}–C_{gb} also in parallel, associated with the grain (g) and grain boundary (gb) phases, respectively. It is well known that the complex impedance of this equivalent circuit is represented by the superposition of arcs corresponding to the two R–C networks [4, 7, 8]. For a given temperature, the conduction processes at the grains are represented by the high frequency arc and those at the grain boundaries by the low frequency arc. In particular, the diameters of the arcs represent the resistance R of the material phases, while the arc maxima are obtained at the corresponding conduction relaxation frequencies ω_0 which satisfy the relation $\omega_0 CR = 1$. In Table I we give R_g and R_{gb} after the fitting of the arcs and we observe that $R_g < R_{gb}$. This result, together with the typical higher dimensions of the grains in comparison with those of the grain boundaries, suggests that the grain conductivity is significantly higher than that for the grain boundaries. In other words, the grain phase is of conductive type while the grain boundary phase is of resistive type.

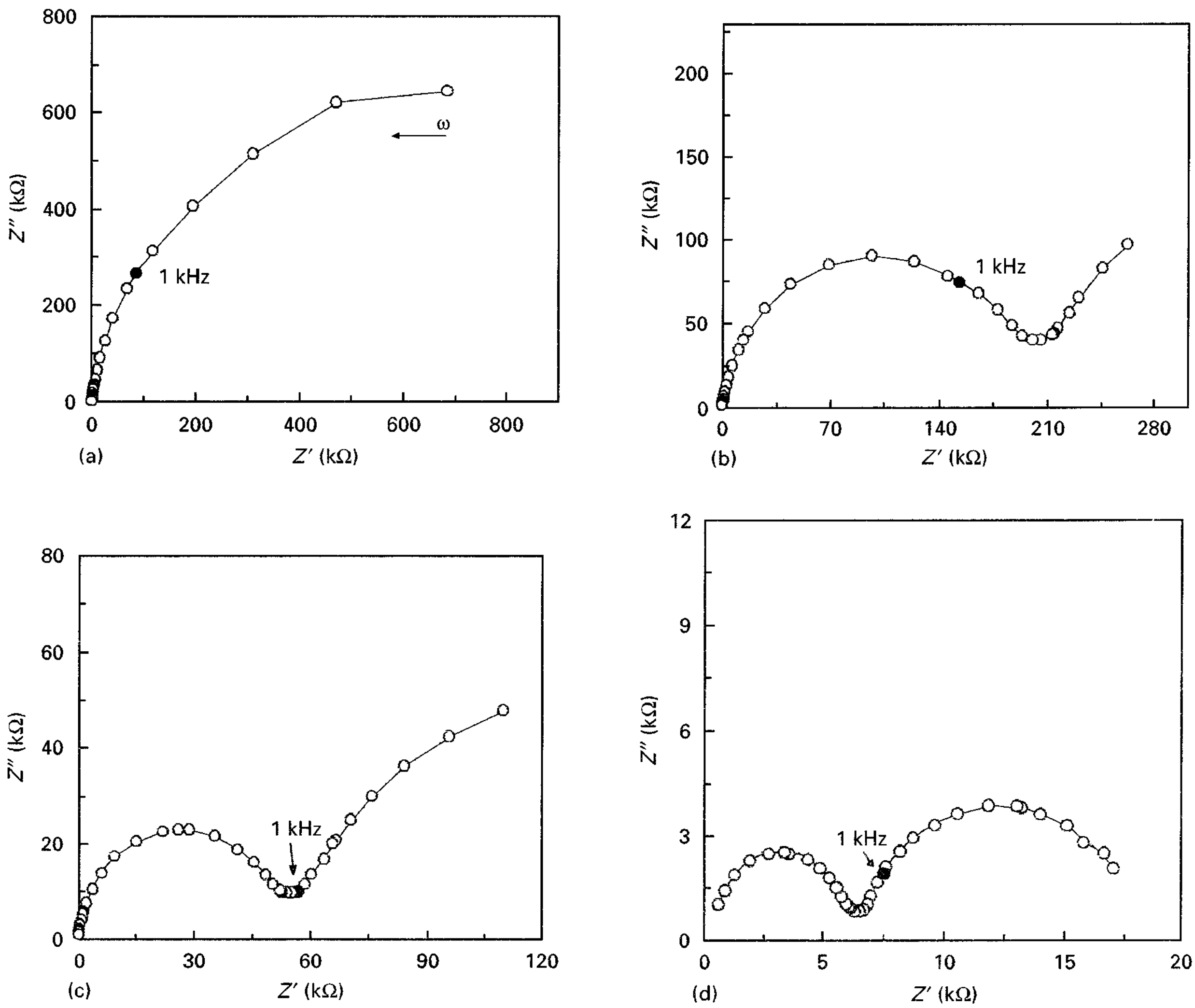

Figure 2 Impedance analysis of $BaTiO_3$ at (a) 250 °C, (b) 310 °C, (c) 350 °C and (d) 410 °C. The frequency of 1 kHz is indicated by a closed circle as a reference for the discussion.

TABLE I Fitted parameters of the arcs: resistance values of grain and grain boundary and arc depression factors below the real axis of the complex impedance plots

T (°C)	R_g (kΩ)	R_{gb} (kΩ)	α_g	α_{gb}
250	1102.9	–	0.046	–
310	216.2	418.6	0.069	0.190
350	53.6	187.1	0.081	0.294
410	6.4	15.6	0.132	0.332

According to the limitation associated with the experimental frequency range of the measurements, the grain boundary arc becomes resolved only with increasing temperature. In this way, at low temperatures up to ~250 °C (Fig. 2a), all the experimental frequencies are on the arc of the grains. As the temperature increases, these frequencies continually shift to the arc of the grain boundaries while the grain arc moves towards higher frequencies. The closed circle in Fig. 2c indicates that in the case of 1 kHz the mentioned shift from the grain arc to the grain boundary arc occurs close to 350 °C, coinciding with the temperature at which the large departure from the Curie–Weiss law starts (Fig. 1). Thus, we can conclude that the observed dielectric anomaly is related to the characteristics of the conduction processes at the material grain boundaries. By the way, the most probable conduction mechanism for the analysed material must come from some impurities and oxygen vacancies created during the ceramic preparation and the sintering process, respectively.

As a second step of this study, we have analysed the frequency-dependent complex permittivity of the material. In particular, it is well known that as the frequency decreases, the real part of permittivity (ε') of $BaTiO_3$ markedly increases at frequencies of $\sim 10^8$–10^9 Hz because of the Debye-like relaxation related to the polarization mechanism from the dipole rotation process [5, 6]. Thereafter, this magnitude must remain essentially constant. Fig. 3 shows the low frequency dependence of ε' here obtained at different temperatures of measurement. Moreover, the data are plotted logarithmically as suggested by Jonscher [9, 10] for a good analysis. We observe that at low temperatures the permittivity is essentially constant. But as the temperature increases, it turns up a continuous dielectric dispersion phenomenon characterized by a notable increment of permittivity at the lower frequencies related to the conduction processes at the grain boundary phase. Thus, besides the high-frequency polarization from the dipole rotation mechanism associated with the grains, there is an additional polarization mechanism associated with the grain boundaries.

In fact, starting from the series combination of the two grain and grain boundary R–C networks, it can be proved that the overall material permittivity ε' should follow the relation

$$\varepsilon'(\omega) = \frac{[\omega^2 R_g^2 R_{fg}^2 C_g C_{fg}(C_g + C_{fg}) + C_g R_g^2 + C_{fg} R_{fg}^2]}{K\varepsilon_0\{[\omega R_g R_{fg}(C_g + C_{fg})]^2 + (R_g + R_{fg})^2\}} \quad (3)$$

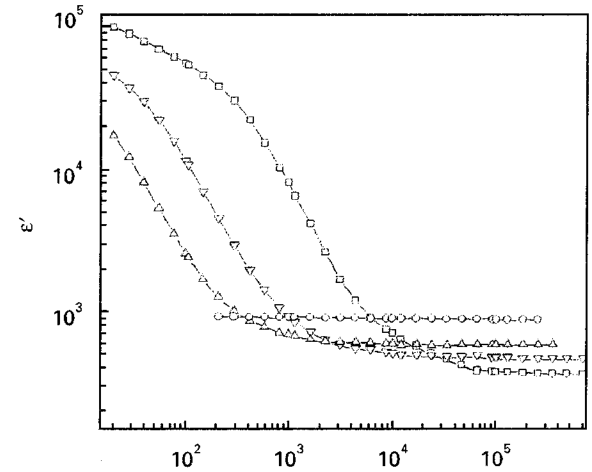

Figure 3 Logarithmic plot of the frequency dependence of the real part of $BaTiO_3$ permittivity. This shows a low frequency dielectric dispersion which is resolved within the experimental frequency window as the temperature increases. (□) 410 °C; (▽) 350 °C; (△) 310 °C; (○) 250 °C.

which involves a dielectric dispersion phenomenon like the Debye-type relaxation from the dipole rotation, but occurring down through lower frequencies. Indeed, this result has been previously pointed out elsewhere [11, 12]. In this way, the low frequency dielectric dispersion can be explained in terms of the storage of several charge carriers at the material inhomogeneities, that is at the grain boundaries. This statement supposes that the grain boundaries necessarily constitute resistive regions as we have pointed out above. In such a case, once these regions are reached, the motion of the electrical charges must occur quite slowly, resulting in an interfacial polarization mechanism leading to an increment of the permittivity over the lower frequencies. Accordingly, this should be the real explanation for the resulting anomalous rise of permittivity shown in Fig. 1, and not necessarily a specific chemical phase nor a structure modification within the material matrix. At all events, the presence of these latter at the intergranular regions must determine of course the intensity of this anomaly by varying the quantitative electrical characteristics of the grain boundary phase.

Moreover, taking into account that the centres of the arcs (Fig. 2) are depressed by an angle of $\alpha\pi/2$ below the real axis, we also give the factor α in Table I. This means that the arcs are not ideal according to the Debye behaviour of lumped circuits with ideal frequency independent capacitance and resistance, and thus the mentioned dielectric dispersion must not be strictly of Debye-type. The factor α is well known to be related to the interaction degree of the charge carriers during the conduction relaxation processes. In this way, and according to Table I, this should be higher for the grain boundaries when accumulating several charges. Starting from the fact that the atomic arrangement of the structure is commonly more disordered near the intergranular regions, on the other hand, the mentioned relaxation process could also involve perhaps some discontinuous jumps or hops of

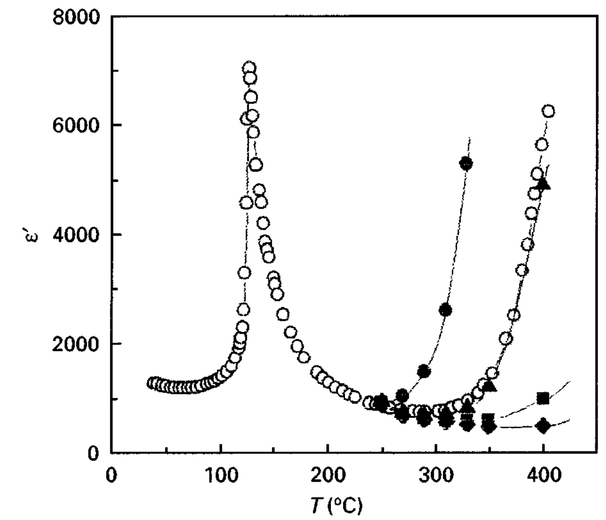

Figure 4 Rebuilding of the temperature dependence of $BaTiO_3$ permittivity at different frequencies. The open circles correspond to Fig. 1 (●) 0.1 kHz; (▲) 1 kHz; (■) 10 kHz; (◆) 100 kHz.

the carriers especially around or across the grain boundaries [9, 10, 13–15].

At the higher frequencies (Fig. 3), corresponding to the conduction processes at the grain phase, the permittivity is practically constant for each temperature, but decreases as the temperature increases. Also, the amount of these frequencies is more and more less in concordance with the shift of the grain arc towards the highest frequencies with increasing temperature. Indeed, the decrease of the high frequency permittivity as the temperature increases means that there is, in principle, no departure from the Curie–Weiss law for the material properties mainly dominated by the ferroelectric response of the grains. In fact, this departure appears as the material properties become strongly influenced by the interfacial phenomena at the grain boundaries downwards through the lower frequencies. In Fig. 4 we show these results by means of the reconstruction of the temperature dependence of the material permittivity for 0.1, 1, 10 and 100 kHz. From this plot, it is clear that the dielectric anomaly is really related to a frequency dispersive behaviour of permittivity.

From all the results presented up to now, we can suggest that for ferroelectric materials having higher Curie points (T_c) and microstructures with conductive-like grains and resistive-like grains, a marked decrease of the maximum of permittivity $\varepsilon(T_c)$ could be seen with increasing frequency, as a result of the mentioned dielectric dispersion. This resembles the results reported in [1–3]. However, the frequency dispersive behaviour of permittivity can have other moving forces from other kinds of polarization mechanisms into the bulk material or interfacial processes at the electrodes [8–12]. The analysis of the frequency-dependent properties of ferroelectric ceramics with a relatively high Curie point will be the content of a later report.

In our laboratory we have also observed in other ferroelectric $BaTiO_3$ ceramics the characteristics given in Fig. 5a for the thermal dependence of permittivity. The curve is really given in terms of capacitance ($C = K\varepsilon_0\varepsilon$). This suggests that the abrupt anomalous rise of permittivity does not occur continuously with increasing temperature. The curve shows a final slow rate of the capacitance increase towards the higher temperatures. Fig. 5b illustrates an example of the corresponding complex impedance analysis which shows the superposition of two arcs according to measurements performed at 401 °C. In fact, the already mentioned circuit model involving a series arrangement of parallel-RC blocks can be assumed for simulating the material properties. Accordingly, a frequency dispersive behaviour of the overall material capacitance is expected as illustrated in Fig. 6. In the specific case of this ceramic sample, even though the arc diameters (Fig. 5b) suggest that the resistance of the grain boundaries is smaller than that of the grains, however, the occurrence of the dielectric dispersion should involve an accumulation of the charge carriers at the intergranular regions. The fact is that these latter must be of resistive type, taking into account their certainly smaller dimensions in comparison with those of the grains.

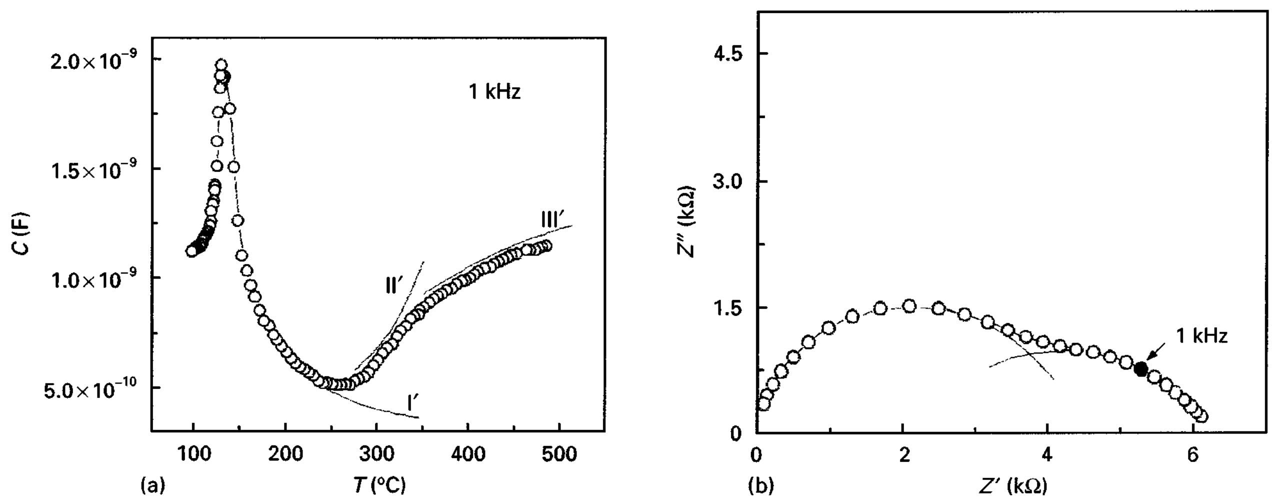

Figure 5 (a) Capacity versus temperature characteristics also seen in $BaTiO_3$ ceramic samples and (b) the corresponding complex impedance analysis according to the a.c. data collected at 401 °C. For the behaviours I′, II′ and III′, see text.

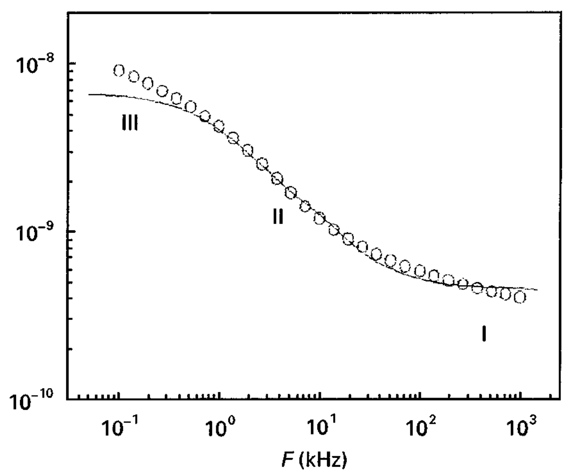

Figure 6 Logarithmic plot of the frequency dependence of capacitance for the $BaTiO_3$ ceramic sample whose other electrical properties are given in Fig. 5. For the behaviours I, II and III, see text. (○) 401 °C.

In fact, three frequency behaviours of the capacitance I, II and III are indicated in Fig. 6. Also, the expected shape of the dielectric dispersion from Equation 3, that is in concordance with the circuit model assumed above, is indicated by a solid line. This shows two frequency plateaus of capacitance over the high- and low-frequency regimes and the capacitance dispersion over the intermediate frequencies. The behaviour I corresponds to the frequency range where the material capacitance is mainly dominated by the grains, while the behaviour II corresponds to the frequency range of the dielectric dispersion phenomenon activated by the charge storage at the grain boundaries. In particular, behaviour III contains the material capacitance after the mentioned dispersion and the start of some additional contribution downwards through the lowest frequencies, probably coming from polarization phenomena at the material–electrode interface and overlapping strongly the low-frequency plateau.

The final consequence of the whole observed frequency spectrum of the material capacitance with increasing temperature are the corresponding tendencies I′, II′ and III′ indicated in Fig. 5a. These are the Curie–Weiss law (I) basically from the electrical response of the grain phase, the abrupt departure from the law (II) from the dielectric dispersion and a final slow capacitance increment (III) containing both the temperature dependence of the material permittivity after the dielectric dispersion as well the possible contribution of the electrodes.

4. Conclusions

The a.c. analysis technique has been shown to be a very good technique for characterizing the electrical properties of the materials, and was applied in this work to study the dielectric anomaly in $BaTiO_3$ ferroelectric ceramics above the Curie point. From the results we can give the following conclusions:

1. The large dielectric anomaly associated with an abrupt rise of permittivity above the Curie point in ferroelectric ceramic materials is related to a low frequency dielectric dispersion phenomenon due to polarization phenomena from charge storage processes at the grain boundaries.
2. The permittivity of the ferroelectric material must always obey the Curie–Weiss law when the operating frequency is only related to the material electrical properties dominated by the grain phase.

According to all these statements, we can emphasize that the material properties taken over wide ranges of frequency and temperature are quite important and needed for the real understanding and interpretation of the many material electrical responses. The temperature dependence of permittivity or any other electrical property measured at a fixed frequency can lead to erraneous conclusions. The experimental procedure of this study and the results of the discussion could be of extensive applicability to several ceramic materials.

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