# Characterization of Electrical Materials, Especially Ferroelectrics, by Impedance Spectroscopy

ANTHONY R. WEST, DEREK C. SINCLAIR & NAOHIRO HIROSE

*University of Aberdeen, Department of Chemistry, Meston Walk, Aberdeen, UK AB24 3UE*

**Abstract.**  A review is given of some of the problems encountered in the analysis and interpretation of impedance data. The importance of choosing the correct equivalent circuit to represent the data is emphasized and it is shown how ferroelectric materials, with their characteristic temperature-dependent capacitance, are particularly suited to discriminating between plausible equivalent circuits. Results are discussed for two materials, $LiTaO_3$ single crystal and $BaTiO_3$ ceramics.

**Keywords:**  impedance data, equivalent circuits, ferroelectric materials, impedance and modulus spectroscopy, lithium tantalate ferroelectric, barium titanate

## Introduction

Ferroelectric materials, especially ceramics, are usually characterized by fixed frequency measurements, typically at 1 kHz. From a practical point of view, this may be appropriate for measuring the key properties of loss tangent and dielectric constant or permittivity. From the viewpoint of scientific understanding, however, such measurements instead of variable frequency measurements, place severe limitations on the amount of information that is readily obtainable, especially with materials that may be electrically heterogeneous.

## Electrical Microstructure and Impedance Spectroscopy

The ready availability of impedance spectroscopy instrumentation covering, routinely, frequencies from millihertz to megahertz offers the possibility of a comprehensive characterization of electroceramics and in particular, characterization of their *electrical microstructure*. The concept of microstructure is, of course, fundamental to ceramics but the link between microstructure and electrical properties is not always obvious or straightforward. For instance, from a

microscopic examination of ceramic texture, it is not usually possible to say whether the electrical properties of grain boundaries are likely to be similar to or significantly different from those of the individual grains. This may depend on whether the electrical properties are intrinsic to the material and are insensitive to minor variations in structure and composition or whether the properties are extrinsic since they could then vary dramatically if impurities are present. In the former case, grains and grain boundaries may be indistinguishable electrically, whereas in the latter their properties may differ greatly, especially if, as often happens, impurities segregate to the grain boundaries. A great strength of impedance spectroscopy is that, with appropriate data analysis, it is often possible to characterize the different electrically-active regions in a material, both qualitatively by demonstrating their existence and quantitatively, by measuring their individual electrical properties.

## Equivalent Circuits: Are They Necessary?

Our belief is that identification of the most appropriate equivalent circuit to represent the electrical properties of a material is absolutely essential as a step towards a

proper understanding of its properties. This is particularly so in materials that are electrically heterogeneous and where the impedance response of one region overlaps, in the frequency domain, with the response of other regions, giving rise to a composite response. From an equivalent circuit analysis, the responses of the different regions may then be deconvoluted and characterized separately. It has to be said, however, that in general, there are severe difficulties in achieving unambiguously this goal of the correct equivalent circuit for a particular material. In the case of ferroelectric materials, fortunately, the goal may be significantly easier to achieve due to the uniquely characteristic variation with temperature of the ferroelectric capacitance; this then enables ferroelectric and non-ferroelectric components of the overall impedance response to be distinguished.

The difficulties associated with choosing the correct equivalent circuit may be summarized as follows. First, as is commonly recognized, it is always possible to find more than one circuit to simulate a particular impedance response. This is shown in Fig. 1, where a sch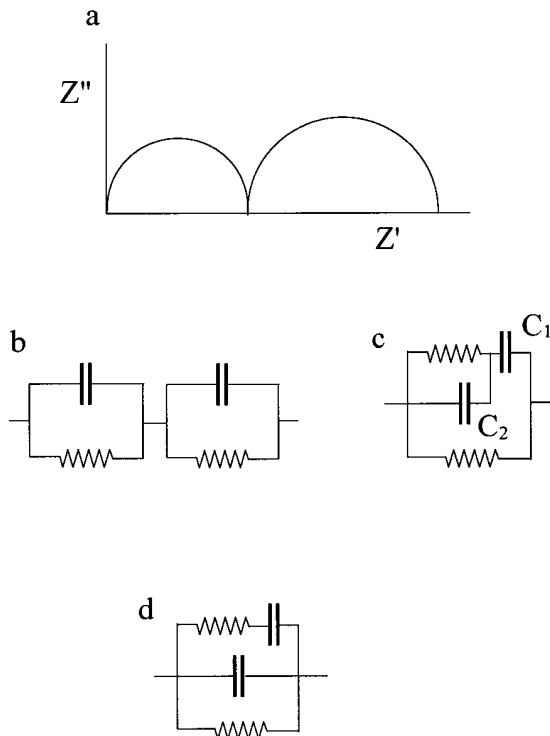ematic, idealized impedance complex plane plot with two semicircular arcs (a) can be modeled equally well by any of the three equivalent circuits shown in (b) to (d). All three of these circuits are widely encountered in the literature {(b) for series-connected bulk and grain boundary phenomena; (c) and (d) for leaky dielectrics} and so each is realistic under a particular set of circumstances.

Second, from an examination of Fig. 1a, there is no *a priori* way to tell which of the three circuits, or indeed some other more complex circuit, is correct. Third, once an equivalent circuit has been identified, the sample is, nevertheless, still a "black box" and it is necessary somehow to make a link between different elements in the circuit and the regions of the sample responsible for each.

Given these difficulties and uncertainties, researches (ourselves included) tend to use a pragmatic approach and adopt a circuit which they *believe* to be most appropriate, given their knowledge of the behavior expected from the material under study and demonstrate that the results are not inconsistent with the circuit used. Thus, the magnitudes of the capacitance values extracted from the analyses are a good pointer to the dimensions of the regions concerned [1] and can be used to diagnose bulk, grain boundary, surface layer and electrochemical phenomena. Also, the temperature dependence of the associated resistances often show Arrhenius behavior and the activation energies should be in the range expected for the phenomena under investigation.

One of the major advantages in using impedance spectroscopy to characterize ferroelectric materials is that the capacitance associated with the ferroelectric
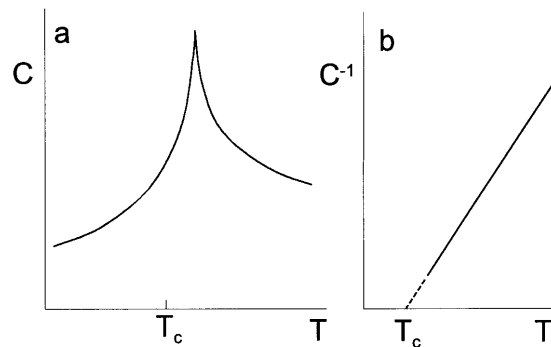


*Fig. 1.* (a) Idealized impedance complex plane plot showing two semicircular arcs and (b–d) plausible equivalent circuits.



*Fig. 2.* (a) Temperature-dependent capacitance of a ferroelectric material and (b) Curie–Weiss plot of reciprocal capacitance for data above $T_c$.

component should show the characteristic sharp maximum at the Curie temperature, with a Curie–Weiss decay at higher temperatures, Fig. 2. This expectation forms the basis of a method [2,3] for testing the validity of various possible equivalent circuits. The choice of an incorrect circuit may lead to the extraction of capacitance values which are composite capacitances that show neither a Curie–Weiss response nor an essentially temperature-independent capacitance. An example of this is discussed later.

## Departures from Ideality: How to Treat Them and Are They Important?

In our experience of a wide range of electronically and ionically conducting materials, both crystalline and amorphous, an ideal Debye-like response is never obtained, i.e., the impedance response can not be treated in terms of simple parallel RC elements. For instance, in glasses, which are presumably homogeneous macroscopically, it has been very well established for many decades that the conductivity–frequency spectrum shows a frequency-independent dc component at low frequencies and a frequency-dependent ac component at high frequencies, Fig. 3. The low frequency component may be represented by a simple parallel RC element, but an additional component is needed to model the high frequency component. An important problem then, is how to model the complete response, taking account of the high frequency behavior.

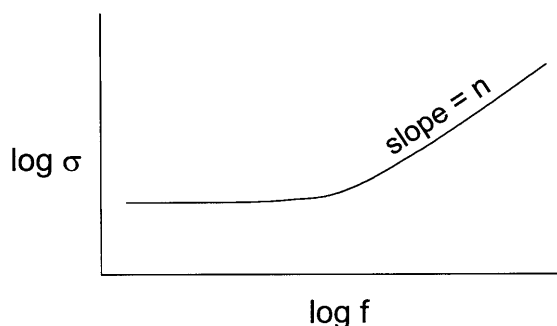This effect is not confined to glasses and is equally apparent in single crystal ionic conductors such as Na



$\beta$-alumina [4]. It is also present in conducting ceramics, although may be less obvious since their conductivity-frequency spectra tend to contain additional regions of frequency dependence associated with, for instance, the relaxation of grain boundary responses; the grain boundary regions themselves may also show non-ideal response; further complexities arise with ceramics if the electrical properties of the individual grains are anisotropic and if additional dielectric losses associated with the reorientation of dipoles are present in the sample. It is probably true to say, though, that all materials show some degree of non-ideality in their impedance response and that the generalized conductivity spectrum shown in Fig. 3 is typical of single phase ''homogeneous'' conductors, both glassy and crystalline.

There are various approaches to modeling the non-ideality and, in particular, the functional form of the high frequency response. Numerous equations are given in the literature; often, these fit the data over certain frequency ranges only. This may be either because the functions used are inappropriate or because overlapping phenomena in the frequency domain give rise to a composite response.

The approach that we favor, and for which, as far as we know, there are no exceptions, is to use a combination of equivalent circuits, with the implicit inclusion of all electrically active components together with constant phase elements, CPEs, to represent the departures from Debye-like ideality of each component. The CPEs describe the widely-observed ''power law'' dependence of the impedance components on frequency, indicated by the linear region of slope $n$ in Fig. 3 and are an expression of this ubiquitous ''Jonscher Law'' behavior [5]. Jonscher Law, or power law response is well established to hold in simple systems over several decades of frequency; departures appear to occur when additional phenomena make a significant contribution to the impedance response, rather than to a breakdown of the power law response.

In its simplest form, the equivalent circuit for an ''ideal'', Debye-like conducting system is represented by a single parallel RC element, Fig. 4a, with impedance, $Z$ and admittance, $Y$ given by:

$$Y^* = (Z^*)^{-1} = R^{-1} + j\omega C \qquad (1)$$

where $j = \sqrt{-1}$. When the power law, high frequency dispersion is taken into account, the circuit

*Fig. 3.* Idealized conductivity–frequency spectrum typical of ionically conducting glasses and crystals.

is modified as shown in Fig. 4b and the admittance is then given by:

$$Y^* = R^{-1} + j\omega C + A\omega^n + jB\omega^n \qquad (2)$$

Whilst this equation gives the admittance, the other three commonly-used formalisms: impedance, $Z$, permittivity, $\varepsilon$ and electric modulus, $M$ can be generated readily by means of the transformations [6,7]:

$$M^* = (\varepsilon^*)^{-1} = j\omega C_0 Z^*$$
$$= j\omega C_0 (Y^*)^{-1} \qquad (3)$$

and the data can then be plotted in many ways, including spectroscopic plots (real, imaginary vs. frequency) and complex plane plots (imaginary vs. real) of all four formalisms.

As a routine part of the general procedures used for data processing, it is important to transform the data between different formalisms and analyse them in various ways since the departures from ideality of a circuit such as Fig. 4b show up differently in the different formalisms. For instance, the ''impedance and modulus spectroscopic plots'' for Fig. 4b, i.e., $Z''$, $M''$ vs. $f$ (shown in Fig. 5b) show that the $Z''$ spectra are broadened on the *low* frequency side of the peak maximum. However, the $M''$ spectra are broadened on the *high* frequency side. In addition, the two peak maxima, which are frequency-coincident for an ideal RC element, Fig. 4a, (shown in Fig. 5a) become separated in the case of a non-ideal element, Fig. 4b (shown in Fig. 5b) [8].

The plots in Fig. 5a, b for the circuits in Fig. 4a, b, respectively, are on log-log scales, instead of the more commonly used, linear-log scales in order to emphasize the departures from ideality and their link to the power law exponent, $n$, Eq. (2). The spectra





*Fig. 5.* Idealized, normalized $Z''$, $M''$ spectra, on logarithmic scales, for the equivalent circuits shown in Fig. 3.

in (b) are somewhat idealized and in the regions of the peak maxima may show deviations from the slopes shown [8]. Nevertheless, the broad features, with peak asymmetries and separations of peak maxima are clear. This separation can become quite large and, in the case of Na $\beta$-alumina which shows a strong high frequency departure from ideality, is almost two decades in frequency [8]. One consequence of basing the analysis of impedance data on equivalent circuits is that apparent discrepancies such as these can be traced directly to a common origin. Whilst quantitative explanation of the meaning of the departures from ideality is still a vexed issue, the problem is simplified greatly with the realisation that the same deviation may manifest itself in different ways in the different formalisms.

The above indicates how departures from ideality may be analyzed, at least empirically. For many purposes, such departures may be ignored since they are essentially ac rather than dc phenomena. Thus, the most important parameters for many electroceramics are the magnitudes of the sample resistances: total, bulk, grain boundary and these are largely unaffected by the presence of high frequency dispersions. Even in such cases, however, recognition of any non-ideality, its influence on for example the impedance complex plane plots and the inclusion of such features in an overall fitting of the electrical response is of value in enabling more accurate values of the resistances to be extracted.
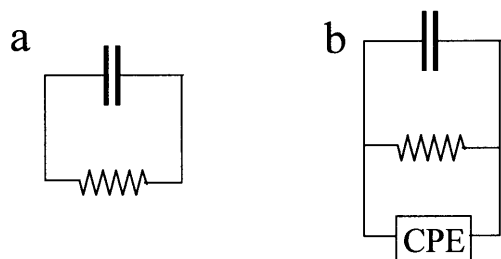


*Fig. 4.* Equivalent circuits for (a) an ideal, parallel RC element and (b) a parallel RC element with an additional parallel constant phase element.
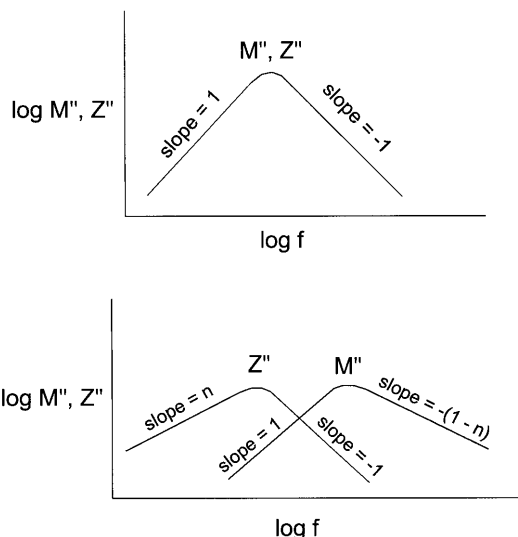
For other purposes, the non-ideality may contain much fundamental information. There has long been interest in conduction mechanisms in solid electrolytes, including glasses and the non-ideal or ac component of the conductivity spectrum is a rich source of information on localized ion movements. The problems are complex, however, due to the cooperative, many body nature of conduction mechanisms. A simple but effective method for separating carrier concentration and ion hopping rate contributions to the conductivity was derived, based on an analysis of non-ideal equivalent circuits and especially, of the power law contribution to the overall conductivity [9].

## Strategy for Data Analysis: A Cautionary Note

It is now becoming standard practice, through the work of Macdonald [10], Boukamp and others, to fit impedance data to equivalent circuits. Such fitting is certainly of value in finishing off an analysis, in checking that not only the impedance but also other formalisms can be fitted well by a particular circuit and in extracting reliable values for the component R, C (and L) parameters. Such analyses do not, however, get around the problems referred to above of choosing which equivalent circuit is most appropriate to a particular material. Computers cannot solve this problem and it is important that the researcher does not attempt to delegate his responsibility to them!

We believe that the best strategy is first to present data graphically, using more than one formalism and extract as much information as possible from a visual inspection of the plots. Thus, one of the strengths of the impedance and modulus spectroscopy combined approach is that the impedance spectra are dominated by the most resistive components in a sample whereas the modulus spectra are dominated by those components with the largest volume fraction: often, peaks are seen in modulus spectra which are hidden in the corresponding impedance spectra, and vice versa. Use of the two analyses together then gives information that is not immediately apparent from either analysis in isolation and this can be crucial in proposing a trial equivalent circuit as a first step in data analysis [1]. Recently, it has been suggested that use of combined plots such as impedance, modulus and dissipation factor may be used to discriminate between localized relaxation and long range conductivity [11].

## Ferroelectric Materials: Two Case Histories

### $LiTaO_3$

Impedance measurements on a single crystal of $LiTaO_3$, with the electric field parallel to the polar c-axis of the crystal, demonstrated a complex response. From its temperature dependence, it was possible to eliminate from consideration two plausible equivalent circuits and leave a single circuit which adequately accounted for the magnitudes and temperature dependences of the component R and C parameters [2]. The key points of the analysis were as follows.

The raw experimental data indicated the occurrence of two RC elements. Each of the three circuits shown in Fig. 1 was therefore a contender but there was no way of telling, from inspection of a particular data set, which circuit was appropriate. The strategy adopted was to calculate the impedance, admittance, etc. for each of the circuits, extract C values from experimental data plotted in the $\varepsilon^*$ formalism and examine their temperature dependence. It became apparent, that only circuit c gave two sets of C data that were both reasonable: one set, $C_1$, showed a sharp maximum at $T_c$ with a Curie–Weiss decay at higher temperature; the other, $C_2$ was largely temperature-independent but showed a small discontinuity at $T_c$.

Further analyses of data sets at different temperatures using the admittance formalism indicated the presence of additional elements in the equivalent circuit and finally, the circuit shown in Fig. 6 was
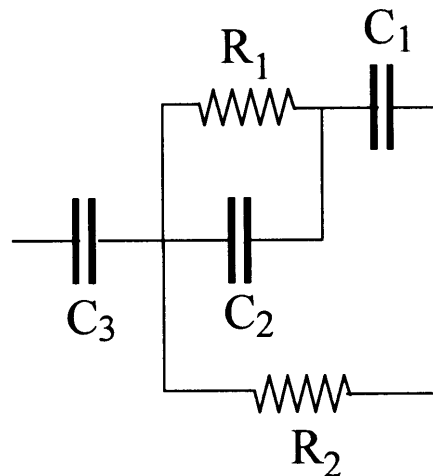


*Fig. 6.* Circuit used to represent the ac response of single crystal $LiTaO_3$.

adopted as representing the overall ac response of the sample. By consideration of the magnitudes and temperature dependences of the component $R$ and $C$ parameters, these were then assigned to the following features of the sample:

$R_1$: the resistance to reorientation of the ferro-electric domains in response to a small applied field; generally, its value was too high to measure at low temperatures, but it decreased increasingly rapidly near $T_c$; well below $T_c$, the domains were presumably ''frozen-in''.

$C_1$: the capacitance associated with reorientation of the domains and dipoles; characteristic ferro-electric behavior.

$R_2$: the resistance associated with leakage conduction of $Li^+$ ions; linear Arrhenius dependence, $E_a = 1.27$ eV.

$C_2$: bulk permittivity of the lattice; high value, approx. 1000, attributable to high polarizability of lattice; largely independent of temperature.

$C_3$: electrode polarization, approximately $1\mu F$.

## $BaTiO_3$

Barium titanate is surely one of the most widely studied ceramic materials and yet, many of the electrical data are confined to fixed frequency permittivity measurements. A major problem in characterizing pure $BaTiO_3$ is that its resistance is too high to be measured by most impedance instrumentation, although donor-doped $BaTiO_3$ is semiconducting and can be readily characterized.

Donor-doped $BaTiO_3$ forms the basis of PTCR devices; the ceramics are electrically heterogeneous and are particularly amenable to characterization by impedance and modulus spectroscopy [12,13]. It has been shown that PTCR ceramics typically have three electrically-distinct regions:
- a conductive core
- a resistive surface layer on the grains, which is ferroelectric
- a resistive surface/grain boundary layer, which is non-ferroelectric

The distinction between the latter two effects was made using capacitance data obtained from modulus, $M''$ spectra for data above $T_c$. Combined impedance and modulus spectra were much more useful than impedance spectra alone in determining the number of electrically-active components and deducing an

equivalent circuit. Once the impedance data had been properly characterized, it then became possible to monitor the variation of each of the electrical components with ceramic processing conditions and the presence of oxidizing/reducing atmospheres.

Impedance measurements of nominally-pure ceramics of $BaTiO_3$ have recently been made [3] at temperatures between 25 and 330°C. Only those data obtained well above $T_c$ could be used for extensive analysis because, at lower temperatures, the high impedance of the samples restricted the amount of useful information that could be obtained to high frequency capacitance data. Inspection of the higher temperature data using different formalisms indicated the presence of two RC elements and again, the question immediately arose as to which circuit was appropriate and, therefore, which equations should be used to extract the component $R$ and $C$ values.

Since the data were recorded above $T_c$ at which ferroelectric domains should be absent, the dielectric circuits, Figs. 1c and d were felt to be unlikely and therefore, subsequent analysis was based on circuit Fig. 1b. The results obtained supported this interpretation. The two RC elements were assigned to bulk and grain boundary regions of the sample, respectively; the bulk region clearly showed a typical ferroelectric response but detailed analysis showed that attention to the equivalent circuit equations was necessary in order to extract the true, bulk capacitance values.

Two reasons were identified for which the use of fixed frequency capacitance data could give misleading or incorrect results. First, as shown earlier [14], the measurement frequency should be high enough for any grain boundary impedances to be
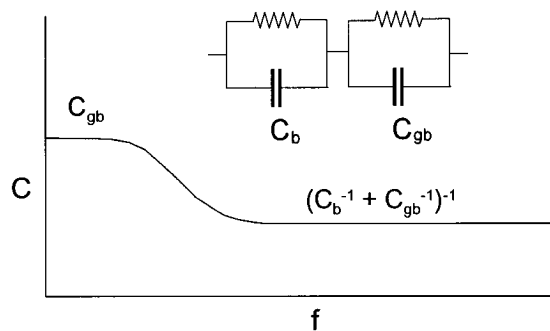


*Fig. 7.* Frequency dependence of capacitance, for the circuit shown; the limiting high frequency capacitance corresponds to the bulk capacitance $C_b$, but modified by the grain boundary capacitance, $C_{gb}$.

relaxed out; if not, the apparent capacitance value would be anomalously high and cause a major deviation from a linear Curie–Weiss plot of $C^{-1}$ vs. $T$. Second, a much more subtle effect was the modification of the high frequency capacitance, even in the region of frequency independence, by the grain boundary capacitance [3], as shown schematically in Fig. 7. This effect may be sufficient to modify the extrapolated Curie–Weiss temperature by a few degrees.

The nature of the grain boundaries in the $BaTiO_3$ ceramics was deduced to be a *constriction grain boundary*, in which the associated capacitance was a combination of the capacitance of the air gaps surrounding the grain-to-grain contacts and the capacitance of the neck region connecting the grains. The latter was ferroelectric but at high temperatures, well above $T_c$, the capacitance of the air gaps became dominant; consequently, the Curie–Weiss plots showed a smooth transition from the expected Curie–Weiss behavior close to $T_c$ to a temperature-independent behavior at higher temperatures. Although constriction grain boundaries had been characterized previously, in poorly sintered LISICON $Li^+$ ion conductors and are usually though to be present in cases where bulk and grain boundary conductivities have identical activation energies [15], the presence of the additional characteristic signature of a ferroelectric capacitance aids the interpretation of such impedances in ferroelectric ceramics.

## Conclusions

Interpretation of impedance data of ceramic materials is often not straightforward. Various candidate equivalent circuits may be used to analyze data and often there is no certain way of discriminating between them. Once the correct circuit has been identified, assignment of the different elements to regions of the sample is usually possible, especially on consideration of the magnitudes of the associated capacitances. At this stage, it may be useful to vary sample geometry, since bulk effects may then alter the magnitude of their impedance response, whereas grain boundary or surface layer effects may not.

The use of equivalent circuits in the analysis of ac data *cannot be avoided* since the equations used to analyze data, such as the intercepts in complex plane plots, are all derived from equivalent circuits.

A major advantage in working with ferroelectric materials is that their capacitance has a characteristic temperature dependence. This means that not only can ferroelectric components be readily distinguished from non-ferroelectric ones, but that, in some cases the adoption of an incorrect equivalent circuit may lead to the extraction of capacitance data that are neither ferroelectric nor non-ferroelectric; this may be used as a clear pointer that the assumed equivalent circuit is incorrect.

## References

1. J.T.S. Irvine, D.C. Sinclair, and A.R. West, *Adv. Mater.*, **2**, 132–138, (1990).
2. D.C. Sinclair and A.R. West, *Phys. Rev. B*, **39**, 13486–13492 (1989).
3. N. Hirose and A.R. West, *J. Am. Ceram. Soc.*, **79**, 1633–1641 (1996).
4. R.J. Grant, I.M. Hodge, M.D. Ingram, and A.R. West, *Nature*, **266**, 42–43 (1977).
5. A.K. Jonscher, *Dielectric Relaxation in Solids*, (Chelsea Dielectric Press, London, 1983).
6. I.M. Hodge, M.D. Ingram, and A.R. West, *J. Electroanal. Chem.*, **58**, 429–432 (1975).
7. I.M. Hodge, M.D. Ingram, and A.R. West, *J. Electroanal. Chem.*, **74**, 125–143 (1976).
8. D.P. Almond and A.R. West, *J. Mat. Sci.*, **18**, 2380–2384 (1983).
9. D.P. Almond, C.C. Hunter, and A.R. West, *J. Mat. Sci.*, **19**, 3237–3248 (1984).
10. J. Ross Macdonald, *Impedance Spectroscopy: Emphasizing Solid Materials and Systems*, (Wiley Interscience Publication, New York, 1987).
11. R. Gerhardt, *J. Phys. Chem. Solids*, **55**, 1491–1506 (1994).
12. D.C. Sinclair and A.R. West, *J. Appl. Phys.*, **66**, 3850–3856 (1989).
13. D.C. Sinclair and A.R. West, *J. Mat. Sci.*, **29**, 6061–6068 (1994).
14. R. Flores-Ramirez, A. Huanosta, E. Amano, R. Valenzuela, and A.R. West, *Ferroelectrics*, **99**, 195–201 (1989).
15. P.G. Bruce and A.R. West, *J. Electrochem. Soc.*, **130**, 662–669 (1983).