

Dielectric and polarization experiments in high loss dielectrics: A word of caution

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The recent quest for improved functional materials like high permittivity dielectrics and/or multiferroics has triggered an intense wave of research. Many materials have been checked for their dielectric permittivity or their polarization state. In this report, we call for caution when samples are simultaneously displaying an insulating behavior and a defect-related conductivity. Many oxides containing mixed valent cations or oxygen vacancies fall into this category. In such cases, most of the standard experiments may result in an effective high dielectric permittivity, which may not be related to ferroelectric polarization. Here we list a few examples of possible discrepancies between measured parameters and their expected microscopic origin. © 2008 American Institute of Physics. [DOI: 10.1063/1.2949752]

Among functional materials, oxides are heavily investigated because of their wide range of properties. ABO_3 perovskites are such a class of materials showing magnetic, ferroelectric, semiconducting, metallic, and superconducting ground state with appropriate selection of the A and B cations. Even more interesting, a coexistence between several of these states may be achieved in a given compound. For example, in $BiFeO_3$, bismuth polarizability and iron magnetism result in the coexistence of ferroelectricity and antiferromagnetism at room temperature, which make this material a very promising multiferroic compound.^{1,2} In many titanates ($B = Ti$), strong dielectric permittivity and net lattice polarization are evidenced, making these the most studied ferroelectrics.³ Coexistence between polarizability and conductivity occurs when polyvalent cations such as Fe, Mn, and Cu are included in perovskite or in other oxides. Indeed, electron transfer between mixed valent states, for example, Fe^{3+} and Fe^{2+} , may lead to increased conductivity depending on the oxygen stoichiometries. Similarly, heterovalent substitution like Nb^{5+} on the Ti^{4+} site profoundly increases the conductivity of $BaTiO_3$, which, in fact, becomes semiconducting⁴ and even superconducting as in the case of $SrTiO_3$.⁵ In all these cases—multivalent cations, heterovalent substitutions, and oxygen vacancies—the materials will exhibit effective dielectric and polarization properties which may not be related to ferroelectricity. In recent years, many materials were shown to display very large or colossal effective dielectric permittivities.^{6–9} In this paper, we show that dielectric and polarization probing may be misleading when conductivity and polarizability do coexist in the same material. Our listing will be split into thermal runs and isothermal scans.

The standard way of testing the polarization of a ferroelectric material is to measure induced pyroelectric current when the sample is heated within the ferroelectric state. This is why the search for new ferroelectrics is usually done by recording pyroelectric current after the sample is poled under electric field cooled conditions. In several cases, a maximum of pyroelectric current and a change in its sign on reversing the sign of the poling bias were taken as evidence for ferroelectricity.^{7,10} There are, however, many examples in lit-

erature of nonferroelectric materials which show clearly such a sign reversal of the pyroelectric depolarization currents. Electrets, which include polymer materials,¹¹ are not ferroelectrics and do show pyroelectric current maxima whose sign follows that of the poling field. Such a change in the polarization state resulting from a change in the poling bias is ascribed to the localization of free charges at interfaces in electrets—the so-called space charge effect. In Fig. 1 we show such a reversal experiment reported for Ta_2O_5 ,^{12,13} a nonferroelectric oxide widely used in microelectronics. The maximum depolarization current was ascribed to the electron detrapping from oxygen vacancies. The nonferroelectric experiment reported in Fig. 1 compares well with similar results reported for $LuFe_2O_4$, CuO , or $CaCu_3Ti_4O_{12}$. In all these cases, heterovalent cations (Fe and Cu) and/or charged oxygen vacancies may act similar to oxygen vacancies in Ta_2O_5 by storing electronic charges during bias cooling and releasing them upon recording the current during the heating. In Ta_2O_5 , $LuFe_2O_4$, CuO , or $CaCu_3Ti_4O_{12}$, the change in sign of the net depolarization currents result from a sign

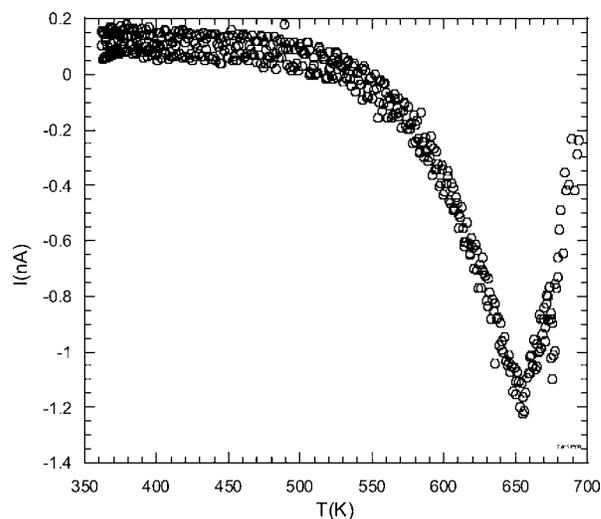


FIG. 1. Zero bias depolarization current of a tantalum oxide nonferroelectric ceramic. The same depolarization can be induced by UV illumination (see Ref. 12) or by poling bias during cooling (see Ref. 13), with the sign of the maximum current being changed on reversing the sign of the poling bias.

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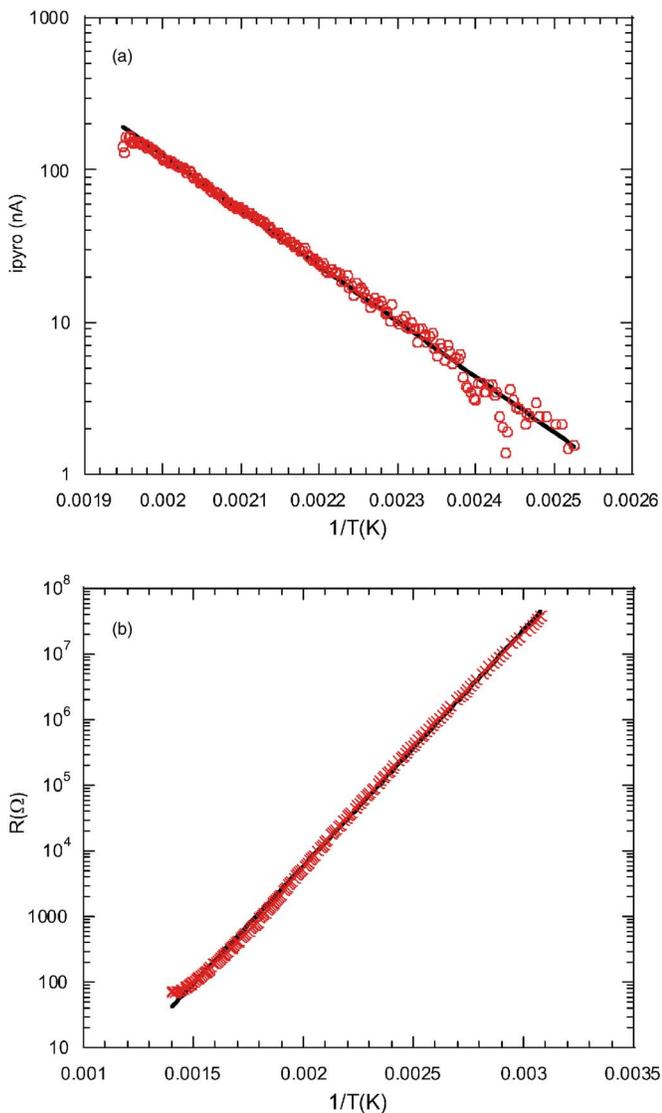


FIG. 2. (Color online) (a) Depolarization current and (b) resistance of a $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic while heating after a poling step. On both plots, lines are fitted to an Arrhenius thermal activation. Both activation energies are 0.7 eV, thus showing that depolarization currents stem from bulk semiconductor in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.

change of the global space charge induced by the poling bias: the density of trapped electrons is not homogeneous in the materials, having gradients of plus or minus sign, and so do the depolarization currents. In some instances,^{7,10} a full detrapping of space charges is achieved at a given temperature, which could be mixed with a possible ferroelectric transition. This temperature is, however, the one where all free charges get enough thermal energy for the space charge to be cancelled. In other instances, continuous increase in dc is recorded, meaning that semiconductor starts to be active before a hypothetical depolarization is reached.¹⁴ We probed the depolarization current using a Keithley 610C electrometer and the resistance with a Keithley 195 multimeter. For both experiments, the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics coated with gold electrodes was set in a homemade cell, allowing temperature to be scan from 77 up to 800 K. As shown in Fig. 2, an Arrhenius increase in the current is observed, which is related to the electrical conduction and is not due to depolarization of the ceramics. This is easily confirmed by comparing the current recorded during a heating run after poling

[Fig. 2(a)] to the dc electrical resistance [Fig. 2(b)]. Since these two independently measured parameters have exactly the same activation energy (0.7 eV), the former can hardly be called “depolarization current.”

While depolarization currents probe the kinetics of the bias induced space charges, low ac voltage dielectric experiments can be used to investigate their dynamics. The collective motion of electrical charge induces mesoscopic as well as macroscopic dipoles, whose relaxation can be seen by scanning the temperature and sweeping the operating frequency. This is well known in electrets based on polymers¹⁵ and inorganic oxides.¹⁶ In the case of oxides such as LuFe_2O_4 , one can note that the temperature at which the depolarization currents are maximum is the same as the one where the effective giant dielectric permittivity undergoes a strong dispersion. This relaxation of Debye type nature and thermally activated conductivity, which follows the same Arrhenius law, was reported in all “giant permittivity materials.”^{6–9} This similarity indicates a common origin of the giant dielectric permittivity and of its relaxation, the space charges.¹⁷ In the case of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, the interplay between grain conductivity and grain boundary insulation was successfully rationalized within the framework of an internal grain boundary layer model,¹⁸ which clearly rejected ferroelectricity as a source of the effective giant permittivity in this compound. In ferroelectrics, however, both the polarization and dielectric permittivity have different behaviors. It is not only the sense of poling which drives the polarization, but also the sign of the temperature slope during the depolarization run.⁵ This is because the polarization arises from an internally built phase transition and not from the poling step. To summarize this first part, neither the depolarization currents nor the dielectric relaxation are ultimate proofs of ferroelectricity in Ta_2O_5 , LuFe_2O_4 , CuO , or $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.

We now turn to isothermal polarization and dielectric experiments, which were also used to probe the expected ferroelectric state of giant permittivity materials and in other lossy dielectrics. At a fixed temperature, the polarization hysteresis loop under electric field cycling is the decisive proof of ferroelectricity. Well saturated and squared loops in ferroelectric perovskites can be found in many textbooks.³ However, in high loss electronics, non-Ohmic dc will occur. When the integrated current is then plotted as a function of electric field, distortions and a slight opening of the loop will occur.¹⁴ This should not be confused with the usual coercivity and saturation of ferroelectric hysteresis loops. To clarify this, the whole process of recording hysteresis loops is detailed in Fig. 3 in the case of the nonferroelectric $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. To evidence the necessary steps required to remove these extrinsic contributions, we have used a fully analog Sawyer–Tower setup to record both the charge and current loops. Moreover, compensating capacitors and resistors could be tuned manually so as to remove spurious impedance contributions to the loops.³ In Fig. 3(a), the Sawyer–Tower integration circuit was used to record charge/electric field loop in this ceramics. At first sight, this looks like a ferroelectric hysteresis with saturation at about $0.03 \mu\text{C}/\text{cm}^2$ and apparent coercive field of 4 kV/cm. To reject dc conductivity from this experiment, one should check the current/electric field loop before integration. This is shown in Fig. 3(b), where a strong dc is seen at zero electric field. The external circuit is then used to compensate for this dc, then leading to the reduced current loop in Fig.

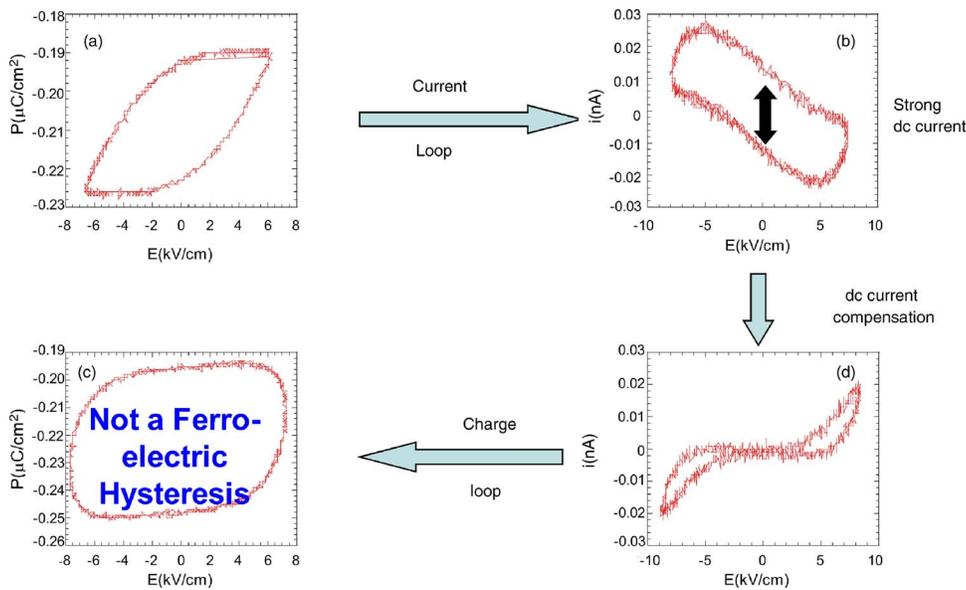


FIG. 3. (Color online) (a) Apparent saturated charge/electric field loop in a $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic at room temperature. (b) Current loop corresponding to the previous charge loop. This shows that a strong current flows through the ceramic at vanishing electric field (c) after appropriate compensation from the external circuit, the zero field current has been minimized, the bending of the current at high field stems from nonlinear conduction (d) after the compensation step of (c), the charge loop no more looks like a saturated hysteresis loop.

3(c), which has no more contribution at zero bias but which undergoes a strong increase at high bias with no sign of bending down. The last step is to turn to the integrated loop in Fig. 3(d), which no more looks like a ferroelectric loop because it is nothing but the integration of the semiconductor shape of the compensated current loop. Whatever the external compensation, it was never possible to get ferroelectric-like loops in the current and charge modes. We then firmly conclude that polarization/electric field loops are not due to the ferroelectric state in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. When true ferroelectric materials such as lead zirconate titanate and BaTiO_3 are subjected to the same process [Figs. 3(a)–3(d)], compensated current and charge loop do lead to consistent ferroelectric polarization reversal. In most of the giant permittivity materials and lossy dielectrics, one should apply the same process in order to reject conductivity contributions to the distortions and opening of electric field loops.¹⁹

Such conductivity contributions can also be seen during isothermal dielectric experiments. In the case of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, the real ϵ_1 and imaginary ϵ_2 parts of the dielectric permittivity were accurately fitted using a modified Jonscher law accounting for both a high frequency dielectric relaxation and a low frequency conductivity contribution.^{16,18,20} A close connection between these two contributions is a further evidence that charge localization is the origin of the giant effective dielectric permittivity involving electrical conduction as evidenced by impedance plots and can be generalized to many giant permittivity materials.^{17,18} Dielectric spectroscopy thus supports the isothermal charge loops as originating from uncompensated dc and not from lattice polarization reversal.

Thus we have shown that thermal and isothermal probing of polarization and dielectric permittivity in oxides are not straightforward when residual conductivity is present. Multivalent cations (Fe, Cu, and Mn) and/or oxygen vacancies are the sources of this residual conductivity, which means that annealing treatments during the processing of ceramics may alter drastically the conductivity and thus the polarization and dielectric parameters. By using well established standard procedures for characterizing ferroelectric materials, one can clearly distinguish between true bulk polarization and extrinsic conductivity contributions.

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