Probing ferroelectricity in highly conducting materials through their elastic response: Persistence of ferroelectricity in metallic $BaTiO_{3-\delta}$

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The question whether ferroelectricity (FE) may coexist with a metallic or highly conducting state or rather it must be suppressed by the screening from the free charges is the focus of a rapidly increasing number of theoretical studies and is finally receiving positive experimental responses. The issue is closely related to the thermoelectric and multiferroic (also magnetic) applications of FE materials where the electrical conductivity is required or spurious. In these circumstances, the traditional methods for probing ferroelectricity are hampered or made totally ineffective by the free charges, which screen the polar response to an external electric field. This fact may explain why more than 40 years passed among the first proposals of FE metals and the present experimental and theoretical activities. The measurement of the elastic moduli, Young's modulus in the present case, versus temperature is an effective method for studying the influence of doping on a FE transition because the elastic properties are unaffected by electrical conductivity. In this manner, it is shown that the FE transitions of $BaTiO_{3-\delta}$ are not suppressed by electron doping through O vacancies; only the onset temperatures are depressed, but the magnitudes of the softenings, and hence of the piezoelectric activity, are initially even increased.

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I. INTRODUCTION

The concept of ferroelectric metal is rather counterintuitive since a material is defined ferroelectric (FE) if it has a spontaneous polarization that can be switched by an external electric field, but within a metal an external electric field is screened out by the free charges so that in this context the term ferroelectric is sometimes put in quotes or substituted by "polar." Nonetheless, noncentrosymmetric displacements of atoms with different charges are possible also in a metal and would produce a local polarization. The first mention of ferroelectric metals regarded V_3Si [1] and Na_xWO_3 [2]. The first is one of the A-15 compounds, which becomes superconductors close to a structural instability, whose order parameter was initially proposed to be a soft transverse optical phonon as for FE transitions [1]. It has later been shown that the structural transition was driven by electronic band splitting [3] rather than a FE-like soft phonon. Also, in tungsten bronze (TTB) Na_xWO_3, which becomes superconducting in a doping range around $x \sim 0.3$, it was suggested that ferroelectriclike distortions are present and might favor superconductivity. Although other TTBs are ferroelectric [4], FE displacements have not been confirmed by diffraction experiments in Na_xWO_3, but in WO_3, corresponding to $x = 0$, the W atoms are antiferroelectrically displaced [5]. On the other hand, x-ray- and electron-diffraction studies on TTB fluorides suggest that ferroelectricity is present in a broader range of temperature and compositions both in TTB fluorides and in oxides [6]. After these early suggestions [1,2,7], the possibility of the coexistence of FE and metallic states received no further consideration except marginally in the context of high-T_c superconductivity [8,9] until the phenomenon has been proposed to occur in the pyrochlore $Cd_2Re_2O_7$ [10], which is superconducting below 1 K, after analyzing the elastic softening with considerations similar to those of Anderson and Blount [1]. Again, no evidence of spontaneous polarization has been found, and the observations may be better explained in terms of a low-temperature piezoelectric but nonferroelectric phase [10,11].

More solid evidence of the coexistence of ferroelectricity and metallic conduction has been provided by heavily doping $BaTiO_{3-\delta}$ with O vacancies (V_O) and showing with a combination of several experimental techniques that the originally FE transition remains with essentially the same characteristics after doping also in the metallic state [12] even though with reduced T_C. It was suggested that the coexistence of metallic and FE states is possible until the Thomas-Fermi screening length does not exceed the FE correlation length [12]. Again, the interpretation of the persistence of the FE transition in the metallic state of $BaTiO_{3-\delta}$ has been criticized on the basis that there would be a phase separation into highly doped metallic and undoped FE phases [13] so that the demonstration by neutron diffraction that the low-temperature phase of $LiOsO_3$ is isostructural with $LiNbO_3$, a well-known FE, could be considered the first clear evidence of coexisting metallic and FE states [14]. Very recently, also the metallic layered perovskite $Ca_3Ru_2O_7$ has been shown by optical second harmonic generation (SHG) and TEM to have polar domains, which, being also ferroelastic, can be switched by mechanical stress [15].

The origin of the polar displacements in $Ca_3Ru_2O_7$ rather than to the usual mechanisms in ferroelectrics would be due to a trilinear coupling involving the polar displacements and two types of tilting of the RuO_6 octahedra [15], a mechanism called hybrid improper ferroelectricity [16]. Another class of polar metals includes a few transition-metal monopnictides, such as TaAs and NbAs [17], where the SHG coefficient is extremely high along the polar axis. It is proposed that this is due to the particular topology of the Fermi surface, characteristic of a Weyl semimetal [17], but also a simple model of a uniaxial polar semiconductor can explain the observations [18].

To our knowledge, further examples of FE metals have been announced in thin films due to the substrate influence [19] or the extremely small thickness that allows the external field to penetrate and switch the polarization [20] but not in other bulk materials, and the brief review of the previous attempts at proving their existence demonstrates that this is not an easy task. Yet, FE metals would not just be rare curiosities but might find technological applications based, for example, on giant nonlinear optical phenomena [17]. New theoretical and computational studies on polar metals are appearing not only dealing with new mechanisms that induce polar displacements, such as improper hybrid ferroelectricity [16] or Weyl semimetals [17], but also considering the effect of electric conductivity on the traditional lattice and electrostatic mechanisms that induce the FE instability [21–23]. The prevailing opinion that the polar distortions cannot develop in a metal due to electrostatic screening [24,25] is evolving. It has been estimated that the polar distortions cannot survive electron doping in $BaTiO_3$ (BT) but may do it in $PbTiO_3$ [26] and the hypothetical (at that time [27]) $SnTiO_3$ [28] thanks to the local influence of the lone pairs of Pb^{2+} and Sn^{2+}. Afterwards, it has been calculated that the FE instability in $BaTiO_3$ is so short ranged that it can persist at high electron densities [29] as previously suggested [12] and the critical electron density for suppressing FE has been calculated as 0.085 electrons/cell [30], much higher than in the previous [12] and present investigations revealing the persistence of FE upon doping. It has also been estimated that the charged impurities are more detrimental than free electrons to FE [31]. More recently, it has been proposed that the electron screening may even favor the polar distortions under certain circumstances [32]. In addition to new FE metals, with their promising but yet unexplored implications and applications, highly doped classic ferroelectrics already find practical applications as thermoelectric materials [33]. Other examples of materials where ferroelectricity is generally accompanied by high electrical conductivity are the multiferroics [34], often obtained by doping magnetic ions in FE materials [35]. In all these cases, the experimental verification of the coexistence of ferroelectricity with a highly conducting or metallic state is a major problem since the traditional tools for probing ferroelectricity, which are directly sensitive to the polarization and require or cause sample poling, are made ineffective by the free charge screening. In these cases, one must resort to indirect methods, such as the determination of the cell structure by diffraction or the nonlinear optic response by SHG.

Recently, it has been shown that the temperature dependence of the elastic moduli across a FE transition may be used to probe the piezoelectric response even in unpoled ceramics [36–38], and, since the elastic response is insensitive to free charges, this seems the ideal tool for the study of coexisting FE and conducting or metallic states. As an example, it will be shown that, in this manner, it is possible with relatively little experimental effort to confirm the persistence of the FE transition in $BaTiO_{3-\delta}$ doped with V_O as initially found by Kolodiazhnyi *et al.* [12] and that, despite the depression of T_C, the piezoelectric coupling may be even enhanced, possibly as suggested in Ref. [32].

II. EXPERIMENT

The measurements were made on $BaTiO_3$ samples prepared in two different laboratories, which we label No. 1 and No. 2. Samples No. 1.1 and No. 1.2 with dimensions $42 \times 6.3 \times 0.68$ mm^3 were cut from the same bar of BT prepared at the Department of Physics of UFSCar-Brazil, starting from commercial high-purity powder of barium titanate (IV) (99.9% pure, Sigma-Aldrich). The powder was initially subjected to a heat treatment at 800 K for 2 h to minimize the presence of undesired organics and then subjected to ball milling for 24 h to get a reduced and homogeneous distribution of particle sizes. Finally, polyvinyl butyral was added as a binder to the powder (3 wt %) and uniaxially pressed at 150 MPa into thick bars, followed by isostatic pressing at 250 MPa, and then conventional sintering at 1350 °C for 2 h. The density measured with Archimede's method was 5.63 g/cm^3, 93.6% of the theoretical density.

For bar No. 2, cut with dimensions $43 \times 4.1 \times 0.59$ mm^3, stoichiometric $BaTiO_3$ was prepared by the conventional mixed-oxide powder technique at the Department of Chemistry of the Martin Luther University Halle (Saale), Germany: 24-h mixing (agate balls and water) of $BaCO_3$ (Solvay, VL600, <0.1 mol % Sr) and TiO_2 (Merck, No. 808), 2 h calcining at 1100 °C, and after it, 24-h fine milling (agate balls and water). Then, the powder was densified (binder polyvinyl alcohol) to a plate of dimensions $53.5 \times 37.0 \times 2.0$ mm^3 with a density of about 3 g/cm^3 and afterwards sintered 1 h in air at 1400 °C (heating and cooling rate 10 K/min). The plate was cut into thin bars which were ground down to a thickness of about 0.6 mm. The relative density was 94%.

The reducing treatments were carried out in a flux of 0.1 CO + 0.9 Ar at ~1 bar. The samples were put into a long envelope of Pt open at both ends with alumina spacers to avoid the direct contact with Pt. The envelope was inserted into a water-cooled quartz tube where the gas flowed and was heated by induction from outside with a coil connected to a rf power source. Each reduction treatment lasted 1.5–2.5 h at temperatures ranging from 950 to 1130 °C and was followed by 1-h homogenization at 800 °C in the same reducing flux. The change in δ was determined from the mass change with a microbalance. Assuming that the mass change was entirely due to O loss; the error on δ was $\sim 10^{-5}$. However, the anelastic and dielectric measurements required the application of Ag paint electrodes, which had to be removed before each high-temperature treatment. During the first part of the research, Ag was mechanically removed with a blade and emery paper and washed away with isopropyl alcohol. In this manner, the removal might sometimes be incomplete, resulting in an overestimation of the O loss from the mass change because the evaporated Ag traces would have been counted as O loss. The error in the determination of each change in δ is estimated as $<10^{-4}$ from the comparison of the cumulative mass losses of sample No. 2 and its mass gain after a final reoxygenation assuming (unrealistically) that every time the same amount of Ag evaporated. In the end, after mechanically removing Ag, the samples were further cleaned in a stirred solution of HNO_3 in water 1:9 in volume ratio at 50–60 °C for 2–10 min in order to dissolve the Ag traces [39]. Reoxygenation was achieved in air at 1100 °C for 1.5 h in a Linn High Therm furnace after which the black samples recovered the white yellowish color.

The complex Young's modulus $E = E' + iE''$ was measured by suspending the bar on two thin thermocouple wires and electrostatically exciting the flexural resonance. Silver paint was applied to the sample in correspondence with the exciting/measuring electrode and in order to short the thermocouple. The measuring system is described in Ref. [40]. The real part was measured from the resonance frequency $f(T)$, being $E' \propto f^2$ [41]. The data are presented as compliance $s = 1/E$ with s' normalized to its minimum value of $s_0 = s(T_0 \simeq 750\ \text{K})$ in the paraelectric (PE) phase; in terms of the resonance frequency, it is $s'(T)/s_0 = [f_0/f(T)]^2$, where $f_0 = f(T_0)$ is the frequency corresponding to s_0. The elastic energy-loss $Q^{-1} = s''/s'$ was measured from the decay of the free oscillations or from the width of the resonance curve [41].

The dielectric permittivity $\epsilon = \epsilon' - i\epsilon''$ was measured by means of a HP 4284A LCR meter with a four-wire probe and an electric field of 0.5 V/mm between 10 kHz and 1 MHz in a Delta Design 9023 chamber for the temperature control.

III. RESULTS

Figure 1 presents the normalized compliance s'/s_0 and elastic energy-loss coefficient Q^{-1} of $BaTiO_{3-\delta}$ of type No. 1 versus temperature at various reduction levels. The curves are a selection from various measurements on the two bars No. 1.1 and No. 1.2: virgin sample No. 1.1 ($\delta = 0$) and sample No. 1.2 before ($\delta = 0.0046$) and after ($\delta = 0.0053$, 0.016) reducing its thickness. In all cases, f_0 ranged between 2.2 and 2.6 kHz. The Curie temperatures T_C and the temperatures T_{OT} of the transition between tetragonal and orthorhombic states are indicated with vertical lines; T_{RO} indicates the transition between the orthorhombic and the rhombohedral phases [37]. All the compliance curves presented here were measured during cooling in order to avoid any possible influence from aging.

The main effect of doping V_O is a progressive shift of T_C to lower temperatures, accompanied by an increase in the steplike softening below T_C (20% at $\delta = 0.016$). Also, T_{OT} steadily decreases, and the increase in the peaked softening at the same temperature is strong (50% at $\delta = 0.0053$), although at the highest doping it becomes broadened and depressed. The last transition at T_{RO} slightly shifts to higher temperatures and noticeably broadens so that at the highest doping it is visible only as a peak in the losses.

The losses are peaked at the structural transitions and exhibit rather high levels in the FE phases due to domain-wall relaxation. Their general lowering with increasing δ can be attributed to the pinning effect of the V_O on the domain walls, which become static with respect to the tested frequencies. On the contrary, in the PE phase the losses increase with δ. This is due to the thermally activated hopping of isolated and clustered V_O as already found in $SrTiO_3$ [42] and will be discussed in a separate paper.

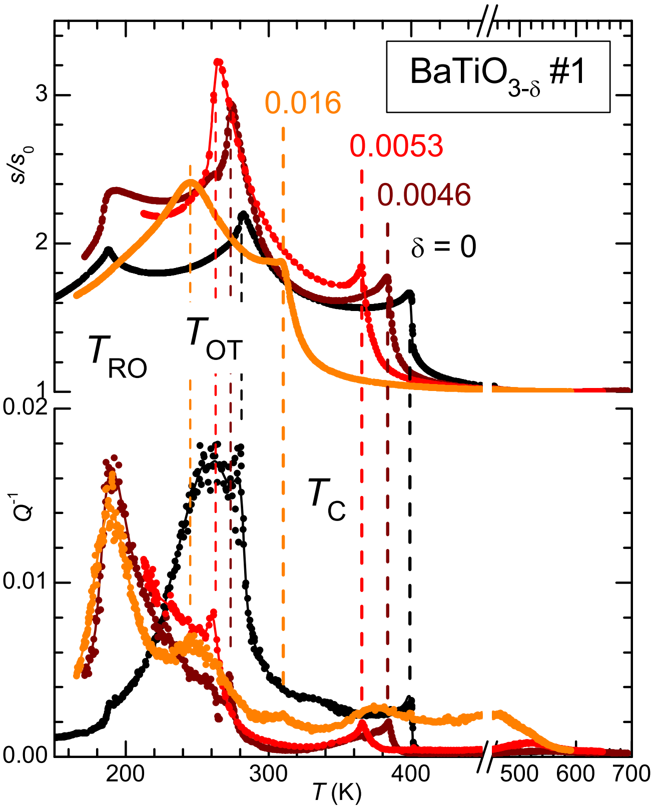

FIG. 1. Compliance s (reciprocal Young's modulus) normalized to its minimum value s_0 in the PE phase and elastic energy-loss coefficient Q^{-1} of $BaTiO_{3-\delta}$ of type No. 1 versus temperature at various reduction levels. The resonance frequency corresponding to s_0 ranged between 2.2 and 2.6 kHz. The curves refer to the virgin sample No. 1.1 ($\delta = 0$) and No. 1.2 before ($\delta = 0.0046$) and after ($\delta = 0.0053$, 0.016) reducing its thickness. The Curie temperatures T_C and the temperatures T_{OT} of the transition between tetragonal and orthorhombic states are indicated with vertical lines. T_{RO} indicates the transition between the orthorhombic and the rhombohedral states.

Figure 2 presents similar results obtained on $BaTiO_{3-\delta}$ No. 2. The Q^{-1} curves, which are of no interest here, are omitted for clarity. The sample was progressively reduced up to a maximum $\delta = 0.0118$ as estimated from the cumulative mass losses, but after reoxygenation, the mass gain corresponded to $\delta = 0.007\,63$. The actual discrepancy between the two values, attributable to the evaporation of residual Ag traces, may be smaller than it appears since also the last estimate might have been affected by the evaporation of the traces of Ag paint, this time underestimating the mass gain under reoxygenation. For our purposes, the exact values of δ are not important, and the results in Fig. 2 are perfectly compatible with those of Fig. 1, in part, obtained with a more effective protocol for removing the Ag electrodes.

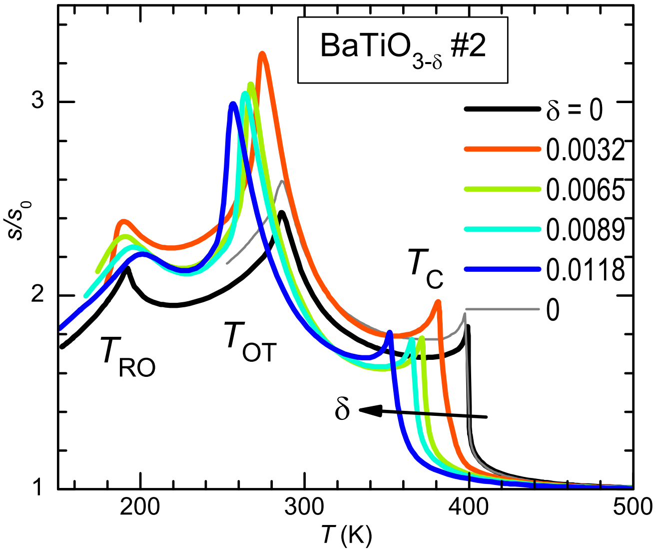

FIG. 2. Compliance s (reciprocal Young's modulus) normalized to its minimum value s_0 in the PE phase of $BaTiO_{3-\delta}$ No. 2 versus temperature after various reducing treatments. The thinner curve was obtained after a final reoxygenation. The resonance frequency corresponding to s_0 was 1.85 kHz.

After reoxygenation, the anelastic spectrum of $BaTiO_{3-\delta}$ No. 2 was measured again and found very close to that in the virgin state except for an overall 6% increase in the compliance in the FE phase. The magnitude of the softening in the FE phase depends on the piezoelectric response of the material [37], and a possible explanation for the observed increase is an improvement in the density, microstructure, and domain configuration after the repeated high-temperature reduction and oxygenation treatments. This fact also excludes any partial conversion of cubic $BaTiO_{3-\delta}$ to the hexagonal phase during the reducing treatments [43]. Anyway, even if some hexagonal phase formed, its effect would be of depressing the elastic anomalies at the transitions because its Young's modulus linearly increases with cooling down to 150 K [44]. This would only reinforce the present observations that V_O doping does not suppress the FE transitions but even slightly enhances the coupling between atomic displacements and strain.

Figure 3 presents the dielectric permittivity and losses measured on $BaTiO_{3-\delta}$ No. 1.2 at the lowest doping $\delta = 0.0046$. The sample was already black and conductive although not metallic.

The highest frequencies from 640 to 960 kHz were tested during a first run, whereas those from 500 kHz down to 10 kHz during a subsequent run. For clarity, only the heating data are reproduced together with the cooling at 500 kHz. These curves have no resemblance at all with the usual permittivity measured in BT [45]: The sharp peaks and steps at the transition temperatures are completely absent, $\epsilon(T)$ steadily increases with temperature also above T_C and increases also with decreasing frequency. The losses are weakly dependent on temperature and are roughly inversely proportional to f below 100 kHz. These features are typical of highly conductive materials and are due to the dynamics of the free charges. The only effect that can be attributed to the transition at T_C is a small step in ϵ' measured at the highest frequencies, but its sign is opposite to what is expected at a polar transition.

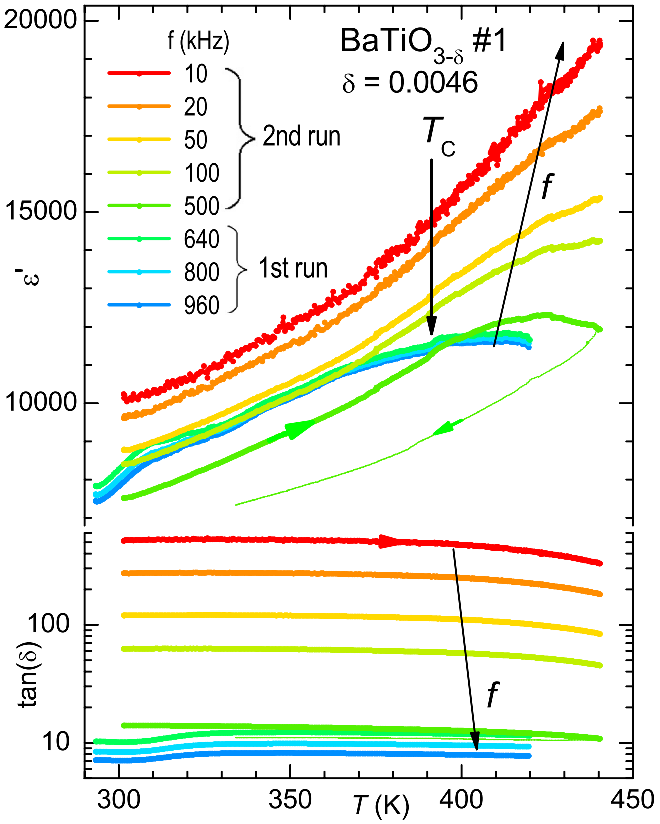

FIG. 3. Dielectric permittivity and losses of $BaTiO_{3-\delta}$ No. 1.2 at the lowest doping, measured during a first heating run at 640, 800, and 960 Hz and during a second run at 10, 20, 50, 100, and 500 kHz. For clarity, the cooling curves are shown only for 500 Hz.

IV. DISCUSSION

The first conclusion that one can draw from the present results is that there is a substantial continuity of the anelastic spectra of $BaTiO_{3-\delta}$ with progress of the O deficiency. There is a shift of T_C to lower temperatures, and some shifting and broadening of the anomalies at T_{OT} and T_{RO} together with changes in their intensities, but they retain all their characteristics. This indicates that doping V_O does not induce any major change in the nature of the three structural transitions, apart from the obvious introduction of lattice and charge disorder. On the contrary, the dielectric spectrum in Fig. 3 is completely changed already at the lowest values of δ and does not retain any of the well-known characteristics of the BT dielectric curves with sharply peaked steps at the three transitions. This fact, however, is due to the overwhelming effect of the charge carriers introduced by the ionized V_O defects, which totally mask any response from the intrinsic electric dipoles. This is a manifestation of the fact that probing the permanence of polar distortions in the bulk of a ferroelectric material with high electrical conductivity cannot be performed with the usual methods directly sensitive to the electric polarization, such as dielectric permittivity, hysteresis loop, or thermally stimulated depolarization current because of the screening effect of the free charges.

It is then clear that the anelastic spectra provide a practical and valuable tool for studying highly doped ferroelectrics in addition to the other techniques used so far, notably optical SHG [15,17,18,46] and Rietveld analysis of diffraction data [14]. The nonlinear optical technique also allows polar domains to be mapped [15,46], although it is not obvious to quantitatively relate the magnitude of the SHG signal with the spontaneous polarization or piezoelectric coefficients. The determination of the full structure by diffraction techniques has been exploited [14] for demonstrating that metallic $\mathrm{LiOsO_3}$ is isostructural with $\mathrm{LiNbO_3}$, a well-known ferroelectric, and hence a "ferroelectriclike metal." This type of experiment, however, is much more demanding than those traditionally performed in laboratories for FE materials. The measurement of the elastic moduli as a function of temperature, on the other hand, is accessible, insensitive to free charge carriers, and the elastic anomalies at the structural transitions provide insight into the distortion modes involved in the transitions and, hence, indirectly of the atomic displacements.

Complex compliance curves, such as those in Figs. 1 and 2, by themselves do not tell that the material is ferroelectric below T_C since any distortion mode that is coupled quadratically to a strain ε or stress σ, for example, antiferrodistortive octahedral tilting by an angle ϕ, would cause a steplike softening below T_C. Yet, when studying the effect of doping on an initially FE material, it is possible, even without structural measurements, to figure out if doping, besides introducing charge carriers, may change the character of the transition from polar to something else. In order to do that, we discuss the types of transitions other than ferroelectric, that might possibly be induced by doping in BT or similar FE perovskites. In this manner, we will discard the possibility that the polar modes of the FE transitions below T_C are fading away, replaced by other types of effects induced by doping and conclude that doping does not depress the polar modes. Certainly, T_C and T_{OT} are depressed as one would expect from the lattice and charge disorder introduced by the V_O and the fact that the induced Ti^{3+} ions, having a radius larger than Ti^{4+}, have a reduced tendency to go off-center. Yet, once the transition occurs, the magnitude of the atomic displacements and their coupling with strain are not depressed at all but rather slightly enhanced. This is especially true for the transition at T_{OT} where the polarization reorients from the $\langle 100\rangle$ to the $\langle 110\rangle$ pseudocubic directions.

A. Elastic anomalies from transitions other than ferroelectric

Limiting our discussion to perovskites, we should take into account: (i) antiferrodistortive octahedral tilting, (ii) cooperative Jahn-Teller (JT), and (iii) antiferromagnetic and ferromagnetic transitions and check whether they can possibly appear as a steplike softening below the transition so replacing the effect from a fading polar mode.

1. Antiferrodistortive octahedral tilting

The coupling energy between the order parameter for octahedral tilting, i.e., the tilt angle ϕ, and the involved shear strain ε is $\propto \varepsilon\phi^2$ because rotations of $\pm\phi$ produce the same ε and the consequent change in free energy must be the same. This is the same form of coupling as between spontaneous polarization P in a FE and strain, namely, the electrostrictive coupling $\propto \varepsilon P^2$, possible also in the PE phase. The simplest situation of this kind is described by Landau's theory of phase transitions with an elastic Gibbs free energy [38,47] (with σ rather than ε as an independent variable),

$$G = \frac{\alpha}{2}(T - T_C)\phi^2 + \frac{\beta}{4}\phi^4 - \frac{1}{2}s^0\sigma^2 - \gamma\sigma\phi^2,$$

where the bilinear coupling $\propto \sigma\phi$ between stress σ and order parameter ϕ is not allowed by symmetry and s^0 is the compliance in the symmetric high-temperature phase. In this case, the compliance $s = d\varepsilon/d\sigma$ with $\varepsilon = -\partial G/\partial\sigma$ remains unaltered until the equilibrium order parameter $\overline{\phi}$ is null above T_C and is softened by γ^2/β below T_C [38,47,48]. Sequences of phase transitions as in BT require additional terms with higher powers of ϕ in the free-energy expansion. The point is that, if both the FE order parameter P and the antiferrodistortive order parameter ϕ can be active, they produce similar types of elastic anomalies and there is no simple manner to weigh their respective influence on the elastic anomalies. Such a situation occurs in $\mathrm{Na_{1/2}Bi_{1/2}TiO_3}$, where octahedral tilting and polar modes are mixed in the various phase transitions, and it is not possible to deduce information on the piezoelectric coupling based only on the elastic anomalies [37,38].

Luckily, in BT there is no tendency at all to octahedral tilting. In fact, this type of distortion occurs in the $AB\mathrm{O_3}$ perovskites (A = Ca, Ba, Pb, etc.; B = Ti, Zr, Sn, etc.) when the rigid $B\mathrm{O_6}$ octahedra are in compression with respect to the A-O sublattice, for example, when cooling causes a larger thermal contraction in the longer, softer, and more anharmonic A-O bonds, and the octahedra tilt in order to fit in the smaller volume without distorting the rigid B-O bonds [49,50]. Barium titanate is the perovskite with the highest ratio of the A-O to B-O bond lengths [51] and, therefore, is the least prone to octahedral tilting. This is true also after doping with V_O because, even though Ti^{3+} has an ionic radius of 0.88 Å, larger than 0.60 of Ti^{4+} [52], the V_O's weaken the networks of both octahedra and Ba-O and, therefore, the strength of the mismatch that produces tilting. This has been observed [50] in $\mathrm{BaCe_{1-x}Y_xO_{3-\delta}}$ where a sequence of tilt transitions occurs during cooling: Doping with Y^{3+} on Ce^{4+} increases the average size of the $\mathrm{(Ce/Y)O_6}$ octahedra because of the larger radius of Y^{3+}, and this should enhance the tilt transition temperature. On the contrary, the temperature of the first tilting transitions is greatly depressed by the larger effect of V_O, which weakens the lattice and relieves the mismatch between octahedra and Ba-O bonds. Similarly, the introduction of V_O in $\mathrm{BaTiO_3}$ should not induce any tendency to tilting, despite the increase in the mean size of the $\mathrm{(Ti^{4+}/Ti^{3+})O_6}$ octahedra.

2. Cooperative Jahn-Teller transition

Each V_O in undoped $\mathrm{BaTiO_3}$ donates up to two electrons, which are generally localized on Ti so that a completely ionized V_O induces the Ti^{3+} state in two Ti^{4+} ions [53,54]. The external electronic shell of Ti^{+3} is $3d^1$, or an electron is doped in the empty $3d$ shell. The five degenerate d orbitals are already split into three T_{2g} (d_{xy}, d_{yz}, and d_{xz}) and two

E_g ($d_{3z^2-r^2}$ and $d_{x^2-y^2}$) orbitals by the octahedral environment of Ti, which can be further split by octahedral distortions, giving rise to the JT effect [55]. The Ti^{3+} ions are usually observed in acceptor-doped titanates [53,54] where, at low concentrations, they form polarons or bipolarons without particular effects on the structure. It is also suggested that the JT distortions of Ti^{3+} in $\mathrm{BaTiO_3}$ may stabilize the hexagonal phase (h-BT) over the cubic one under strongly reducing conditions, but this occurs at the very high sintering temperatures ∼1400 °C , which can be slightly lowered by doping strongly JT active ions in the Ti site [56,57]. It is out of the question that the major lattice rearrangement necessary for the hexagonal/cubic transition may occur also down to T_C; if the formation of minor amounts of h-BT occurred in the present investigation, it was during the reducing treatments at high temperatures. Yet, as explained in the previous section, this could only decrease the amplitude of the elastic anomalies by reducing the fraction of BT, in fact, h-BT has no phase transitions down to 150 K, and above that temperature its Young's modulus exhibits the usual linear anharmonic stiffening [44].

Therefore, the only possible effect on the elastic anomalies from the JT active Ti^{3+} ions would be a tendency to a cooperative JT transition [49], namely, ordering of the $3d^1$ orbitals and the associated octahedral distortions into a coherent pattern. Also, this scenario could not explain the observed persistence of the steplike anomaly below T_C for, at least, two reasons. The first reason is that at temperatures as low as T_C most Ti^{3+}'s are trapped next to a V_O, which can have up to two axially arranged nearest-neighboring Ti^{3+}. These electrons cannot participate in an orbital order transition because their occupation, presumably $d_{3z^2-r^2}$ [54,58], is determined by the position of the neighboring V_O, which can be considered as static in this respect. Then, the fraction of Ti^{3+} free from V_O and available for a cooperative JT transition is much smaller than the maximum possible concentration of Ti^{3+}, namely, $2/3 \times \delta \leqslant 0.01$ in the present investigation, and this is far below the threshold for cooperative orbital ordering to occur [49]. Finally, an orbital order transition would cause stiffening rather than softening [38,59], apart from a minor initial softening above the transition. This is due to the fact that, above the transition temperature, in the cubic phase, the orbitals are randomly occupied among the T_{2g} and/or E_g multiplets, and their populations can almost instantaneously relax under the influence of the stress from the sample vibration, causing anelastic relaxation and softening the elastic modulus. Such a softening disappears below the orbital order transition where the orbitals are frozen, appearing as a stiffening [59].

3. Magnetic transition

The electrons that occupy the Ti^{3+} ions accompanying the V_O carry also unpaired spins and, therefore, are potential sources of magnetic ordering [60]. Various theoretical papers have been devoted to predicting possible magnetism in highly deficient $\mathrm{BaTiO}_{3-\delta}$, but the experimental evidence, when not negative, is for very small or controversial effects.

In $\mathrm{BaTiO}_{3-\delta}$ the magnetic susceptibility has been measured at various reduction levels, characterized with the electron concentration n at 400 K from the Hall effect [58], finding a paramagnetic behavior down to LHe temperature. The paramagnetic rise of χ below 50 K persists also at the highest dopings, corresponding to $\delta > 0.033$, and excludes any magnetic ordering at higher temperatures. No magnetism has been found even in extremely reduced $\mathrm{SrTiO}_{3-\delta}$ with $\delta \leqslant 0.28$ [61], whereas very weak ferromagnetism has been deduced from field-cooling and zero-field-cooling splitting of the magnetic susceptibility [62], but without any Curie-Weiss peak, under certain reducing conditions and after irradiation with specific ions and fluences [62]. Ferromagnetism has been reported in nanocrystalline $\mathrm{BaTiO_3}$, but it disappears after high-temperature annealing with onset of grain growth [63] so that it can be ruled out in the present case of well-developed grains. In addition, these effects in the M-H curves are so small to be comparable with those from usual sources of contamination [64]. In order to obtain more substantial magnetic responses in $\mathrm{BaTiO_3}$, one must dope magnetic ions, but even then the effect of V_O is weak: In $\mathrm{EuBaTiO}_{3-\delta}$ the Eu $4f$ spins order antiferromagnetically, and the V_O with δ as high as 0.15 induces a ferromagnetic transition but only below 3 K [65].

It can be concluded from the existing experiments that no magnetic ordering of the spins introduced by V_O is expected at the presently tested O deficiencies. Even conceding that our samples become strongly magnetic below T_C under doping, the temperature dependence of the magnetic contribution to the elastic constants would be different from the sharp step found at T_C. In fact, depending on the strain derivatives of the exchange constants, there can be either a softening [66] or a stiffening [67] below the ferromagnetic transition, which, however, is proportional to the square of the magnetization and, therefore, is progressive [66] rather than steplike. Therefore, a magnetic transition could not replicate the anomaly observed here below T_C and even less the peaked softening at T_OT.

B. Interpretation of the elastic anomalies in $\mathrm{BaTiO}_{3-\delta}$ as piezoelectric softening

After examining the effects of the other types of transitions occurring in perovskites, we conclude that only octahedral tilting can produce an anomaly similar to the piezoelectric softening below T_C. On the other hand, due to the large Ba ionic size, stoichiometric $\mathrm{BaTiO_3}$ is far from unstable against octahedral titling and even more after the lattice is weakened by the introduction of O vacancies. It can be concluded that the magnitude of the softening below T_C in $\mathrm{BaTiO}_{3-\delta}$ is a measure of the piezoelectric coupling and, therefore, of the tetragonal distortion and the associated off-centering of Ti. In fact, the softening in the FE phase can be written in terms of the electrostrictive coupling Q, dielectric susceptibility χ, and spontaneous polarization P_0 as [36,38,68]

$$\Delta s = 4\chi_0 Q^2 P_0^2 \qquad (1)$$

ignoring for simplicity the tensorial nature of the various terms. This softening is also of piezoelectric origin since in this case the piezoelectric coefficient is $d = 2\chi_0 Q P_0$ [36,38,68]. The dielectric susceptibility has been written as χ_0 in order to stress the fact that it is defined as $\chi_0 = \partial P_0/\partial E$, namely, the change in the FE polarization under application of an electric field. However, in a conducting sample the permittivity $\epsilon \simeq \chi$ rather measures the response of the free charges to the external electric field. The free charges screen E outside the sample and, therefore, do not allow the FE dipoles within the sample to feel it. Then, the appropriate susceptibility to insert in Eq. (1) is not ϵ' of Fig. 3 but rather the response that the spontaneous polarization would have in the absence of screening from the free charges, because the compliance s is measured in the absence of E. None of the quantities in Eq. (1) can be directly measured in a conducting sample, but their product is the elastic softening Δs. If, upon doping, Δs remains constant or even increases, the most likely situation seems that all of them vary little. In fact, if one assumes that P_0 vanishes as commonly implied until recently, at least one or both Q and χ_0 should correspondingly increase. The electrostrictive coupling Q is essentially of ionic origin, resulting from the strengths and geometry of the bonds and ionic effective charges [69] and is usually weakly dependent on temperature and composition even through the FE transition [70]. In the descriptions of FE materials and phase diagrams, Q is one of the coefficients of the Landau expansion of the free energy, independent of temperature [68] and sometimes of composition [71]. Then, in order to compensate for a hypothetical vanishing P_0, one should assume that upon doping $\chi_0 \sim 1/P_0$, for which no ground can be found.

We conclude that the enhancement of the softening below T_C and in correspondence with the subsequent structural transitions reflects the persistence of ferroelectricity in the presence of free charge carriers even in the metallic state. In fact, the critical concentration of electrons above which $BaTiO_{3-\delta}$ is metallic is [12] $n_c = 1 \times 10^{20}$ cm^{-3} or 0.0064 mol^{-1}, which is reached with $\delta = 0.0096$ assuming two electrons per V_O. Our highest doping $\delta = 0.016$ should, therefore, have induced a metallic state, even assuming that part of the V_O are aggregated and possibly contribute each with less than two electrons to doping. These data confirm the initial finding of the persistence of ferroelectricity in $BaTiO_3$ through the insulator-metal transition, obtained by a combination of resistivity, specific heat, x-ray diffraction, and optical conductivity measurements [12] and demonstrates the effectiveness of studying highly doped or metallic ferroelectrics by means of elastic measurements.

The results of Kolodiazhnyi *et al.* [12] have been criticized on the basis of neutron-diffraction measurements on $BaTiO_{3-\delta}$ with $\delta = 0.09$ and 0.25, according to which there is a separation into insulating and metallic phases rather than coexistence of FE and metallic states [13]. Apart from the recent observation of FE in $BaTiO_3$ made metallic by La^{3+} doping [72], there are various replies to the argument of a phase separation. First, the O deficiencies of the experiment where the phase separation is found [13] are far higher than those we are considering here and during reductions at those levels $BaTiO_{3-\delta}$ should, at least partially, transform into the hexagonal phase [43,56,57]. On the other hand, even if a phase separation occurred in the present case, the steplike softening below T_C would not shift to lower temperatures without reducing amplitude and sharpness; rather, it would decrease in amplitude with the same T_C, corresponding to the fraction that remains insulating FE.

Before concluding, we comment on the initial increase in the magnitude of the piezoelectric softening with doping. The increase in the softening below T_C is certain at the initial stage of doping, whereas it might be influenced by the next transition at T_{OT} at higher doping due its proximity and broadening. Also, the transition at T_{OT} is of FE nature, consisting of the change in the direction of the spontaneous polarization from (001) to (011), and the associate softening is enhanced by doping even more than that below T_C; this fact would deserve further investigation, but we will limit to the FE/PE transition below T_C. The initial enhancement of the softening below T_C upon doping might be an exciting confirmation of the theoretical prediction that the polar distortions may even be reinforced by metallization, especially if they are mainly due to local chemical or steric effects [32]. Yet, some caution is necessary since the elastic softening, such as the piezoelectric effect, is affected by the depolarization field E_{dep}. The use of Eq. (1) relies on the assumption that the depolarization field is negligible, a condition that it is argued to be approximated for unpoled samples probed by vibrations whose wavelengths exceed the domain size [36–38]. There is, however, no quantitative assessment in this sense yet, and it cannot be excluded that at the present conditions E_{dep} partially restrains the piezoelectric softening in the absence of free charges. In this case, the charge carriers introduced by doping would neutralize the polarization charges and the associated E_{dep}, resulting in an enhancement of the observed piezoelectric softening. On the other hand, the magnitude of the piezoelectric softening in these undoped ceramic samples has been quantitatively compared with the intrinsic piezoelectric $\mathbf{d}$ and dielectric constant $\epsilon \simeq \chi_0$ from the literature on single crystals through the appropriate average of the tensor Eq. (1), written as $\Delta s = \langle \mathbf{d}^+ \cdot \chi^{-1} \cdot \mathbf{d} \rangle$, and good agreement was found [37,38]. This fact suggests that in unpoled ceramics probed at kilohertz frequencies E_{dep} is indeed negligible in the majority of domains. In addition, one would expect that the depolarization charges are already neutralized at the lowest doping $\delta =$ 0.0046 of sample No. 1 where the mobile charges already totally mask the dielectric response (Fig. 3); instead, Fig. 1 shows that further doping to $\delta \simeq 0.0053$ still increases the softening below T_C. We do not consider the highest dopings where an influence of the transition at T_{OT} is possible.

V. CONCLUSION

The topic of coexistence of ferroelectric and highly conducting states is of both fundamental and practical interests. On one hand, it regards the fundamental ionic and electronic interactions responsible for ferroelectricity and possible new mechanisms of the electron-phonon interaction, which might, for example, favor superconductivity. On the other hand, there are applications of ferroelectrics, for example, in the fields of thermoelectricity and multiferroics where the electric conductivity is either required or an unwanted but frequent by-product of the material engineering. In these cases, the major experimental obstacle is probing the FE state since the traditional experiments for this purpose apply electric fields and/or detect electric currents and, hence, probe the free charges rather than the FE response, not to mention the difficulties of poling such samples.

Here, it has been shown that purely elastic measurements are a practical and effective tool for probing the FE state of materials independently of their conducting state. This is possible because in the FE state there is an additional softening of piezoelectric origin, which can be probed also on unpoled samples and without the application of electric fields. Therefore, by following the evolution of the elastic compliance versus temperature at various doping levels, it is possible to assess how ferroelectricity is affected by doping. It is also possible to obtain information on unknown FE transitions in new conducting materials with an appropriate analysis of the possible types of structural transitions and couplings to strain.

The method is demonstrated by following the evolution of the Young's modulus of $BaTiO_{3-\delta}$ versus temperature with δ up to 0.016, which corresponds to a metallic state. It turns out that doping shifts the temperatures of the first two FE transitions T_C and T_{OT} to lower temperature but the piezoelectric softening below T_C is little affected and even enhanced. After analyzing the possible alternative mechanisms that might contribute to maintaining the softened state below T_C under doping through O vacancies, it is concluded that only the FE transitions originally observed in undoped $BaTiO_3$ can be responsible for the observations. Therefore, doping with V_O and the concomitant lattice and charge disorder depress the onset temperature T_C but not the magnitude of the FE displacements and their coupling with macroscopic strain. This confirms earlier conclusions based on a combination of other techniques [12].

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[1] P. W. Anderson and E. I. Blount, Symmetry Considerations on Martensitic Transformations: 'Ferroelectric' Metals? Phys. Rev. Lett. **14**, 217 (1965).

[2] Ch. J. Raub, A. R. Sweedler, M. A. Jensen, S. Broadston, and B. T. Matthiasg, Superconductivity of Sodium Tungsten Bronzes, Phys. Rev. Lett. **13**, 746 (1964).

[3] E. Pytte, Theory of the Structural Transition in NbSn and V_3Si, Phys. Rev. Lett. **25**, 1176 (1970).

[4] X. Zhu, M. Fu, M. C. Stennett, P. M. Vilarinho, I. Levin, C. A. Randall, J. Gardner, F. D. Morrison, and I. M. Reaney, A crystal-chemical framework for relaxor versus normal ferroelectric behavior in tetragonal tungsten bronzes, Chem. Mater. **27**, 3250 (2015).

[5] K. R. Locherer, I. P. Swainsond, and E. K. H. Salje, Transition to a new tetragonal phase of WO_3 : crystal structure and distortion parameters, J. Phys.: Condens. Matter **11**, 4143 (1999).

[6] S. Fabbrici, E. Montanari, L. Righi, G. Calestani, and A. Migliori, Charge order and tilt modulation in multiferroic $K_xM^{II}_xM^{III}_{1-x}F_3$ ($0.4 < x < 0.6$) transition metal fluorides with tetragonal tungsten bronze structure, Chem. Mater. **16**, 3007 (2004).

[7] G. Bonera, F. Borsa, M. L. Crippa, and A. Rigamonti, Transient nuclear-magnetic-resonance study of phase transitions in metallic sodium tungsten bronzes, Phys. Rev. B **4**, 52 (1971).

[8] G. Cannelli, M. Canali, R. Cantelli, F. Cordero, S. Ferraro, M. Ferretti, and F. Trequattrini, Low temperature phase transformations in $YBa_2Cu_3O_{6+x}$ by anelastic relaxation measurements and possible formation of ferroelectric and antiferroelectric domains, Phys. Rev. B **45**, 931 (1992).

[9] J. L. Birman and M. Weger, Theory of coexistence of superconductivity and ferroelectricity: A dynamical symmetry model, Phys. Rev. B **64**, 174503 (2001).

[10] I. A. Sergienko, V. Keppens, M. McGuire, R. Jin, J. He, S. H. Curnoe, B. C. Sales, P. Blaha, D. J. Singh, K. Schwarz, and D. Mandrus, Metallic "Ferroelectricity" in the Pyrochlore $Cd_2Re_2O_7$, Phys. Rev. Lett. **92**, 065501 (2004).

[11] Y. Ishibashi and M. Iwata, Structural and elastic aspects in phase transitions of superconducting pyrochlore oxide $Cd_2Re_2O_7$, J. Phys. Soc. Jpn. **79**, 044604 (2010).

[12] T. Kolodiazhnyi, M. Tachibana, H. Kawaji, J. Hwang, and E. Takayama-Muromachi, Persistence of Ferroelectricity in $BaTiO_3$ through the Insulator-Metal Transition, Phys. Rev. Lett. **104**, 147602 (2010).

[13] I. K. Jeong, S. Lee, S. Y. Jeong, C. J. Won, N. Hur, and A. Llobet, Structural evolution across the insulator-metal transition in oxygen-deficient $BaTiO_{3-\delta}$ studied using neutron total scattering and Rietveld analysis, Phys. Rev. B **84**, 064125 (2011).

[14] Y. Shi, Y. Guo, X. Wang, A. J. Princep, D. Khalyavin, P. Manuel, Y. Michiue, A. Sato, K. Tsuda, S. Yu, M. Arai, Y. Shirako, M. Akaogi, N. Wang, K. Yamaura, and A. T. Boothroyd, A ferroelectric-like structural transition in a metal, Nature Mater. **12**, 1024 (2013).

[15] S. Lei, M. Gu, D. Puggioni, G. Stone, J. Peng, J. Ge, Y. Wang, B. Wang, Y. Yuan, K. Wang, Z. Mao, J. R., and V. Gopalan, Observation of quasi-two-dimensional polar domains and ferroelastic switching in a metal, $Ca_3Ru_2O_7$, Nano Lett. **18**, 3088 (2018).

[16] N. A. Benedek and C. J. Fennie, Hybrid Improper Ferroelectricity: A Mechanism for Controllable Polarization-Magnetization Coupling, Phys. Rev. Lett. **106**, 107204 (2011).

[17] L. Wu, S. Patankar, T. Morimoto, N. L. Nair, E. Thewalt, A. Little, J. G. Analytis, J. E. Moore, and J. Orenstein, Giant anisotropic nonlinear optical response in transition metal monopnictide Weyl semimetals, Nat. Phys. **13**, 350 (2017).

[18] S. Patankar, L. Wu, B. Lu, M. Rai, J. D. Tran, T. Morimoto, D. E. Parker, A. G. Grushin, N. L. Nair, J. G. Analytis, J. E. Moore, J. Orenstein, and D. H. Torchinsky, Resonance-enhanced optical nonlinearity in the Weyl semimetal TaAs, Phys. Rev. B **98**, 165113 (2018).

[19] T. H. Kim, D. Puggioni, Y. Yuan, L. Xie, H. Zhou, N. Campbell, P. J. Ryan, Y. Choi, J. W. Kim, J. R. Patzner, S. Ryu, J. P. Podkaminer, J. Irwin, Y. Ma, C. J. Fennie, M. S. Rzchowski, X. Q. Pan, V. Gopalan, J. M. Rondinelli, and C. B. Eom, Polar metals by geometric design, Nature (London) **533**, 68 (2016).

[20] Z. Fei, W. Zhao, T. A. Palomaki, B. Sun, M. K. Miller, Z. Zhao, J. Yan, X. Xu, and D. H. Cobden, Ferroelectric switching of a two-dimensional metal, Nature (London) **560**, 336 (2018).

[21] G. Giovannetti and M. Capone, Dual nature of the ferroelectric and metallic state in $LiOsO_3$, Phys. Rev. B **90**, 195113 (2014).

[22] N. A. Benedek and T. Birol, "Ferroelectric" metals reexamined: fundamental mechanisms and design considerations for new materials, J. Mater. Chem. C **4**, 4000 (2016).

[23] I. Lo Vecchio, G. Giovannetti, M. Autore, P. Di Pietro, A. Perucchi, J. He, K. Yamaura, M. Capone, and S. Lupi, Electronic correlations in the ferroelectric metallic state of $LiOsO_3$, Phys. Rev. B **93**, 161113 (2016).

[24] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, Oxford, 1977).

[25] R. E. Cohen, Origin of ferroelectricity in perovskite oxides, Nature (London) **358**, 136 (1992).

[26] X. He and K. J. Jin, Persistence of polar distortion with electron doping in lone-pair driven ferroelectrics, Phys. Rev. B **94**, 224107 (2016).

[27] R. Agarwal, Y. Sharma, S. Chang, K. C. Pitike, C. Sohn, S. M. Nakhmanson, C. G. Takoudis, H. N. Lee, R. Tonelli, J. Gardner, J. F. Scott, R. S. Katiyar, and S. Hong, Room-temperature relaxor ferroelectricity and photovoltaic effects in tin titanate directly deposited on a silicon substrate, Phys. Rev. B **97**, 054109 (2018).

[28] C. Ma, X. He, and K. J. Jin, Polar instability under electrostatic doping in tetragonal $SnTiO_3$, Phys. Rev. B **96**, 035140 (2017).

[29] Y. Wang, X. Liu, J. D. Burton, S. S. Jaswal, and E. Y. Tsymbal, Ferroelectric Instability under Screened Coulomb Interactions, Phys. Rev. Lett. **109**, 247601 (2012).

[30] Y. Iwazaki, T. Suzuki, Y. Mizuno, and S. Tsuneyuki, Doping-induced phase transitions in ferroelectric $BaTiO_3$ from first-principles calculations, Phys. Rev. B **86**, 214103 (2012).

[31] H. K. Chandra, K. Gupta, A. K. Nandy, and P. Mahadevan, Ferroelectric distortions in doped ferroelectrics: $BaTiO_3 : M$ ($M =$ V-Fe), Phys. Rev. B **87**, 214110 (2013).

[32] H. J. Zhao, A. Filippetti, C. Escorihuela-Sayalero, P. Delugas, E. Canadell, L. Bellaiche, V. Fiorentini, and J. Íñiguez, Meta-screening and permanence of polar distortion in metallized ferroelectrics, Phys. Rev. B **97**, 054107 (2018).

[33] S. Lee, G. Yang, R. H. T. Wilke, S. Trolier-McKinstry, and C. A. Randall, Thermopower in highly reduced $n -$ type ferroelectric and related perovskite oxides and the role of heterogeneous nonstoichiometry, Phys. Rev. B **79**, 134110 (2009).

[34] S. Dong, J. M. Liu, S. W. Cheong, and Z. Ren, Multiferroic materials and magnetoelectric physics: symmetry, entanglement, excitation, and topology, Adv. Phys. **64**, 519 (2015).

[35] F. Craciun, M. Cernea, V. Fruth, M. Zaharescu, I. Atkinson, N. Stanica, L. C. Tanase, L. Diamandescu, A. Iuga, and C. Galassi, Novel multiferroic $(Pb_{1-3x/2}Nd_x)(Ti_{0.98-y}Fe_yMn_{0.02})O_3$ ceramics with coexisting ferroelectricity and ferromagnetism at ambient temperature, Mater. Des. **110**, 693 (2016).

[36] F. Cordero, F. Craciun, F. Trequattrini, and C. Galassi, Piezoelectric softening in ferroelectrics: ferroelectric versus antiferroelectric $PbZr_{1-x}Ti_xO_3$, Phys. Rev. B **93**, 174111 (2016).

[37] F. Cordero, Quantitative evaluation of the piezoelectric response of unpoled ferroelectric ceramics from elastic and dielectric measurements: Tetragonal $BaTiO_3$, J. Appl. Phys. **123**, 094103 (2018).

[38] F. Cordero, Elastic and dielectric evaluation of the piezoelectric response of ferroelectrics using unpoled ceramics, Ceramics **1**, 211 (2018).

[39] C. Ozmetin, M. Copur, A. Yartasi, and M. M. Kocakerim, Kinetic investigation of reaction between metallic silver and nitric acid solutions in the range 7.22-14.44 M, Ind. Eng. Chem. Res. **37**, 4641 (1998).

[40] F. Cordero, L. Dalla Bella, F. Corvasce, P. M. Latino, and A. Morbidini, An insert for anelastic spectroscopy measurements from 80 K to 1100 K, Meas. Sci. Technol. **20**, 015702 (2009).

[41] A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).

[42] F. Cordero, Hopping and clustering of oxygen vacancies in $SrTiO_3$ by anelastic relaxation, Phys. Rev. B **76**, 172106 (2007).

[43] A. Recnik and D. Kolar, Exaggerated growth of hexagonal barium titanate under reducing sintering conditions, J. Am. Ceram. Soc. **79**, 1015 (1996).

[44] F. Cordero, H. T. Langhammer, and T. Müller (unpublished).

[45] W. J. Merz, The electric and optical behavior of $BaTiO_3$ single-domain crystals, Phys. Rev. **76**, 1221 (1949).

[46] S. A. Denev, T. T. A. Lummen, E. Barnes, A. Kumar, and V. Gopalan, Probing ferroelectrics using optical second harmonic generation, J. Am. Ceram. Soc. **94**, 2699 (2011).

[47] B. A. Strukov and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals* (Springer, Heidelberg, 1998).

[48] J. C. Slonczewski and H. Thomas, Interaction of elastic strain with the structural transition of $SrTiO_3$, Phys. Rev. B **1**, 3599 (1970).

[49] J. B. Goodenough, Electronic and ionic transport properties and other physical aspects of perovskites, Rep. Prog. Phys. **67**, 1915 (2004).

[50] F. Cordero, F. Trequattrini, F. Deganello, V. La Parola, E. Roncari, and A. Sanson, Effect of doping and oxygen vacancies on the octahedral tilt transitions in the $BaCeO_3$ perovskite, Phys. Rev. B **82**, 104102 (2010).

[51] F. A. Kassan-Ogly and V. E. Naish, The immanent chaotization of crystal structures and the resulting diffuse scattering. II. Crystallochemical conditions of perovskite chaotization, Acta Crystallogr., Sect. B: Struct. Sci. **42**, 307 (1986).

[52] R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[53] S. Lenjer, O. F. Schirmer, H. Hesse, and Th. W. Kool, Conduction states in oxide perovskites: Three manifestations of Ti_{3+} Jahn-Teller polarons in barium titanate, Phys. Rev. B **66**, 165106 (2002).

[54] S. Lenjer, O. F. Schirmer, H. Hesse, and Th. W. Kool, Reply to "Comment on 'Conduction states in oxide perovskites: Three manifestations of Ti^{3+} Jahn-Teller polarons in barium titanate", Phys. Rev. B **70**, 157102 (2004).

[55] N. Tsuda, K. Nasu, A. Yanase, and K. Siratori, *Electronic Conduction in Oxides* (Springer-Verlag, Heidelberg, 1991).

[56] H. T. Langhammer, T. Müller, K. H. Felgner, and H. P. Abicht, Crystal structure and related properties of manganese-doped barium titanate ceramics, J. Am. Ceram. Soc. **83**, 605 (2000).

[57] H. T. Langhammer, T. Müller, R. Böttcher, and H.-P. Abicht, Structural and optical properties of chromium-doped hexagonal barium titanate ceramics, J. Phys.: Condens. Matter **20**, 085206 (2008).

[58] T. Kolodiazhnyi, Insulator-metal transition and anomalous sign reversal of the dominant charge carriers in perovskite $BaTiO_{3-\delta}$, Phys. Rev. B **78**, 045107 (2008).

[59] F. Cordero, F. Trequattrini, V. B. Barbeta, R. F. Jardim, and M. S. Torikachvili, Anelastic spectroscopy study of the metal-insulator transition of $Nd_{1-x}Eu_xNiO_3$, Phys. Rev. B **84**, 125127 (2011).

[60] D. Cao, M. Q. Cai, Y. Zheng, and W. Y. Hu, First-principles study for vacancy-induced magnetism in nonmagnetic ferroelectric $BaTiO_3$, Phys. Chem. Chem. Phys. **11**, 10934 (2009).

[61] W. Gong, H. Yun, Y. B. Ning, J. E. Greedan, W. R. Datars, C. V. Stager, N. Shanthi, and D. D. Sarma, Oxygen-deficient $SrTiO_{3-x}$, $x = 0.28$, 0.17, and 0.08. Crystal growth, crystal structure, magnetic, and transport properties, J. Solid State Chem. **90**, 320 (1991).

[62] K. Potzger, J. Osten, A. A. Levin, A. Shalimov, G. Talut, H. Reuther, S. Arpaci, D. Bürger, H. Schmidt, T. Nestler, and D. C. Meyer, Defect-induced ferromagnetism in crystalline $SrTiO_3$, J. Magn. Magn. Mater. **323**, 1551 (2011).

[63] Z. Y. Chen, Z. Q. Chen, D. D. Wang, and S. J. Wang, Correlation between interfacial defects and ferromagnetism of $BaTiO_3$ nanocrystals studied by positron annihilation, Appl. Surf. Sci. **258**, 19 (2011).

[64] M. A. Garcia, E. Fernandez Pinel, J. de la Venta, A. Quesada, V. Bouzas, J. F. Fernández, J. J. Romero, M. S. Martín González, and J. L. Costa-Krämer, Sources of experimental errors in the observation of nanoscale magnetism, J. Appl. Phys. **105**, 013925 (2009).

[65] W. Li, R. Zhao, L. Wang, R. Tang, Y. Zhu, J. H. Lee, H. Cao, T. Cai, H. Guo, C. Wang, L. Ling, L. Pi, K. Jin, Y. Zhang, H. Wang, Y. Wang, and S. H. Yang, Oxygen-vacancy-induced antiferromagnetism to ferromagnetism transformation in $Eu_{0.5}Ba_{0.5}TiO_{3-\delta}$ multiferroic thin films, Sci. Rep. **3**, 2618 (2013).

[66] G. Hausch, Magnetic exchange energy contribution to the elastic constants and its relation to the anomalous elastic behavior of invar alloys, Phys. Status Solidi A **15**, 501 (1973).

[67] G. A. Alers, J. R. Neighbours, and H. Sato, Temperature dependent magnetic contributions to the high field elastic constants of nickel and an Fe-Ni alloy, J. Phys. Chem. Solids **13**, 40 (1960).

[68] A. F. Devonshire, Theory of barium titanate-Part II, Philos. Mag. **42**, 1065 (1951).

[69] V. Sundar and R. E. Newnham, Electrostriction and polarization, Ferroelectrics **135**, 431 (1992).

[70] F. Li, L. Jin, Z. Xu, and S. Zhang, Electrostrictive effect in ferroelectrics: An alternative approach to improve piezoelectricity, Appl. Phys. Rev. **1**, 011103 (2014).

[71] A. Amin, M. J. Haun, B. Badger, H. McKinstry, and L. E. Cross, A phenomenological Gibbs function for the single cell region of the $PbZrO_3$:$PbTiO_3$ solid solution system, Ferroelectrics **65**, 107 (1985).

[72] J. Fujioka, A. Doi, D. Okuyama, D. Morikawa, T. Arima, K. N. Okada, Y. Kaneko, T. Fukuda, H. Uchiyama, D. Ishikawa, A. Q. R. Baron, K. Kato, M. Takata, and Y. Tokura, Ferroelectric-like metallic state in electron doped $BaTiO_3$, Sci. Rep. **5**, 13207 (2015).