Persistence of Ferroelectricity in $BaTiO_3$ through the Insulator-Metal Transition

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The ferroelectric $BaTiO_3$ is a band-gap insulator. Itinerant electrons can be introduced in this material by doping, for example, with oxygen vacancies. Above a critical electron concentration of $n_c \approx 1 \times 10^{20}$ cm^{-3}, $BaTiO_{3-\delta}$ becomes metallic. This immediately raises a question: Does metallic $BaTiO_{3-\delta}$ still retain ferroelectricity? One may expect itinerant electrons to destroy ferroelectricity as they screen the long-range Coulomb interactions. We followed the phase transitions in $BaTiO_{3-\delta}$ as a function of n far into metallic phase. Although their stability range decreases with n, the low-symmetry phases in metallic $BaTiO_{3-\delta}$ are still retained up to an estimated concentration of $n^* \approx 1.9 \times 10^{21}$ cm^{-3}. Moreover, it appears that the itinerant electrons partially stabilize the ferroelectric phases in metallic $BaTiO_{3-\delta}$ by screening strong crystal field perturbations caused by oxygen vacancies.

The problem of the coexistence of two distinct states of matter that, from common knowledge, may seem mutually incompatible, has been attracting significant attention. For example, it is generally considered that ferromagnetism or antiferromagnetism destroys superconductivity. Yet, recent findings reveal that several materials show both superconductivity and magnetic ordering [1]. (Partial) occupancy of d orbitals in transition metal perovskites is a prerequisite for magnetic ordering, whereas the absence of the d electrons is an important condition for ferroelectricity, which explains the scarcity of magnetic ferroelectrics [2]. Another relevant problem—a possible existence of ferroelectric (FE) metal—has been treated theoretically by Anderson and Blount [3]. Normally, one may expect that the fragile balance of the long- and short-range forces that stabilizes FE ground state will be altered by the screening effect of itinerant electrons, thus destroying ferroelectricity in metals. The authors of Ref [3], however, suggest that FE metals may exist providing that the interaction between the itinerant electrons and the soft "FE" phonon mode is weak.

For almost four decades no experimental evidence of FE metal has been reported. Recently, a loss of a center of symmetry at the cubic-to-tetragonal phase transition in $Cd_2Re_2O_7$ has been discussed in light of elastic moduli measurements [4]. According to Ref [4], $Cd_2Re_2O_7$, a metallic pyrochlore, might be the first example of FE metal. One may realize, however, that the Fermi surface energy in $Cd_2Re_2O_7$ is fixed by the chemical formula. Therefore, this leaves little room for understanding the effect of free carrier concentration on the stability range of the FE phase in $Cd_2Re_2O_7$.

In an attempt to confirm a new class of materials—FE metal—we undertook a different approach by starting with $BaTiO_3$—a classical FE perovskite. $BaTiO_3$ is an insulator that undergoes a series of phase transitions from paraelec-tric cubic (C) to FE tetragonal (T), orthorhombic (O), and rhombohedral (R) phases at 403, 287, and 197 K, respectively. Electron transport in semiconducting n-type $BaTiO_3$ has been studied for decades [5]; however, only recently was it reported [6] that $BaTiO_3$ doped with oxygen vacancies becomes metallic above a critical electron concentration n_c of 1×10^{20} cm^{-3}. Thus, by following the phase transformations in $BaTiO_{3-\delta}$ across the insulator-to-metal transition, deep into metallic phase, we can provide evidence of the FE metal and explore its phase stability range.

A FE hysteresis loop cannot be measured in conducting materials as external field induces a flow of electric current instead of polarization switching. In this sense, ferroelectricity in metals and semiconductors is absent. However, it does not immediately follow that the underlying coopera-tive crystallographic distortions that lead to ferroelectricity vanish as soon as material becomes metallic. Therefore, we focus here on finding evidence of the low-symmetry phases in conducting $BaTiO_3$ that may support the FE ground state. For this purpose, we utilize several techniques in-cluding x-ray diffraction, dc and optical conductivity, as well as differential scanning calorimetry (DSC).

According to Cohen, hybridization between the empty Ti $3d$ and occupied O $2p$ orbitals reduces the short-range repulsion and allows off-center displacement of Ti ions that drives the FE instability [7]. Therefore, electrical conduc-tivity is extremely sensitive to the changes in the Ti-O hybridization and positional degeneracy of Ti ions [6,8] and can be used as an indirect evidence of the low-symmetry crystallographic phase transitions in $BaTiO_{3-\delta}$.

Figure 1(a) shows a transition from insulating- to metallic-type behavior of electrical resistivity, $\rho(T)$, for a series of $BaTiO_{3-\delta}$ single crystals with different electron concentrations. The low-symmetry phase transitions are seen as distinct $\rho(T)$ anomalies at the corresponding tem-
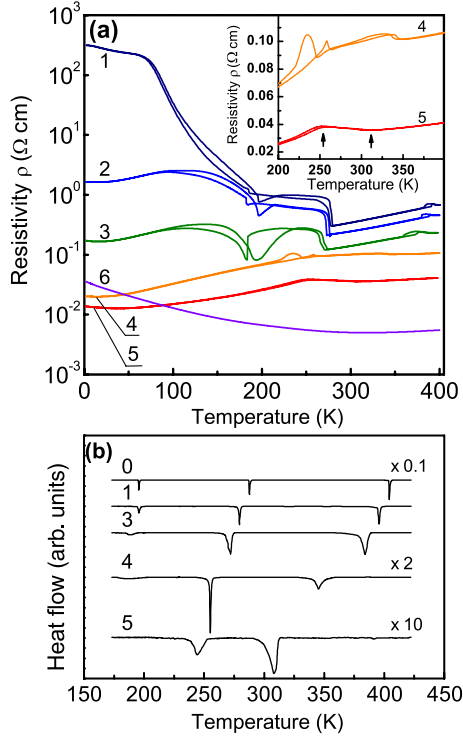
FIG. 1 (color online). (a) Temperature dependence of resistivity of BaTiO$_{3-\delta}$ measured on both cooling and heating to reveal temperature hysteresis of the phase transitions. Electron concentration n was determined from the Hall effect. Samples 1, 2, 3, 4, 5 correspond to $n = 1.9 \times 10^{19}$, 3.1×10^{19}, 6.1×10^{19}, 1.6×10^{20}, and 3.5×10^{20} cm^{-3}. Sample 6 is a BaTi$_{0.875}$Nb$_{0.125}$O$_3$ polycrystal with $n \approx 2.0 \times 10^{21}$ cm^{-3}. The $\rho(T)$ dependence changes from insulating (curves 1 and 2) to metallic (curves 4 and 5). Structural phase transitions are manifested by pronounced $\rho(T)$ anomalies at corresponding temperatures. The inset shows an enlarged part of resistivity for metallic samples 4 and 5 in the region of the *O-T* and *T-C* phase transitions. The *O-T* and *T-C* phase transitions for sample 5 are indicated by arrows. (b) DSC of selected BaTiO$_{3-\delta}$ samples. The samples' labels correspond to those of (a). Sample 0 is undoped BaTiO$_3$ with $n \leq 1 \times 10^{12}$ cm^{-3}.

peratures. It should be noted that the resistivity anomalies with hysteretic nature associated with the FE phase transitions are also observed in metallic samples 4 and 5. Metallic ground state in these latter samples has been also confirmed by finite contribution of itinerant carriers to the low-temperature specific heat (not shown). As is evident from the $\rho(T)$ data, the effect of the doping with oxygen vacancies, V_O, is to decrease the *C-T*, and, to a lesser extent, the *T-O* transition temperatures. The lowest symmetry *R* phase seems to be the least affected by doping with V_O. These findings are also confirmed by the DSC data shown in Fig. 1(b). The DSC peaks corresponding to the phase transitions shift to lower temperatures and broaden as n increases. The structural phase transitions are detected in all the samples including metallic ones (samples 4 and 5).

Although Fig. 1 shows evidence of the low-symmetry phase transformations in metallic BaTiO$_3$, their FE nature can only be confirmed by diffraction study. X-ray diffraction analysis of sample 5 ($n = 3.5 \times 10^{20}$ cm^{-3}) with the highest concentration of the V_O has been performed at the BL02B2 beam line at SPring-8 of JASRI using an x-ray wavelength of 0.49893(2) Å at 100, 150, 200, 250, 300, 350, 400, and 450 K [Fig. 2(a)]. Refined low-symmetry crystal structures were best fitted with noncentrosymmetric *P4/mmm* tetragonal ($T = 250, 300$ K), *Amm*2 orthorhombic ($T = 200$ K), and *R*3*m* rhombohedral ($T = 100, 150$ K) space groups. Diffraction data confirm that sample 5 with metallic ground state undergoes a series of FE phase transitions that are structurally identical to those of stoichiometric BaTiO$_3$ [Fig. 2(b)]. It was found, however, that the phase transitions are shifted to lower temperatures and the degree of tetragonal, orthorhombic, and rhombohedral distortions is substantially reduced in metallic phase which can be explained by the effect of partial disorder introduced by oxygen vacancies that drives the system towards higher symmetry. A detailed account of the structural differences between metallic and insulating
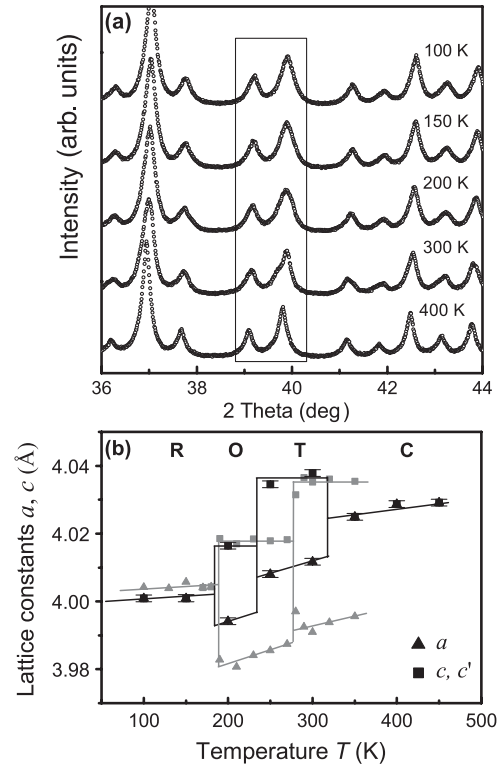

FIG. 2. (a) Selected x-ray diffraction profiles for sample 5 at 100, 150, 200, 300, and 400 K. Lowering of the crystal symmetry can be noticed by visual changes in the profile of the {512} reflection at $2\Theta \approx 39.8°$. (b) Temperature evolution of the lattice constants for sample 5 refined with the Rietveld method. For comparison, the data for stoichiometric BaTiO$_3$ from Ref. [17] are shown as gray symbols. The lines are guides for the eye.

BaTiO$_3$ based on synchrotron diffraction studies will be reported elsewhere.

Further evidence of the structural phase transitions in metallic BaTiO$_{3-\delta}$ is found in the optical conductivity $\sigma_1(\omega)$ data. Part of the $\sigma_1(\omega)$ spectra at ω corresponding to the TO phonon mode at around 500 cm^{-1} is shown in Fig. 3. The mode at $\omega = 500$ cm^{-1} is associated with the vibration of the TiO$_6$ octahedron against Ba atoms and shows strong changes upon lowering the crystal symmetry not only in insulating [Fig. 3(a)] but also in metallic BaTiO$_{3-\delta}$ [Fig. 3(b)]. Detailed analysis of the doping and temperature dependent optical properties of BaTiO$_{3-\delta}$ are given elsewhere [9].

The phase diagram that shows electron concentration dependence of the phase transition temperatures in BaTiO$_{3-\delta}$ is presented in Fig. 4. The stability range of all three FE phases extends far into the metallic part of the phase diagram. In this study, we have used oxygen vacancies, V_O, as donor dopants. Therefore, the data in Fig. 4 should be treated as a combined effect of both n and V_O defects. It is well known that defects in BaTiO$_3$ cause a decrease in the Curie temperature, T_C, even in the absence of free electrons. For example, alloying of BaTiO$_3$ with SrTiO$_3$ causes linear decrease in T_C by ca. 3.8 K per

1 mol % of SrTiO$_3$ [10]. In contrast to Sr, oxygen vacancy represents much stronger perturbation to the lattice; it causes a decrease in T_C by ca. 50 K per 0.1 at. % [V_O] and irreversibly transforms perovskite BaTiO$_{3-\delta}$ into hexagonal polymorph at [V_O] $\gtrsim 0.5$ at. % [11].

According to the first principles calculations, V_O strongly perturbs the Ti-O hybridization by adding electrons to the otherwise empty Ti 3d band and causing a change in the orbital symmetry ($t_{2g} \to e_g$) of the Ti 3d electrons in close proximity to the V_O [12]. Modern FE theories also predict that as soon as the d shell of transition metal ion becomes partially occupied, its tendency for off-center distortion in the oxygen octahedral environment is eliminated [2]. Remarkably, in spite of these destabilizing effects, we find that the FE ground state in BaTiO$_{3-\delta}$ metal is quite robust. Although it is difficult to separate individual contributions of itinerant electrons and V_O, a closer analysis of Fig. 4 indicates that the decrease in T_C with n gradually changes slope at $n \approx n_c = 0.8$–1×10^{20} cm^{-3}. A similar effect has also been reported for BaTiO$_{3-\delta}$ ceramics [13]; however, the origin of the turning point at $n \approx 0.8$–1×10^{20} cm^{-3} has been left unexplained. We believe that the turning point in the $T_C(n)$ dependence is closely related to the insulator-to-metal transition at $n \approx n_c = 0.8$–1×10^{20} cm^{-3}. As soon as BaTiO$_{3-\delta}$ enters metallic phase, the strong destabilizing effect of the oxygen vacancies is effectively screened by itinerant electrons. As a result, the $T_C(n)$ dependence changes slope from 50 to 25 K per 1×10^{20} cm^{-3}. Therefore, we arrive at the rather unexpected conclusion that ferroelectricity in metallic BaTiO$_{3-\delta}$ is partially stabilized by the itinerant electrons.
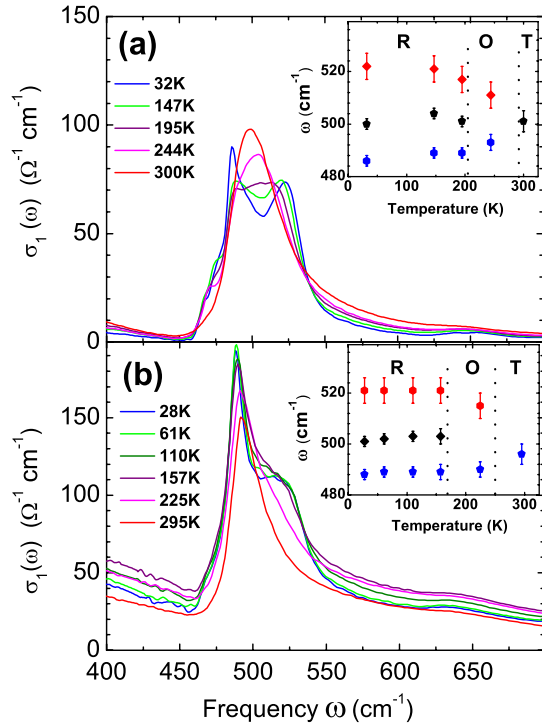

FIG. 3 (color online).   Real part of the optical conductivity of BaTiO$_{3-\delta}$ that shows infrared active TO mode near 500 cm^{-1} for sample with $n = 3.9 \times 10^{17}$ cm^{-3} (a) and $n = 2.0 \times 10^{20}$ cm^{-3} (b). The insets show the temperature evolution of the mode frequency in R, O, and T crystal phases. We fit the phonon mode with Lorentzians to obtain peak frequencies at given temperature.
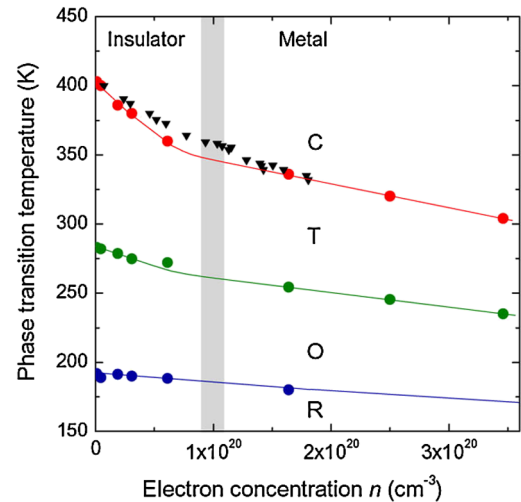

FIG. 4 (color online).   Temperature-electron concentration phase diagram of BaTiO$_{3-\delta}$. The phase transition temperatures for different electron concentrations were compiled from the resistivity and DSC data. Black triangles indicate the C-T phase transition temperature adopted from Ref. [13] for polycrystalline BaTiO$_{3-\delta}$.

Linear extrapolation of the C-T transition temperature (Fig. 4) to $T = 0$ K yields an electron concentration $n^* \approx 1.9 \times 10^{21}$ cm^{-3}. Given the high frequency dielectric constant of BaTiO$_3$ of $\varepsilon \approx 4.5$, this translates into a critical Thomas-Fermi screening length $\lambda_s^* \approx 20$ nm [14]. It is expected that at $n \geq n^*$ the screening of the long-range Coulomb interactions is too strong to stabilize the FE ground state. We suggest that the estimated λ_s^* value can provide a lower limit of the critical correlation length of the FE polarization ξ required to stabilize the FE phase in metals. This value is in very good agreement with $\xi = 10$–50 nm given in [15].

To confirm that at $n > n^* \approx 1.9 \times 10^{21}$ cm^{-3} the FE ground state in metallic BaTiO$_3$ is destroyed, we prepared a BaTi$_{0.875}$Nb$_{0.125}$O$_3$ sample with $n = 2.0 \times 10^{21}$ cm^{-3} that is slightly higher than n^* [16]. Based on the DSC, neutron diffraction [8], and resistivity measurements (Fig. 1, curve 6), we confirm that this sample remains paraelectric (cubic) down to the minimum accessible temperature of 2 K. Although this sample shows no sign of the long-range FE order, it was found, however, that on the atomic scale Ti ions are still displaced from the center of the oxygen octahedra along one of the cubic body diagonals [8]. The driving force for the off-center displacement of the Ti $3d^\gamma$ ions with $\gamma \neq 0$ ($\gamma \approx 0.125$) remains a puzzle, but it provides solid experimental evidence that partial occupancy of Ti $3d$ orbitals in BaTiO$_3$ perovskite does not eliminate the tendency for off-centering.

In conclusion, we have confirmed a series of the low-symmetry phase transitions in metallic BaTiO$_3$ that may support FE phase. Since ferroelectricity is a cooperative phenomenon, we suggest that metallic and FE ground states may coexist as long as the $\lambda_s^* > \xi$ criterion is satisfied. What seems to be much more surprising and deserves further investigation is a clear tendency for the Ti $3d^\gamma$ ion with $\gamma \neq 0$ to retain the off-center displacement even in the absence of the long-range FE ordering. Owing to its simple and well understood structure, we hope that a novel functionality of BaTiO$_3$ as FE metal will stimulate further theoretical and experimental efforts into the search for the $3d^{\gamma \neq 0}$ perovskites with both FE and magnetic ordering.

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[16] The Nb dopant was chosen for two reasons. First, we could not prepare BaTiO$_{3-\delta}$ with $n \approx 1 \times 10^{20}$ cm^{-3} having a cubic perovskite structure since perovskite BaTiO$_{3-\delta}$ is stable only at $[V_O] \leq 0.5$ at. %. Above this concentration, the crystals transform into hexagonal polymorph (space group $P6_3/mmc$). Second, among the possible donor ions, the ionic radii of Nb^{5+}/Nb^{4+} is very close to that of Ti^{4+}/Ti^{3+}, thus minimizing the effect of the size mismatch on the ferroelectric instability.

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