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Coexistence of ferroelectric and relaxor properties in epitaxial films of $Ba_{1-x}Sr_xTiO_3$

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Dielectric response of epitaxial thin films of perovskite $Ba_{1-x}Sr_xTiO_3, x=0$, 0.2, 0.6, was experimentally studied as a function of temperature, frequency, and amplitude of ac electric field. Decrease of temperatures of dielectric maxima T_m with respect to those in bulk, Curie-Weiss behavior above T_m, and ferroelectriclike behavior around T_m were found to coexist with relaxorlike behavior below T_m. The results are discussed in terms of the frustrated transition between two ferroelectric phases in the films.

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Barium titanate $BaTiO_3$ is known to be a perovskite ferroelectric undergoing a cubic-to-tetragonal structural phase transition at the Curie temperature T_C. The ferroelectric transition is generally considered to be the first-order displacive type. Respectively, the phase diagram of $BaTiO_3$ can be described in the frame of the phenomenological Landau-Ginzburg-Devonshire theory.[1] However, the first principles calculations[2] have shown that although the typically assumed potential (sixth-order expansion in polarization) can properly reproduce the behavior of the system, it requires a nontrivial temperature dependence for all the coefficients in the expansion. Simultaneously, recent NMR studies[3] and Raman scattering studies[4] have experimentally evidenced the coexistence of the displacive character of the TO soft mode with the order-disorder dynamics of Ti ions, in agreement with the earlier detected disorder in $BaTiO_3$.[5] A model combining the order-disorder and displacive features of the phase transition in $BaTiO_3$ is currently under development.[6]

A crossover from ferroelectric to relaxor behavior has been observed in doped $BaTiO_3$ ceramics with the substitution beyond a certain level.[7–9] High-pressure Raman studies of such ceramics[9] have revealed the features typical for ferroelectrics rather than for a model relaxor (such as $PbMg_{1/3}Nb_{2/3}O_3$), indicating a kind of possible coexistence of ferroelectric and relaxor properties. Despite the lack of the proper model of $BaTiO_3$, such a coexistence of ferroelectric and relaxor behavior might be supposedly related to the coexistence of order-disorder and displacive features in $BaTiO_3$.

In the last years, thin films of $BaTiO_3$ and $(Ba,Sr)TiO_3$ have been under intensive studies due to their potential for various applications in microelectronics. The Landau-Ginzburg-Devonshire-type approach has been used to calculate the temperature-strain phase diagrams for epitaxial $(Ba,Sr)TiO_3$ films[10–14] and to analyze the dielectric properties of the films.[13–15] Although the predicted diagrams can satisfactorily explain the most of the experimental observations, some unusual features have been detected, too. In particular, indications of a non-Debye dielectric relaxation have been found in ferroelectric thin films of $Ba_{0.5}Sr_{0.5}TiO_3$.[16] A model considering a distribution of the domain sizes at the nanometer scale and, respectively, a distribution of the relaxation times, has been proposed.[17] In $(Ba,Sr)TiO_3$ films, the existence of such nanodomains has been experimentally evidenced using the high-resolution near-field and confocal scanning optical microscopy.[18,19] Existence of nanodomains, or polar nanoregions, has been suggested to explain the peculiarities of the Raman spectra of $(Ba,Sr)TiO_3$ thin films, too.[20] The absence of the low-temperature structural phase transitions has been found in $BaTiO_3$ films.[21] Both the frustration of the structural transitions and the existence of polar nanoregions are features typical for relaxors rather than for ferroelectrics. Based on the recent findings in $(Ba,Sr)TiO_3$ films and doped $BaTiO_3$ ceramics, it would be possible to expect a coexistence of ferroelectric and relaxor features in the dielectric behavior of $(Ba,Sr)TiO_3$ films. An experimental evidence of such a coexistence is presented here.

Epitaxial heterostructures of 400 nm thick $Ba_{1-x}Sr_xTiO_3$ (BSTO) films, with $x=0$, 0.2, and 0.6, were grown by pulsed laser deposition on MgO (001) single-crystal substrates using 250 nm thick layers of $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) as a bottom electrode. The room-temperature x-ray diffraction analysis showed that BSTO films were pseudocubic perovskite, with (001) planes parallel to the (001) substrate surface, and with an in-plane epitaxial relationship $BSTO[100]\|LSCO[100]\|MgO[100]$. The out-of-plane lattice parameters were 4.007, 3.986, and 3.945 Å for $x=0$, 0.2, and 0.6, respectively. The dielectric response of the heterostructures with Pt top electrodes was measured as a function of temperature $T=100-650$ K, frequency $f=10^2-10^6$ Hz, and amplitude of the probing ac electric field $E_{ac}=(0.25-50)\times 10^5$ V/m using an HP4824A *LCR* meter.

In heterostructures, the real part of the small-signal dielectric permittivity $\varepsilon'(f,T)$ exhibited broad, frequency dependent peaks [Figs. 1(a) and 1(b)]. The temperatures T_m of maxima in ε' were lower than those of the cubic-to-tetragonal transitions (T_C) in BSTO ceramics[22] and depended on frequency. In $BaTiO_3$ heterostructure, besides the main higher-temperature peak in ε', another lower-temperature peak was present [Fig. 1(a)]. Although less expressed, a similar lower-temperature peak in ε' was detected in $Ba_{0.8}Sr_{0.2}TiO_3$ [Fig. 1(b)]. Respectively, two peaks were present in tan δ [Figs. 1(a) and 1(b)]. The lower-temperature peaks in tan δ in $BaTiO_3$ and $Ba_{0.8}Sr_{0.2}TiO_3$ [Figs. 1(a) and 1(b)] and a peak in tan δ in $Ba_{0.4}Sr_{0.6}TiO_3$ [Fig. 1(c)] exhibited relaxorlike shifts of maxima towards higher T with increasing frequency f.

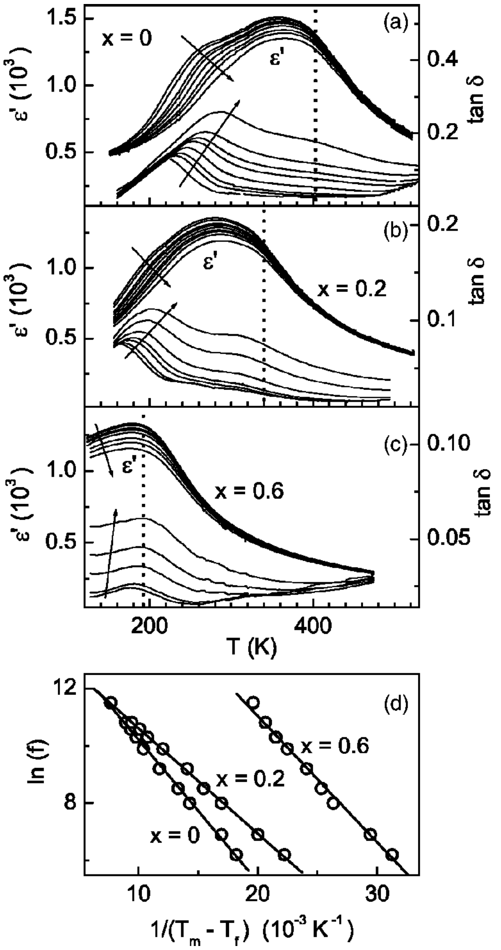

FIG. 1. (a)–(c) The real part of the dielectric permittivity ε' and loss factor tan δ as a function of temperature T and frequency f measured in $Ba_{1-x}Sr_xTiO_3$ thin-film heterostructures on cooling. Amplitude of ac electric field $E_{ac}=2.5\times10^4$ V/m. Frequency $f=0.5-100$ kHz from the upper (or lower) curves down (or up) for ε' (or loss factor). The temperature T_C of the corresponding ceramics is shown by dashed lines. (d) Relationship between the temperature T'_m (see text) and the frequency f in thin-film heterostructures of $Ba_{1-x}Sr_xTiO_3$. Straight lines show fits to the Vogel-Fulcher relationship.

In ferroelectric thin-film heterostructures, the presence of the film-electrode interfaces can result in ε', which is smaller than that of the bulk prototype.[23] Respectively, the peak in $\varepsilon'(T)$ may broaden. Also a frequency dispersion of ε' in the whole range of T can be connected with the presence of such an interface.[23] However, the peculiar behavior of BSTO thin-film heterostructures [Figs. 1(a)–1(c)] cannot be explained by the interface contribution solely. For example, an interface related frequency dispersion of ε' would be similar both above and below T_m, in contrast to the observations [Figs. 1(a)–1(c)].

To clarify the nature of the dielectric relaxation in BSTO films, the imaginary part of the dielectric permittivity $\varepsilon''(f,T)=\varepsilon'(f,T)\tan\delta(f,T)$ was analyzed. For the lower-temperature peaks of $\varepsilon''(f,T)$, a frequency dependence of the positions T'_m of maxima in ε'' was found to satisfy the Vogel-Fulcher relationship [Fig. 1(d)]: $f=f_0\exp[-T_A/(T'_m-T_f)]$, where T_f, f_0, and T_A are the parameters. For $x=0$, 0.2, and 0.6, respectively, the freezing temperatures T_f were 170, 130, and 145 K. For $x=0.6$, possible overlapping of two peaks in ε'' could prevent correct estimation of T'_m and result in a nonmonotonic dependence of T_f on x.

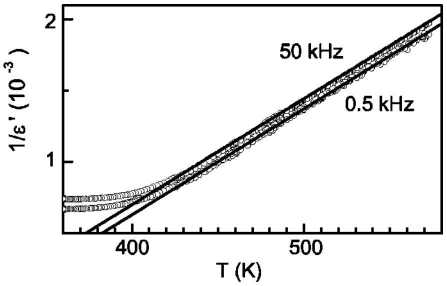

FIG. 2. Inverse of the real part of the dielectric permittivity $1/\varepsilon'$ as a function of temperature T in $BaTiO_3$ thin-film heterostructure. Frequency $f=0.5$ kHz (lower curve) and $f=50$ kHz (upper curve). Straight lines show linear fits.

The validity of the Vogel-Fulcher relationship [Fig. 1(c)] could indicate the relaxor nature of the dielectric response of BSTO films at $T\leqslant T_m$. At higher temperatures $(T>T_m)$, the analysis of the temperature dependence of the inverse dielectric permittivity $1/\varepsilon'$ revealed the Curie-Weiss behavior $\varepsilon'=c/(T-\Theta)$, where c is the Curie constant and Θ is the Curie temperature (Fig. 2). In BSTO heterostructures, the relatively small $c=(1.0-1.3)\times10^5$ K and the Curie-Weiss behavior just 30–50 K above T_m were in contrast to the observations in typical relaxors[24] and agreed with those in normal ferroelectrics.

Further analysis of such a coexistence of both ferroelectriclike and relaxorlike behavior was based on the difference in the dynamic nonlinear dielectric responses of normal ferroelectrics and relaxors. In normal ferroelectrics at the amplitude of ac electric field E_{ac} below the coercive field, the nonlinear dielectric response is dominated by the contribution from the domain wall motion with $\varepsilon'\propto(E_{ac})$.[25] In relaxors, with increasing E_{ac} in the range below a certain threshold, the permittivity ε' increases following $\varepsilon'\propto(E_{ac})^2$, and the temperatures T_m shift to lower T.[26] In BSTO thin-film heterostructures, the dielectric nonlinearity was studied using both cooling at different E_{ac} and varying E_{ac} at different T.

With increasing amplitude E_{ac} from 2.5×10^4 V/m to 5×10^6 V/m, a strong increase in ε' around and below T_m was observed [Figs. 3(a)–3(c)]. The temperatures T_m shifted to lower T by more than 50 K [Fig. 3]. The Vogel-Fulcher relationship between f and positions T'_m of the low-temperature peaks in ε'' was preserved, indicating relaxorlike behavior. Also a decrease in T_f was detected, in agreement with that in relaxors at large E_{ac}.[26] Applying biasing dc electric field $E_B=5\times10^6$ V/m resulted in a decrease of ε' and disappearance of the frequency dispersion (dashed lines in Fig. 3).

In $BaTiO_3$ film exhibiting the most pronounced separation between the two peaks in ε', the dependence of ε' on E_{ac} was analyzed in more detail (Fig. 4). Around $T\approx T_m$, changes in ε' were minor. At T few degrees below T_m, the permittivity ε' increased with increasing E_{ac}, tending to saturation at high E_{ac}. The initial part of $\varepsilon'(E_{ac})$ could be satisfactorily

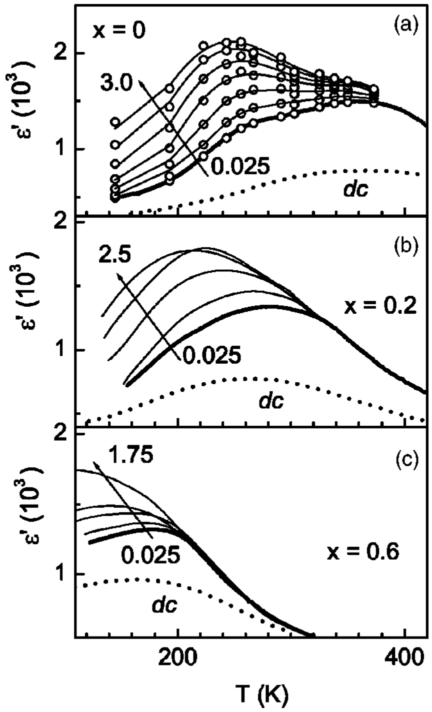

FIG. 3. The real part of the dielectric permittivity ε' as a function of temperature T measured in $Ba_{1-x}Sr_xTiO_3$ thin-film heterostructures on cooling at frequency $f=1$ kHz and at the amplitude of ac electric field E_{ac} (a) 0.025-3 MV/m, (b) 0.025-2.5 MV/m, and (c) 0.025-1.75 MV/m (from the lower curves up as shown by arrows). Dashed curves correspond to $E_{ac}=2.5\times10^4$ V/m and biasing dc electric field $E_B=5$ MV/m. Open symbols in (a) correspond to the measurements performed at fixed temperature T and varying the amplitude E_{ac}.

fitted by a linear dependence $\varepsilon' \cong \varepsilon'_\alpha + \alpha E_{ac}$, where the coefficient α was about 15×10^{-5} m/V, close to that of 7.5 $\times10^{-5}$ m/V in ferroelectric PZT films.[27] Such a dielectric nonlinearity could be considered as a ferroelectriclike. At T much below T_m, with increasing E_{ac} to about 3×10^6 V/m, the permittivity ε' followed a square law $\varepsilon' \cong \varepsilon'_\beta + \beta(E_{ac})^2$, where the coefficient β was about 1×10^{-10} m^2/V^2, comparable with that in relaxor films at $T<T_m$.[28] In the reconstructed response of the films (details in Ref. 23) with the interface contribution $\varepsilon'_{int}=100-5000$, both the linear and the square field dependencies were preserved, with the coefficients α and β changing by factor 2–10.

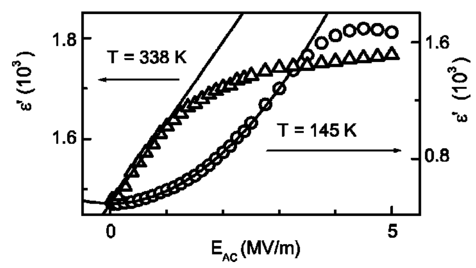

FIG. 4. The real part of the dielectric permittivity ε' as a function of amplitude of ac electric field E_{ac} measured in $BaTiO_3$ thin-film heterostructure at frequency $f=1$ kHz and temperature $T=338$ K (triangles) and $T=145$ K (circles). Solid lines show linear fit $\varepsilon' \propto E_{ac}$ and square fit $\varepsilon' \propto (E_{ac})^2$, respectively.

On cooling from high T, the films could undergo paraelectric to ferroelectric transition, as evidenced by the Curie-Weiss behavior, lack of frequency dispersion at $T>T_m$, and linear field dependence of ε' around T_m. The relatively small Curie constant and validity of the Curie-Weiss law even close to T_m were different from the behavior of typical relaxors. The temperatures T_m were lower than T_C in ceramics, in contrast to the temperature-strain phase diagrams predicted for both epitaxial monodomain $(Ba,Sr)TiO_3$ films[10,11,13,14] and polydomain $BaTiO_3$ films.[12] According to the mentioned diagrams at $T<T_C$, a structural transition between two polar phases is possible. However, the corresponding peak in ε' is expected to be rather small[11] and cannot explain the observed T_m. The shift of T_m to lower temperatures with respect to T_C could be connected with the influence of the depolarization field[29,30] and surface effects.[14,30]

The low-temperature (at $T\leqslant T_m$) dielectric response of the BSTO films exhibited relaxorlike features, that could be induced due to disrupted Ti-O bonds.[7] The presence of oxygen vacancies might be one of the contributing factors.[31] Respectively, a corresponding increase of the unit-cell volume[32] and a high-temperature diffuse dielectric anomaly[33] would be present. None of them was detected in the studied BSTO films. Moreover, an oxygen vacancy related mechanism cannot explain the observed temperature evolution from the ferroelectriclike to relaxorlike behavior.

The temperature-strain phase diagrams of epitaxial BSTO films accounting for both the displacive and order-disorder features would, probably, explain the origin of the relaxorlike behavior. Meanwhile neither such diagrams, nor a proper model for $BaTiO_3$ are developed. However qualitatively, the observed relaxorlike behavior could be ascribed to the frustrated transition between two ferroelectric phases in the films. In particular, the position of the lower-temperature peak of $\tan\delta(f,T)$ in $BaTiO_3$ [Fig. 1(a)] was close to that of 280 K, corresponding to the tetragonal-orthorhombic transition in the crystal $BaTiO_3$.[22] On cooling in pseudocubic (100) oriented epitaxial films, the 5-10 nm long chains[5] of tetragonal phase with the direction of polarization along [100] and $[\bar{1}00]$ (and/or [001] and $[00\bar{1}]$) crystal directions could remain stable and coexist with the chains of orthorhombic phase with the direction of polarization along [010] and $[0\bar{1}0]$ crystal directions resulting in an ensemble of randomly distributed polar clusters with the relaxorlike dielectric response. Such a mechanism of onset of relaxorlike behavior in $BaTiO_3$ and $(Ba,Sr)TiO_3$ films is different from that suggested for relaxor behavior in doped $BaTiO_3$ ceramics.[7–9]

In summary, the dielectric response of epitaxial thin films of perovskite $Ba_{1-x}Sr_xTiO_3, x=0$, 0.2, 0.6, was studied as a function of temperature, frequency, and amplitude of ac electric field. Decrease of temperatures of dielectric maxima T_m with respect to those in bulk, Curie-Weiss behavior above T_m, and ferroelectriclike behavior around T_m were found to coexist with relaxorlike behavior below T_m. The observed relaxorlike behavior could be ascribed to the frustrated transition between two ferroelectric phases in the films.

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