Impact of critical point on piezoelectric and electrocaloric response in barium titanate

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The prediction that the piezoelectric tensor is diverging at the critical point is verified for BaTiO$_3$ (BTO), which is the oldest perovskite structured ferroelectric material with an extremely long and eventful research history. Here we investigate experimentally by dielectric and calorimetric measurements the existence and the position of the critical point in the electric-field-temperature (E-T) phase diagram of BTO in the vicinity of the paraelectric to ferroelectric phase transition. Measurements of the piezoelectric coefficient d_{31} as a function of the temperature and the electric field applied along the [001] direction show a critical enhancement of the piezoelectric response in the vicinity of the critical point, in agreement with recent calculations by Porta *et al.* [J. Phys.: Condens. Matter **22**, 345902 (2010)]. The electrocaloric responsivity is found to be enhanced due to the latent heat on the paraelectric to ferroelectric transition locus below the critical point.

I. INTRODUCTION

Despite a long research history, BaTiO$_3$ (BTO) still remains a basic ferroelectric material for fundamental studies because of its availability, well-understood structure, and applicability.[1–8] Recently much effort has been invested into understanding the giant electromechanical effect observed in perovskite ferroelectrics near the morphotropic phase boundary.[9–14] The largest values of piezoelectric coefficients have been reported in single crystals of relaxor ferroelectrics, where the electric fields have been applied along axes other than the polar axes.[11,15–17] However, the enhancement of the piezoelectric response can be a result of several different interplaying factors: (i) proximity to the morphotropic phase boundary,[9,10,15] (ii) engineered domain configuration,[13,15,18–20] and (iii) proximity of the critical point.[12] The experimental[12,21–26] and theoretical[22,27–29] results demonstrate that in the latter case a significant enhancement (by almost an order of magnitude) of the electromechanical or piezoelectric response is possible. In this case, it has been proposed[22] and later confirmed[27] that the divergence of the dielectric susceptibility can drive the divergence of the piezoelectric tensor in the vicinity of the critical point. In particular, the presence of the electric-field-induced critical point at a ferroelectric transition in disordered ferroelectrics and in relaxor ferroelectrics (relaxors) has been experimentally observed in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)[30–33] and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PMN-xPT) solid solution, where x is the fraction of PbTiO$_3$.[12] In addition, in the case of the PMN-PT system the influence of the criticality on the piezoelectric response has been clearly demonstrated.[12,22,23]

Recently a theoretical study of the piezoelectric response of BaTiO$_3$ in the vicinity of the paraelectric to ferroelectric phase transition as a function of temperature and the applied electric field along the [001] direction has been presented by Porta *et al.*,[27] who investigated the influence of disorder and the presence of the critical point on the piezoelectric properties by using a Ginzburg-Landau model. Within the presented model they calculated the electric field temperature (E-T) phase diagram for the single domain BaTiO$_3$ and showed that the first-order transition line ends at a critical

point, where the calculated piezoelectric tensor diverges.[27] The theoretically calculated position of the critical point[27] differs significantly from the one observed experimentally in Ref. 34. It has been shown recently both theoretically and experimentally that the electrocaloric responsivity $\Delta T/E$ also exhibits a maximum near the critical point in bulk relaxor ferroelectric ceramics.[35] However, the enhancement of the electrocaloric responsivity near the critical point has not yet been experimentally confirmed in BTO single crystals.

Here we report a series of dielectric, high resolution calorimetric, direct electrocaloric, and piezoelectric experiments, which were conducted in order to verify experimentally the above theoretical predictions, in particular, the position of a critical point for the paraelectric to ferroelectric phase transition, the divergence of the piezoelectric response, and the enhancement of the electrocaloric responsivity in a BaTiO$_3$ single crystal.

II. EXPERIMENTAL PROCEDURES

A thin plate of a BaTiO$_3$ single crystal oriented in the [001] direction with thickness of 390 μm was covered by silver paste electrodes. Temperature dependence of the complex dielectric constant at various constant bias electric fields applied along the [001] direction was measured at a frequency of 1 kHz by using an HP4282 Precision LCR Meter. The amplitude of the probing ac electric signal was 1 V. After heating the sample up to ∼425 K for 30 min the sample was cooled down to 300 K in zero field (ZFC). The dielectric response measured along the [001] direction was then obtained in a field-heating (FH) run between 300 and 425 K with a typical heating rate of 1 K/min.

The piezoelectric coefficient as a function of the electric field and temperature was determined by using the resonance method, in which the sample acted like a piezoelectric bar resonator, and the resonance response of the complex dielectric constant was probed at various temperatures and electric fields. The resonance response of the complex dielectric constant was scanned between 200 kHz and 1.2 MHz, and from the data the

complex piezoelectric constant d_{31} was calculated. Details of the resonance method can be find in Refs. 36 and 37.

The calorimetric measurements were performed by a high-resolution calorimeter that allows precise temperature stabilization of the bath (within 0.1 mK), and by high-resolution measurements of the heat capacity and enthalpy variations as functions of the temperature and applied bias electric field.[38,39] For that purpose a heater and a thermistor were attached to the opposite sides of the sample. The high-resolution calorimeter is capable of operating in the ac and relaxation mode. The combination of the two modes is used to probe both the continuous and discontinuous (i.e., latent heat L) changes.[38] The heat capacity measurements in the ac mode were carried out at various different bias electric fields during the heating runs with a typical scanning rate of 1 K/h in the vicinity of the ferroelectric transition temperature $T_C = 405$ K. The relaxation mode was modified in such a way that it was capable of tracing a variation of the sample temperature at constant bath temperature, while the electric field applied parallel to the sample direction was linearly cycled. In these experiments the sample was also heated up to 425 K for 30 min and zero-field cooled to a specific temperature, which was stabilized and kept constant. Then the electric field was increased linearly in time from 0 to 16 kV/cm in a time of 250 seconds. After reaching 16 kV/cm the field was linearly reduced to zero using the same slew rate of 16 kV/cm per 250 seconds. During such a cycle, the temperature of the sample was measured every 0.6 seconds with a resolution within 0.1 mK in order to detect any temperature changes of the sample due to the latent heat, which should be released at the electric-field-induced first-order phase transition (i.e., an electrocaloric effect due to the discontinuous change of the polarization order parameter). The electric field slew rate was kept slow enough to avoid the temperature gradients within the sample, but fast enough to avoid losing most of the released latent heat to the bath.

The direct electrocaloric measurements were performed as described in Refs. 35 and 40–42 by applying a steplike electrical signal to the sample and measuring the heating and cooling electrocaloric temperature change ΔT of the sample in the vicinity of the electric signal positive (field on) and negative (field off) slopes, respectively.

III. RESULTS AND DISCUSSION

In this section, the dielectric and calorimetric results are presented and discussed. $BaTiO_3$ is an especially suitable material for investigating the influence of the electric field on the ferroelectric transition and the behavior of the piezoelectric coefficient at the transition because of the structural ferroelectric transition sequence at $E = 0$: high-temperature paraelectric cubic phase $\xrightarrow{405\,K}$ ferroelectric tetragonal $\xrightarrow{281\,K}$ orthorhombic $\xrightarrow{193\,K}$ rhombohedral.[6] Of these transitions we have focused our attention on the predicted[27] electric-field-induced critical point terminating the line of first-order paraelectric to ferroelectric phase transitions. Special interest has been paid to its influence on the piezoelectric response. The existence of the critical point induced by an electric field at the ferroelectric transition has already been observed in the relaxor systems PMN-PT[12,22] and PMN.[12,22,30–33] The critical point is the only second-order
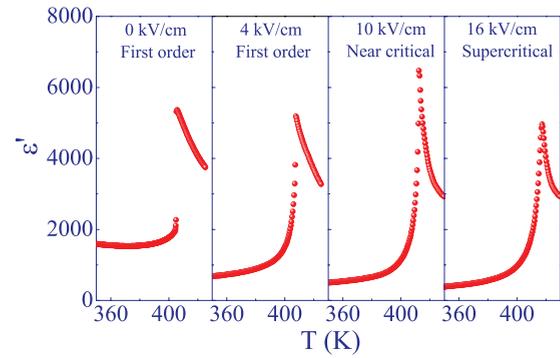

FIG. 1. (Color online) Temperature dependence of the dielectric data of a $BaTiO_3$ single crystal obtained in ZFC-FH experiment at various bias electric fields applied along the [001] direction.

transition point at which the first-order transition line is terminated in an E-T phase diagram. Above the critical point, the transition disappears and a supercritical regime is observed with the so-called Widom line[43] at which the anomalies in various physical properties become noncritical and smeared out. The best way to find out whether the first-order transition line ends in a critical point is to observe the released latent heat along the line, which should disappear at the critical point.

Figure 1 shows the temperature dependence of the dielectric constant measured at various constant electric fields. The observed sharp and narrow discontinuous step in the dielectric constant at 405 K is in good agreement with previously reported dielectric anomalies[4,5] at the paraelectric to ferroelectric phase transition in the absence of the electric field. With increasing electric field up to 10 kV/cm, the discontinuous dielectric anomaly moves towards higher temperatures and the value of the dielectric constant increases. In addition, the shape of the dielectric anomaly gradually becomes continuous. At 12 kV/cm and above, the dielectric anomaly starts to decrease and becomes suppressed above the critical point as an indication of supercritical behavior. It should be mentioned that the birefringence also exhibits a crossover from the sharp discontinuous to continuous evolution between 10 and 12 kV/cm.[5] At higher fields the birefringence anomaly becomes smeared and suppressed, as typical for the supercritical regime.[5] The decreasing of discontinuity when approaching the critical point was observed also in the behavior of the lattice constant as a function of the electric field and temperature.[34]

The temperature dependence of the excess specific heat Δc_p of a $BaTiO_3$ single crystal obtained in the vicinity of the paraelectric to ferroelectric phase transition is displayed in Fig. 2 for different bias electric fields. Similar to the dielectric response, the specific heat shows a sharp and discontinuous anomaly at the transition temperature. By increasing the bias electric field the transition temperature shifts from ~405 K at zero field to ~412 K at 10 kV/cm. However, the ac measurements cannot quantitatively detect a latent heat and thus cannot provide enough information about the crossover from first-order to second-order phase transition induced by the applied electric field. In order to detect the released latent heat, we used a modified relaxation method in which the electric field is linearly ramped with time, and the sample temperature is recorded. Such measurements were performed at several
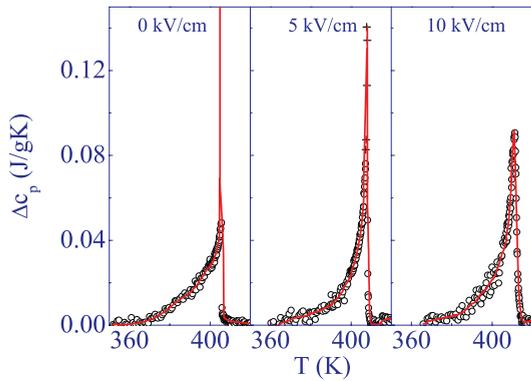
FIG. 2. (Color online) Temperature evolution of the excess specific heat data obtained in the ac mode at various constant electric fields. The solid line is a guide to the eye, whereas open circles and crosses are the c_p data obtained outside and inside the coexistence rang, respectively. In the first panel the anomalous response of c_p in the coexistence range is so huge that it is out of the drawing limit.

different bath temperatures, which were stabilized and held constant during the experiment.

The variation of the sample temperature (ΔT_s) with increasing electric field is presented in Fig. 3. At the field-induced ferroelectric transition a sharp increase in the sample temperature is observed as a consequence of the released latent heat. At lower values of the electric field, which also induces a transition at lower temperatures, ΔT_s exceeds the value of 1 K. The released latent heat is subsequently dissipated into the surrounding heat bath, resulting in an exponential decay of the sample temperature back to the initial bath temperature. On increasing the bath temperature the magnitude of ΔT_s gradually decreases, whereas the electric field necessary to induce the transition increases. The decrease of ΔT_s with increasing temperature is mainly due to the decrease of the latent heat.

The exponential decay of the sample temperature can be in a first approximation fitted by the simple exponential decay ansatz $\Delta T(t) = \Delta T_s \exp(-t/\tau)$, where τ is the external thermal time scale.[38] By analyzing the data from such an experiment we can precisely determine ΔT_s and thus the latent heat $L = c_p \Delta T_s$ released at the transition. This approximation can
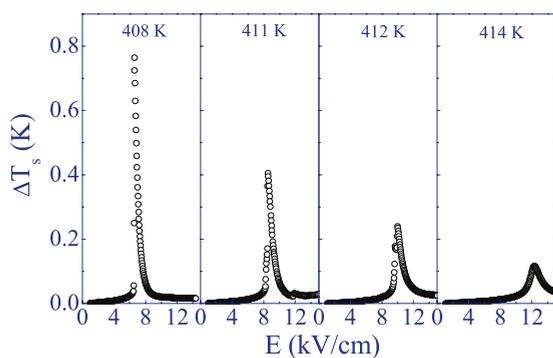

FIG. 3. (Color online) Change of the sample temperature for the BaTiO$_3$ single crystal due to the released latent heat at the field-induced cubic to tetragonal phase transition, measured at several constant bath temperatures.

be used as long as the electro-caloric effect (ECE) stemming from the continuous changes of the polarization can be neglected.[32] This can be experimentally achieved by slewing the electric field sufficiently slowly in order to lose most of the electrocaloric heat generated by the continuous polarization changes to the surrounding bath. Since the polarization variation still remains sharp in the vicinity of the critical point (corresponding to the divergence of the susceptibility), one can expect to observe some smeared ECE response with a small apparent ΔT_s even slightly above the critical point. This is due to the fact that the heat released by the ECE due to continuous changes of polarization is still large and is mostly released in a relatively narrow range of the scanning electric field. Thus, the large released ECE heat does not relax completely into the surroundings, and part of it can still be detected. In the case of BaTiO$_3$, ΔT_s does not vanish up to 414 K, whereas in contrast, the discontinuity in the ECE response can be observed only up to 412 K, in agreement with dielectric results.

From the dielectric measurements and the relaxation experiments probing the above described discontinuous electrocaloric response due to the released latent heat, it is possible to estimate the critical point in a BaTiO$_3$ [001] single crystal as $T_{CP} \cong 412$ K and $E_{CP} \cong 10$ kV/cm. Our estimate of the coordinates of the critical point is in good agreement with the theoretical prediction by Porta *et al.*,[27] in which the critical point for the monodomain crystal and for the crystal with a small amount of disorder is set at $T_{CP} = 414.32$ K, $E_{CP} = 14.6$ kV/cm, and $T_{CP} = 415$ K, $E_{CP} = 9.55$ kV/cm, respectively. The experimentally determined E-T phase diagram for a BaTiO$_3$ [001] single crystal is presented in Fig. 4(a).

Figure 4(b) shows the temperature dependence of the piezoelectric coefficient d_{31} obtained in the BaTiO$_3$ single crystal poled along the [001] direction at four different values of the electric field. The value of d_{31} found at the room temperature is in good agreement with previously published results.[19,29,44] By plotting the maximum values of $d_{31}(T)$ obtained at a specific bias field as a function of that field, one can follow the evolution of d_{31} along the phase transition line in an E-T phase diagram [cf. Fig. 4(a)]. Both plots show that the obtained piezoelectric response clearly exhibits a maximum at the temperature and electric field close to the critical point, i.e., 412 ± 3 K and 10 ± 2 kV/cm, respectively. These findings of the piezoelectric response enhancement at the critical point in a BaTiO$_3$ [001] single crystal are in a good qualitative agreement with the theoretical predictions of the piezoelectric tensor divergence at the critical point in BaTiO$_3$[27] due to the divergence of the dielectric susceptibility.

Figure 5 shows the electrocaloric results obtained in a BTO [001] single crystal. Details of experiments and analysis are given in Refs. 40 and 35. Here the steplike voltage signal was applied to the sample, and the electrocaloric heating and cooling temperature changes were recorded as functions of time close to the moments at which the electric field was switched on and off (see the inset of Fig. 5). The maximum electrocaloric response was found at the ferroelectric transition temperature, where $\Delta T = 1.6$ K was observed at the electric field of 30 kV/cm. These results, including the magnitude of the electrocaloric response, are in good agreement with recent calculations of the ECE response in a BaTiO$_3$ single crystal based on the specific heat measurements.[45] The
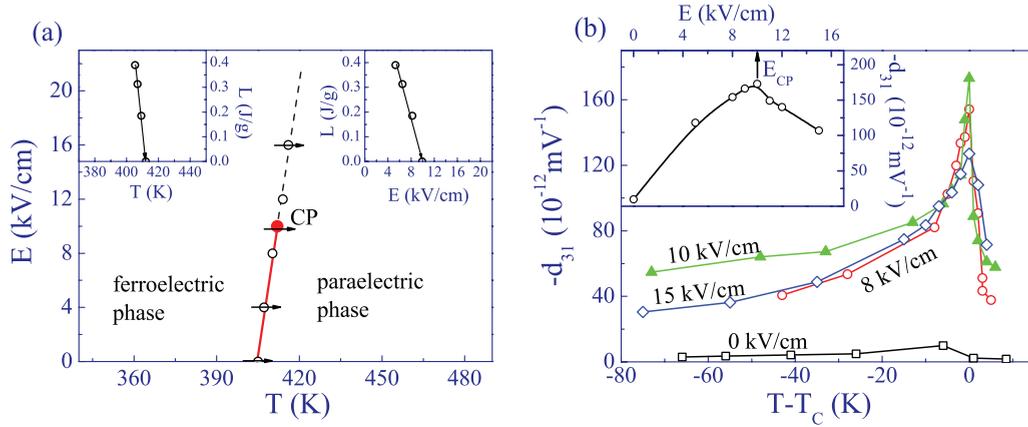
FIG. 4. (Color online) (a) E-T phase diagram for a BaTiO$_3$ single crystal constructed from the calorimetric and dielectric data. Solid line represents the electric-field-induced first-order transition line between the paraelectric and ferroelectric phases, which ends in a critical point at T_{CP} ~412 K and E_{CP} ~10 kV/cm. The dashed line denotes the Widom line, and the solid arrows denote values of the electric field at which the piezoelectric response was measured. The two insets represent the temperature and electric field variation of the latent heat. (b) The temperature dependence of the piezoelectric coefficient d_{31} obtained in a BaTiO$_3$ single crystal poled along the [001] direction at four different values of the bias electric field below and above E_{CP}. The inset shows the electric field dependence of the piezoelectric coefficient d_{31} at $T = T_{CP}$, which exhibits a maximum at the critical field E_{CP} (arrow).

temperature dependence of the EC sample temperature change is qualitatively similar to the experimental and theoretical results obtained in ferroelectrics PZT,[46] 0.92PZN-0.08PT,[47] and LiNbO$_3$.[48]

Figure 5 also shows the electrocaloric responsivity $\Delta T/E$ as a function of the electric field strength. Here the solid line represents the experimentally deduced electrocaloric responsivity in a BTO [001] single crystal as determined along the ferroelectric transition line; i.e., the corresponding temperature at a given electric field can be read off the ferroelectric transition line shown in Fig. 4(a). In the case that the discontinuous entropy change L/T is small compared to the total entropy change induced by the electric field, the maximum ECE responsivity is predicted to occur near

the critical point[49] (see the dashed line in Fig. 5). Such a case has recently been realized in bulk relaxor ferroelectric ceramics.[35] In BTO, however, an appreciable latent heat can still be observed relatively close to the critical point, resulting in an additional enhancement and a shift of the maximum of the ECE responsivity towards lower fields (solid line in Fig. 5).

IV. CONCLUSIONS

By using dielectric, calorimetric, and piezoelectric experiments the existence of the electric-field-induced critical point for paraelectric to ferroelectric phase transition and the divergence of the piezoelectric response in a BaTiO$_3$ [001] single crystal were investigated. Both dielectric and calorimetric results confirmed the presence of the critical point in a BTO single crystal. The crossover from first-order to second-order transition was estimated to take place at $T \sim 412$ K and $E \sim 10$ kV/cm by monitoring the vanishing latent heat. The dielectric and calorimetric response at fields and temperatures above the critical point is reminiscent of a supercritical regime. Piezoelectric experiments utilizing the resonance method show that the obtained piezoelectric response is significantly enhanced in the vicinity of the critical point, which is in good agreement with direct theoretical predictions for a BaTiO$_3$ system.[27] The electrocaloric responsivity exhibits a maximum and significant enhancement on a ferroelectric transition line just below the critical point, due to the significant latent heat involved in a ferroelectric conversion. The appreciable latent heat at strongly first-order ferroelectric transitions can thus be explored for additional enhancement of the electrocaloric response.
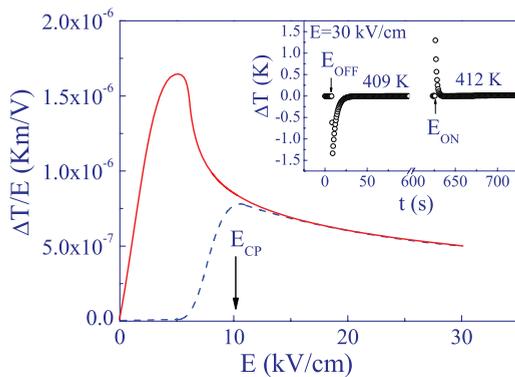

FIG. 5. (Color online) The electric-field dependence of the electrocaloric responsivity $\Delta T/E$ determined along the ferroelectric transition line shown in the E-T phase diagram [Fig. 4(a)] for a BaTiO$_3$ [001] single crystal. Solid line is obtained from the direct electrocaloric measurements (shown in the inset) at different temperatures and magnitudes of the electric field. Dashed line: Schematic field dependence of the electrocaloric responsivity for a system with vanishingly small latent heat; in such a case, the maximum of $\Delta T/E$ occurs near the critical field E_{CP}.[49]

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