Direct and indirect determination of electrocaloric effect in $Na_{0.5}Bi_{0.5}TiO_3$

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Direct and indirect studies of electrocaloric effect were performed in poled and depoled $Na_{0.5}Bi_{0.5}TiO_3$. For this purpose polarization and electrocaloric effect temperature change measurements were made at different electric field pulses as a function of temperature. Applicability of the widely-used indirect electrocaloric effect determination method, using the Maxwell relation, was critically analyzed with respect to the reliable direct measurements. Quantitative differences were observed between the results obtained by both approaches in case of the poled $Na_{0.5}Bi_{0.5}TiO_3$ sample. These differences can be explained by the temperature-dependent concentration of domains oriented in the direction of the applied electric field. Whereas in the depoled $Na_{0.5}Bi_{0.5}TiO_3$, which is characterized by electric field dependence of polar nanoregions embedded in a nonpolar matrix, the Maxwell relation is not applicable at all, as it is indicated by the obtained results. Possible mechanisms which could be responsible for the electrocaloric effect in the relaxor state were considered. The results of this study are used to evaluate the numerous results obtained and published by other authors, using the Maxwell relation to indirectly determine electrocaloric effect. The reason of the negative electrocaloric effect values, obtained in such a way and widely discussed in literature in case of $Na_{0.5}Bi_{0.5}TiO_3$, have been explained in this study.

I. INTRODUCTION

After a long period of rather modest studies of electrocaloric effect (ECE), which had left unfulfilled expectations of potential application of ECE in cooling devices, this research direction has revived in the recent years. It started from the publications of Mischenko [1] and Neese [2], demonstrating a possibility to obtain much higher values of a temperature change, caused by ECE, (ΔT) compared to earlier results. Two characteristic features are inherent to the mentioned publications. Firstly, the results were obtained for thin films and high electric fields, which are not accessible in bulk materials. Secondly, instead of direct measurements, one of the Maxwell relations in integral form was used to calculate ΔT from electric field (E) and temperature dependence of polarization (P) in a

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certain temperature range:

$$\Delta T = -\frac{T}{c_E} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE \ , \tag{1}$$

where T is absolute temperature and c_E is heat capacity at fixed electric field. Starting from this milestone, a huge number of works, devoted to studies of ECE, has been published. They mostly follow the same path – measurements of P(T,E) and calculation of ΔT according to Eq. (1). The choice of such an approach is quite natural. Measurements of polarization are much easier to perform, compared to direct ECE measurements. Moreover, although direct measurements of the temperature change in thin films are successfully accomplished in some cases, they are very tricky, in general due to extremely small heat capacity and very good thermal contact with the substrate [3,4].

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) -based compositions in the concentration region of rhombohedral phase and the morphotropic phase boundary (MPB), which are widely studied due to promising piezoelectric properties, have been recently considered also with respect to ECE [5-17]. Except for [11,17], all studies based on the indirect measurements of ECE revealed temperature regions with remarkable so-called negative ECE – decreasing of temperature if the electric field is applied and increasing of temperature if the electric field is removed.

Taking into account the large number of publications and very promising values of ECE obtained using the Maxwell relation, validity of the Maxwell relation in concrete cases is an important question. Results of studies, devoted to this issue, create an impression that application of the indirect method in most cases is justified [18-23]. However, a relaxor state (sometimes just non-ergodic) or contribution of lattice energy at ultra-high electric fields are assumed as the reason for the disagreement in some cases [15,24-28]. Some considerations about influence of measurement conditions on values of P(E) have also been discussed [29]. Considering NBT-based compositions, only partial correspondence between direct and indirect ECE measurements has been found in NBT-$KNbO_3$ and NBT-$K_{0.5}Bi_{0.5}TiO_3$ solid solutions in the region of MPB [9,11], while even the opposite signs of the effect have been revealed, using both of the methods for NBT-$BaTiO_3$ solid solutions in the region of MPB [15].

Use of the Maxwell relations is very popular in studies of magnetocaloric effect (MCE). So-called giant MCE with values of magnetic field-induced entropy changes, even exceeding the theoretical limit available for a magnetic

system, are obtained from the Maxwell relation in case of the first order phase transition [30,31]. Unfortunately, the reason of such large values sometimes is an incorrect application of the Maxwell relation [32]. The conditions, under which using of the Maxwell relations is not correct in studies of MCE, are considered also in the references [33,34].

This work is devoted to direct measurements of ECE in poled and depoled NBT and critical discussion of applicability of the Maxwell relation (Eq. (1)) to evaluate ECE in ferroelectrics. Poled and depoled states in NBT are essentially different. While the poled NBT is in the ferroelectric state with symmetry R3c [35], the depoled state can be apparently characterized only by coexistence of phases with different symmetry and corresponds to behavior of relaxor ferroelectrics [36,37]. Since the critical electric field (E_c) between the relaxor and the ferroelectric states in NBT is high and a phase transition occurs in a narrow electric field range (inset on the left in Figure 1), both states are well separated, which makes such a comparison reasonable.
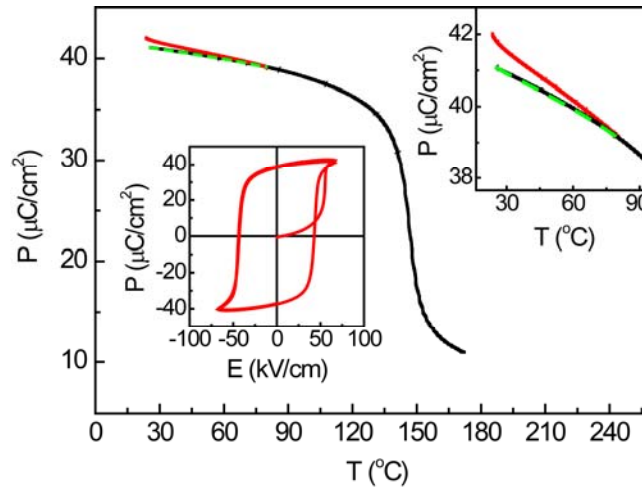

FIG. 1. Temperature dependence of the remnant polarization P_{rem}, obtained from heating measurements of the sample poled at room temperature. Temporary alternation of the direction of temperature change is also shown (a more detailed view in the inset on the right: first, the temperature was increased from room temperature to 70°C – red solid line, then decreased to room temperature – green dashed line, then increased till 170°C – black solid line). Inset on the left: polarization hysteresis loop of a virgin NBT sample.

II. EXPERIMENTAL DETAILS

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) was synthesized with 2mol% Bi over stoichiometry to compensate expected losses of Bi during processing. Besides depressing of conductivity at high temperatures, this also stimulates reduction of T_d [38]. NBT ceramics was prepared by the conventional solid state reaction method. Chemical-grade oxides and carbonates Na_2CO_3, Bi_2O_3, and TiO_2 (purity>99.5%) were used as starting materials. The powders were weighed according to the formula, mixed with ethanol and milled in an agate ball mill for 24 h. The dried powders were calcined for the

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first time at 850°C for 2 h. Afterwards they were milled again in the same conditions for 24 h and calcined for the second time at 1000°C for 2 h. After milling in the same conditions for 24 h again, the powders were pressed uniaxially into a disk-shaped pellet with diameter of ~17 mm and height of ~10 mm and then compacted under a pressure of 30 MPa using a hydraulic press. The disk was sintered at 1200°C for 4 h. In order to decrease evaporation of Bi, calcination was carried out in covered platinum crucibles, whereas during the sintering, the disk was embedded in a powder of the same composition and placed under platinum crucibles on a platinum pallet.

A sample with thickness of 0.3 mm was cut and polished. Electrodes were made by firing of Au paste at 500°C for ECE and polarization measurements. Polarization of the sample was performed by applying electric field of 70 kV/cm at room temperature. The same sample was used for measurements in the poled and the depoled states. Measurements in the poled state were performed first. As a consequence, depolarization was ensured by heating till 280°C.

During ECE measurements, the sample was connected with alumel wires and 3M polyimide adhesive tape on a sample holder. A chromel-alumel thermocouple was attached to one side of the sample on top of the polyimide adhesive for direct temperature measurements. The sample with the electrical wires was placed inside a closed beaker to ensure a long enough thermal time constant compared to the measurement period.

Response of the thermocouple, attached on the sample surface, was measured by a multimeter (34420A, Agilent Technologies Inc.) while applying 2.5 s long DC electric field pulse (including 0.125 s rise and fall times) from a function generator (33120A, Agilent Technologies Inc.), connected with a high voltage amplifier (RT6000HVA, Radiant Technologies Inc.). During the measurements, the polarization current through a shunt resistor was detected with an Agilent 34411A multimeter. The ECE temperature change was calculated from thermocouple response by subtracting the thermocouple voltage response after the electric field pulse from the thermocouple voltage during the electric field pulse. Thus the sign of ΔT in the graphs presented further does not reflect the sign of ΔT at a particular direction of electric field change (increasing at applying electric field or decreasing at removing electric field). The sign is used to distinguish between the positive and the negative ECE in terms characterized in the Introduction section.

The measurements were made by step-like increasing of temperature with 40 min levelling time at each temperature. Thermal loads of the electrodes and adhesive tape were estimated (~3-7 %) to correct the direct temperature measurements. All measurements were made under computer control in a Memmert UFP400 oven.

Additionally, polarization hysteresis P(E) measurements were performed using the Sawyer-Tower method in a quasistatic limit. Temperature dependence of the remnant polarization $P_{rem}(T)$ was measured after measurement of P(E) on the same experimental setup, keeping E=0, with rate of the temperature change 3 K/min.

III. RESULTS AND DISCUSSION

Temperature dependences of the directly measured ECE temperature change ΔT(T) for the poled and the depoled NBT sample are presented in Figure 2. In case of the poled NBT sample, ΔT(T) has a well-expressed maximum of 0.37^{o}C (at electric field pulse E=20 kV/cm) at temperature T_m=150°C, which corresponds to the temperature range, where depolarization takes place, and vanishes at temperatures above 210°C (Figure 2(a)). Slight
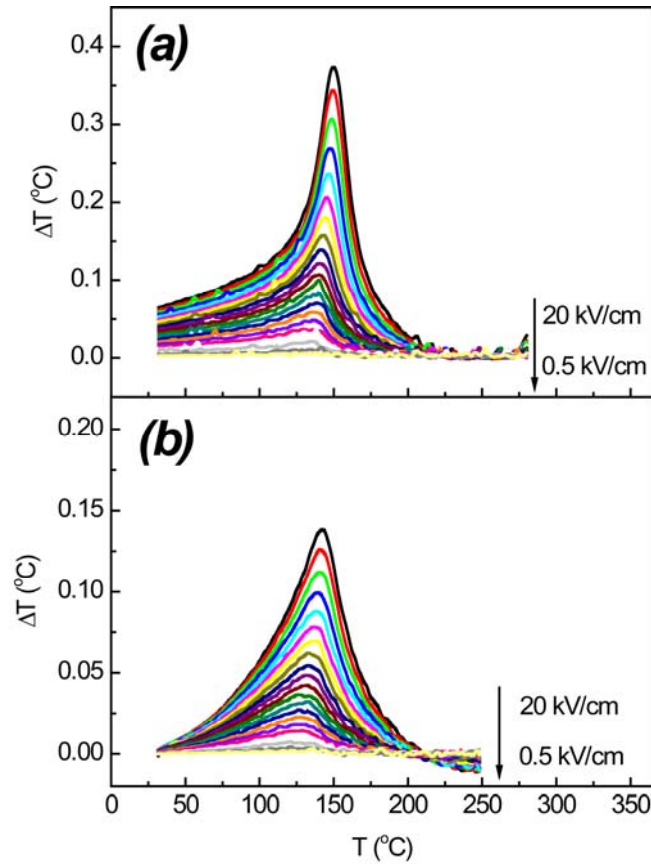

FIG. 2. ECE temperature change ΔT(T) on removing of electric field at various electric field pulses for the poled (a) and the depoled (b) NBT samples.

decreasing of T_m can be observed upon lowering of the electric field. ΔT(T) is positive at all temperature range where it is observed. Vanishing of ΔT above 210°C apparently does not correspond to what could be expected in the

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paraelectric state, where a small, but detectable ECE temperature change should be observed in a wide range of temperature above T_c due to the temperature dependence of dielectric permittivity (the Curie-Weiss law). In the ferroelectric state, up to 130°C, ECE temperature change as a function of P_i, which is the electric field-dependent part of polarization at unipolar electric field pulses, at different temperatures follows a common path (Figure 3), although $P_i(T)$ varies significantly upon changing temperature. Such behavior was observed earlier also in NBT-containing solid solutions in the ferroelectric state [39].
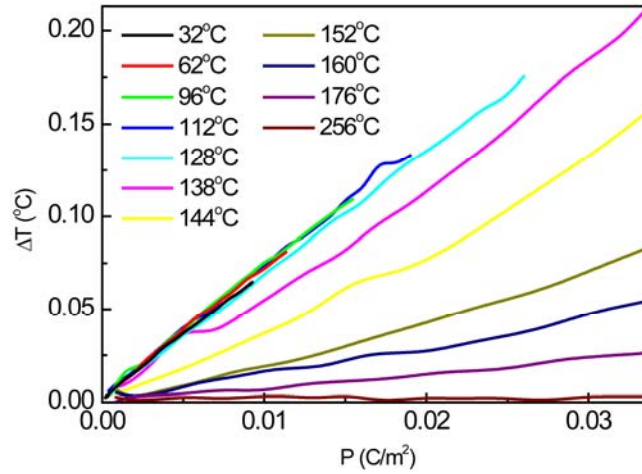

FIG. 3. ECE temperature change as a function of electric field-dependant part of polarization $\Delta T(P_i)$.

In the case of the depoled NBT sample, the maximum of $\Delta T(T)$ is lower and more diffused than in the poled sample − $\Delta T=0.14^o$C at $T_m=142^o$C (at electric field pulse E=20 kV/cm) (Figure 2(b)). Another difference is the change of sign of ΔT in the temperature range above 210°C, where ΔT vanishes in the case of the poled NBT. The negative ΔT, observed upon removal of the electric field, is very small and, apparently, in ΔT measurements upon application of the electric field, is masked by the Joule heat. Obviously, the different behavior indicates different states of the poled and the depoled sample even in the temperature range, where the poled state is destroyed. A different behavior was observed also for the temperature and frequency dependences of dielectric permittivity [37]. The dependence $\Delta T(P_i)$ at different temperatures follows different paths and, in a wide temperature interval, can be considered as quasilinear with a slope which significantly decreases in the direction of lower temperatures (for the purpose of following analysis, it is illustrated as $\Delta T/P_i$ versus electric field pulse value in Figure 4).
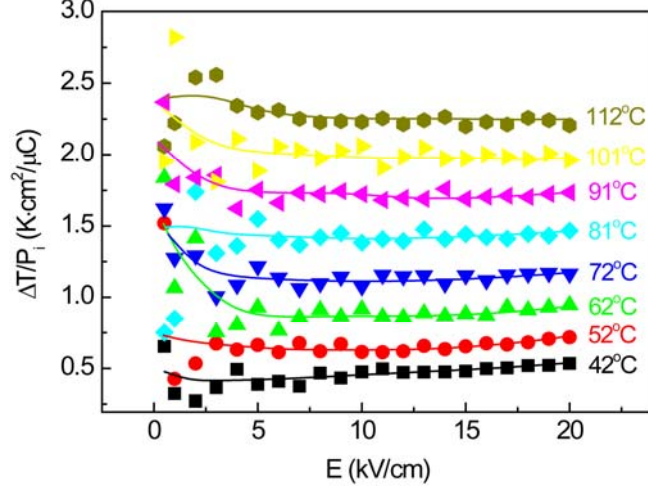
FIG. 4. ECE temperature change and polarization ratio $\Delta T/P_i$ as a function of the electric field at various temperatures in the depoled state of NBT.

Results of polarization measurements for the poled and the depoled NBT samples, utilized to calculate ECE according to the widely-used indirect method of ECE determination, are presented in Figure 5. The temperature region was chosen far enough from the depolarization temperature T_d, where nonlinearity of both $P_i(E)$ and $\Delta T(E)$ is weak. Since the change of polarization was obtained simultaneously with the direct ECE measurements at unipolar electric field change, at the poled state it represents the change of $P_i(E)$ (Figure 5(a)) instead of the total polarization $P_{tot}=P_{rem}+P_i$ (where P_{rem} is remnant polarization). In order to obtain the total polarization, results of $P_{rem}(T)$ measurements were added (Figure 1). P_{rem} smoothly decreases upon increasing of the temperature, which is followed by a steep drop in the region of T_d, as it is expected in the poled state of NBT. For calculation of the ECE temperature change, the measured $P_{rem}(T)$ in the considered temperature range was replaced by 3rd order polynomial fit, while $P_i(E)$ – by 2nd order polynomial fit ($P_i(E)=\varepsilon_1 \times E+\varepsilon_2 \times E^2$), where the linear term represents the linear part and the 2nd order term – the nonlinear part of quasistatic dielectric permittivity. Both ε_1 and ε_2 are smoothly increasing functions of temperature (inset in Figure 5(a)). If dP/dT in Eq. (1) is replaced by the sum of all three contributions, the ECE temperature change can be calculated as follows:

$$\Delta T = -\frac{T}{c_E}\left(\frac{dP_{rem}}{dT}E+\frac{1}{2}\frac{d\varepsilon_1}{dT}E^2+\frac{1}{3}\frac{d\varepsilon_2}{dT}E^3\right). \tag{2}$$
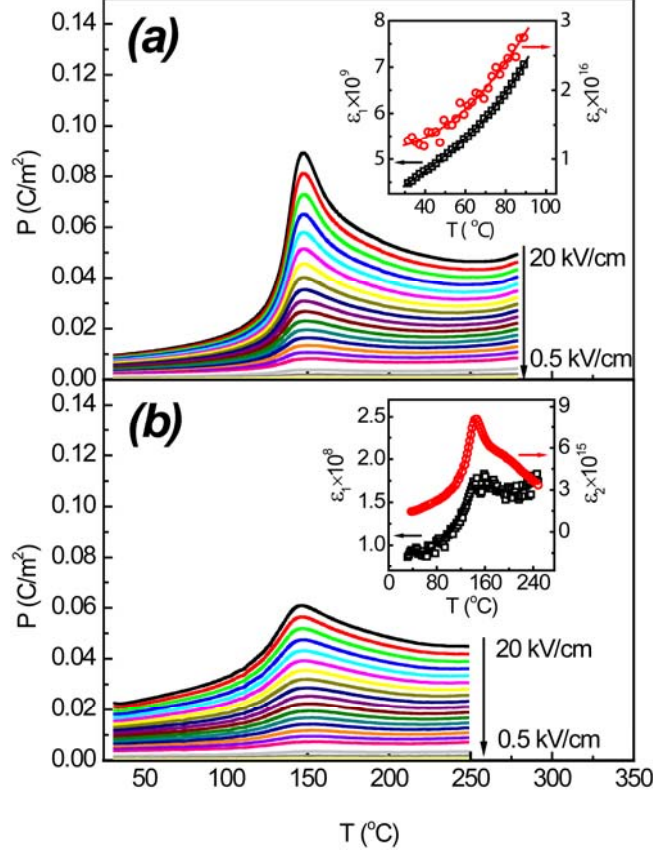
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FIG. 5. Polarization as a function of temperature $P_i(T)$ at various unipolar electric field pulses for the poled (a) and the depoled (b) NBT samples, measured simultaneously with ECE temperature change ΔT. The insets in (a) and (b) illustrate temperature dependence of the extracted linear (ε_1) and nonlinear (ε_2) parts of dielectric permittivity for the poled and the depoled NBT sample correspondingly.

Like in other published calculations of ECE in ceramics, the one-dimensional approach is used, assuming that spontaneous polarization P_s and E are oriented in one direction and allowing one to simply replace P_s by P_{rem}. P_i in such case is purely induced (or intrinsic in terms used in the reference [40]) polarization. This issue will be discussed later. Values of temperature dependent c_E, necessary for calculation of ΔT, were taken from [10].

Now, the contribution to ECE temperature change will be compared from the different terms. Since the slope of $dP_{rem}(T)$ is negative, contribution from this term to ΔT is positive, while contribution from both linear and nonlinear parts of dielectric permittivity is negative. Contribution from the nonlinear part of dielectric permittivity to ΔT is negligible, while contribution from the linear part is insignificant at low fields, but reaches up to 12% of the total ΔT at E=20 kV/cm in the considered temperature range. The calculated ΔT values are larger than the directly measured, but can be aligned with them in the whole electric field and temperature range, where the comparison is made, by simple rescaling, multiplying all calculated values roughly by 0.6 (Figure 6). The role of dP_{rem}/dT as a plausible

reason of this difference can be illustrated in the following way. As it follows from Eq. (2), the slope of $\Delta T/E(E)$ at $E \rightarrow 0$ corresponds to dP_{rem}/dT. The directly measured $\Delta T(E)$ was fitted by polynomial function and dP_{rem}/dT was calculated from the linear term. The obtained results show approximately the same discrepancy between the calculated dP_{rem}/dT and the one obtained from the measured temperature dependence of remnant polarization. Moreover, experimentally observed nonlinearity of $\Delta T(E)$ is insignificant, which, according to Eq. (2), means that the whole value of ΔT can be attributed to dP_{rem}/dT, but $d\varepsilon_1/dT$ is insignificant.
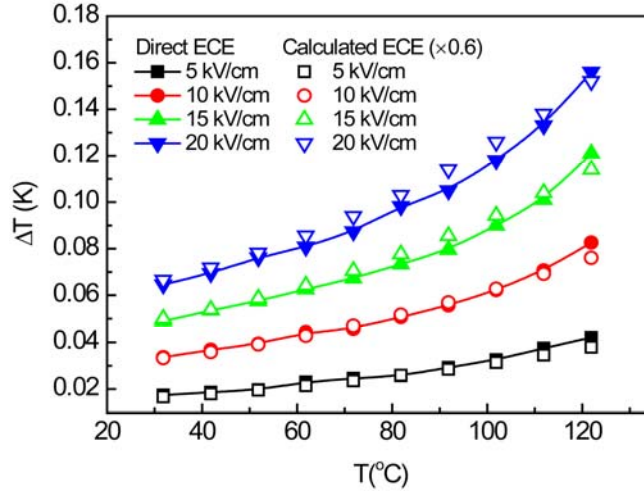

FIG. 6. Comparison between the directly measured ECE temperature change $\Delta T(T)$ and $\Delta T(T)$, calculated from Eq. (2) at four different values of electric field pulses (5, 10, 15 and 20 kV/cm) for the poled NBT. The calculated values are multiplied by 0.6.

The simplest way to explain the difference between the measured and calculated dP_{rem}/dT is to assume that P_{rem} depends on the difference (n_{or}) between concentrations of the domains oriented in the direction of the electric field and the domains oriented in the opposite direction (in the one-dimensional approach), earlier considered in [25]. So the remnant polarization and pyroelectric coefficient, taking into account that n_{or} also can depend on temperature, can be expressed in the following way:

$$P_{rem} = n_{or}(T) \times P_s(T),$$ (3)

$$\frac{dP_{rem}}{dT} = n_{or}\left(\frac{\partial P_s}{\partial T}\right)_{n_{or}} + P_s\left(\frac{\partial n_{or}}{\partial T}\right)_{P_s}.$$ (4)

Contrary to the earlier assumption, now P_{rem} and P_s are mutually different, since presence of domains is taken into account when calculating P_{rem}. While measurements of thermally stimulated depolarization and P(E) loops at E=0 reflect P_{rem}, only the first term in Eq. (4) contributes to ECE. Therefore, the difference between the directly and the indirectly measured ΔT is caused by temperature dependence of $n_{or}(T)$. In order to illustrate the possible contribution of the second term in Eq. (4), let us assume that $P_s(T)$=const in a certain temperature range, particularly between 25 and 125°C. Simple calculations using Eq. (4) show that the experimentally observed decreasing of $P_{rem}(T)$ in the considered temperature interval corresponds to decreasing of n_{or} by 18%.

The role of $n_{or}(T)$ can be confirmed by the irreversibility of $P_{rem}(T)$ upon switching the direction of the temperature change (Figure 1). It can be assumed that, during cooling, if it is started at a temperature $T<<T_d$, domain configuration is more stable against temperature change and $dP_{rem}(T)/dT$ approaches $n_{or}\times dP_s/dT$. Indeed, dP_{rem}/dT at cooling is equal to 70-80% from the value obtained at heating and, to a large extent, reduces the discrepancy, previously observed between the calculated and the directly measured ECE. It is remarkable that $P_{rem}(T)$ at subsequent heating follows the same path, which was observed at cooling, before it joins the first heating curve (Figure 1).

In spite of the difference between the results of the direct and the indirect measurements of ECE, the fact that $\Delta T(P_i)$ in the ferroelectric state follows the same path independently from temperature (Fig.3, similar behavior was observed in NBT-based solid solutions [38]) creates an impression that P_i can be considered as a variable, which solely characterizes ΔT in the ferroelectric state. As it follows from the Ginsburg-Devonshire theory [41]:

$$\Delta T = -\frac{2\pi T}{c_E C_w}\left(P_{tot}^2 - P_s^2\right), \tag{5.1}$$

which, taking into account that

$$P_{tot}^2 = (P_s + P_i)^2, \tag{5.2}$$

can be rewritten as

$$\Delta T = -\frac{2\pi T}{c_E C_w}\left(2P_s P_i + P_i^2\right). \tag{5.3}$$

Here C_w is the Curie-Weiss constant. The part of Eq. (5.3) before the brackets is almost temperature-independent in the considered temperature range (far enough from T_d). Unfortunately, the value of the Curie-Weiss constant, which can be extracted from the nonlinear $\Delta T(P_i)$ dependence as tangent at $P_i=0$ ($C_w=6.8\times10^5$ K), is remarkably larger than for such reference ferroelectric material of perovskite structure as $BaTiO_3$ [42]. The reason for this inconsistence apparently is contribution to P_i from other components of the dielectric permittivity tensor in the three-dimensional system. Indeed, contrary to P_{rem}, which is rather close to P_s after averaging over various directions of crystallographic axes of rhombohedral lattice in ceramics (87% from value of P_s [43]), the averaged value of P_i contains remarkable contribution from dielectric permittivity components in nonpolar directions. They usually are much higher than dielectric permittivity in direction of P_s [44] and can even give the main contribution in the total value of P_i. The positive curvature of $\Delta T(P_i)$, which contradicts with Eq. (5.3), can be also explained by contribution of dielectric permittivity in nonpolar directions. For this reason, estimation of C_w from Eq. (4) is not possible even if the Ginsburg-Devonshire theory (in three-dimensional case) is applicable.

When considering the measured $P_i(T)$ of the depoled sample (Figure 5(b)), already at first glance the Maxwell relation is not applicable in this case. dP_i/dT is positive below T_m, but $P_{rem}=0$, unlike in the poled state. As a consequence, calculated ΔT is purely negative at $T<T_m$ (Figure 7). Naturally, due to the maximum in $P_i(T)$ dependence, the calculated $\Delta T(T)$ changes sign in the region of T_m, becoming positive in a certain temperature region above T_m. Upon approaching T_m, ε_2 has much more pronounced temperature dependence than ε_1 (inset in Figure 5(b)), giving the main contribution to the calculated ΔT. Temperature region, where small negative directly measured ΔT was observed (above 210^oC) (Figure 2(b)), coincides with the temperature region, where $d\varepsilon_1/dT$ changes sign and the correspondingly calculated contribution to ΔT becomes negative again (inset in Figure 7). For the total calculated $\Delta T(T)$, this temperature is shifted in the direction of high temperatures due to contribution of $d\varepsilon_2/dT$ (Figure 7). Since nature of the electric field-induced polarization is rather complicated in the temperature range between T_d and T_m, where relaxor properties continuously diminish and diffused phase transition to orthorhombic phase is approached upon increasing of temperature [37], it is hard to comment such coincidence at the moment.

Nature of polarization in the depoled state of NBT is different compared to the poled state, as it should be considered as a relaxor state [37], consisting of polar nanoregions (PNR) of rhombohedral structure, embedded in
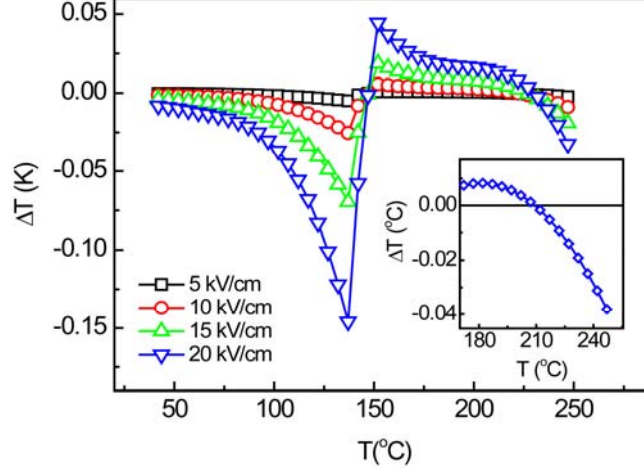
FIG. 7. Total ECE temperature change $\Delta T(T)$ calculated according Eq. (2) at four different values of electric field pulses (5, 10, 15 and 20 kV/cm) for the depoled NBT. The inset illustrates solely contribution of $d\varepsilon_1/dT$ to $\Delta T(T)$ at 20 kV/cm pulse.

the nonpolar matrix. It means that, besides the induced polarization, $P_i(E)$ contains other relevant contributions, such as reorientation and breathing of PNR [45]. Earlier, the breathing mechanism was used to interpret the frequency dispersion of dielectric permittivity in NBT at low temperatures [46]. Remarkable reduction of $\Delta T(P_i)$ slope upon decreasing of temperature, expressed in Figure 4 as $\Delta T/P_i$ as a function of E, can be attributed to PNR breathing mechanism, extended to moderate electric fields. Namely, change of PNR volume upon application/removing of electric field essentially is a temporary local phase transition between the polar and the nonpolar states. It corresponds to increasing of volume (v_+) for PNR oriented parallelly and decreasing of volume (v_-) for PNR oriented antiparallelly to the electric field. Let us assume that both v_+ and v_- at low enough electric field are linear functions of the electric field – $v_+=m \times E$ and $v_-=n \times E$. Contribution of PNR volume change to ΔT and polarization can be expressed in following way:

$$\Delta T = -\frac{T}{c_p}\left[(m-n)E\Delta S^{PT} + \frac{1}{2}\frac{dP_s}{dT}(m+n)E^2\right] \text{ and} \tag{6}$$

$$P_i = (m+n)EP_s, \tag{7}$$

where ΔS^{PT} is the entropy jump at the electric field-induced phase transition. Contribution from the nonpolar matrix in Eq. (6), as well as intrinsic induced polarization of PNR and nonpolar phases in Eq. (7) is neglected. If the first term in Eq. (6) dominates (if m>>n), $\Delta T(E)$ is linear, while, in case if only the second term gives contribution (if

m=n), $\Delta T(E)$ is proportional to E^2. Indeed, reducing of $\Delta T/P_i$, observed in the direction of low temperatures, can be explained by reducing of contribution to ΔT from the electric field-induced phase transition, if the difference m–n is reduced:

$$\frac{\Delta T}{P_i} = -\frac{T(m-n)\Delta S^{PT}}{c_p(m+n)P_s}.$$

(8)

This ratio is also electric field-independent in accordance with the experiment (Figure 4).

The obtained results of direct ECE measurements in NBT are in deep contrast to the published results obtained using the indirect ECE determining method [5,7,8,14]. The negative ΔT of NBT, obtained by measurements of bipolar polarization hysteresis loops in the ferroelectric state and by applying of the Maxwell relation, can be explained by the increased resistance of domain reorientation to the change of the electric field if the temperature is lowered [9,25,47]. Increasing of the coercive field E_{coerc}, usually observed in direction of low temperatures, also reflects this trend. Like in case of $P_{rem}(T)$ considered above, the contribution of $n_{or}(T)$ (Eq. (3)) can be used in the interpretation of $P(T)_{E=const}$, obtained from polarization hysteresis loops. This contribution is remarkable in case if E_{max} does not exceed E_{coerc} much [7,8,14] or in case of inclined polarization hysteresis loops with weakly expressed saturation [5]. In both cases a completely poled state is not achieved and P_{rem} depends on E_{max}.

The contradiction between the directly and the indirectly measured values of ECE should not be a surprise, since the Maxwell relations, strictly speaking, are applicable only for homogeneous systems where electric field-induced polarization has purely induced (intrinsic) nature. In none of the large number of publications, where ECE is calculated from the Maxwell relation, this requirement is fulfilled due to the presence of domains, or even worse – coexistence of PNR and nonpolar matrix in case of relaxor ferroelectrics. Finding an answer to the relevant question – in which cases and why the Maxwell relations give appropriate results – is outside the scope of the present study. According to considerations presented in this manuscript, Eq. (1) leads to correct results in the ferroelectric phase, if the first term in Eq. (4) prevails and $n_{or} \approx 1$. Application of the Maxwell relation in the relaxor state is more controversial due to the presence of PNR. Agreement with the direct measurements in case of 0.9PMN-0.1PT films [23] is observed at large electric fields, where contribution of PNR could be already exhausted. Since Eq.(1) is valid also at the first order phase transition [48], interpretation of ECE as a result of local or macroscopic field induced

first order phase transition perhaps could be used to explain, why, in some cases, the Maxwell equation gives a reasonable agreement with the direct measurements of ECE in relaxor ferroelectrics also below the high electric field limit [22].

IV. CONCLUSIONS

Directly measured ECE in the poled and the depoled NBT are not in agreement with the results of indirect ECE measurements, obtained from polarization as a function of applied electric field at different temperatures, measured simultaneously with electrocaloric response. Reason of the disagreement in the ferroelectric state is the temperature-dependent concentration of domains oriented in the poling direction. The almost temperature-independent path of $\Delta T(P_i)$ can be interpreted in the framework of the Ginsburg-Devonshire theory, even taking into account that values of the thermodynamic parameters cannot be extracted due to contribution of the nonpolar direction components of the dielectric permittivity tensor to P_i.

In the relaxor state of NBT, direct application of the Maxwell relation leads to a negative ECE temperature change values, which essentially contradicts with the results of the direct ECE measurements. One of the various $P(E)$ mechanisms, existing in the relaxor state that can be used to explain the behavior of $\Delta T(P_i)$, is the movement of PNR boundaries.

The directly measured ECE in the poled and the depoled NBT reveals remarkable differences from the earlier published results of the indirect measurements, where negative ECE temperature change values were observed. Due to different possible contributions to polarization inherent to inhomogeneous systems, the nature of polarization measured in a particular experiment should be evaluated before application of the Maxwell relation.

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