Direct measurement of electrocaloric effect in lead-free Ba(Sn$_x$Ti$_{1-x}$)O$_3$ ceramics

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In this study, we report on investigation of the electrocaloric (EC) effect in lead-free Ba(Sn$_x$Ti$_{1-x}$)O$_3$ (BSnT) ceramics with compositions in the range of $0.08 \leq x \leq 0.15$ by the direct measurement method using a differential scanning calorimeter. The maximum EC temperature change, $\Delta T_{\text{EC-max}}$ = 0.63 K under an electric field of 2 kV/mm, was observed for the composition with $x = 0.11$ at ~44 °C around the multiphase coexistence region. We observed that the EC effect also peaks at transitions between ferroelectric phases of different symmetries. Comparison with the results of indirect EC measurements from our previous work shows that the indirect approach provides reasonable estimations of the magnitude of the largest EC temperature changes and EC strength. However, it fails to describe correctly temperature dependences of the EC effect for the compositions showing relaxor-like behaviour ($x = 0.14$ and 0.15) because of their non-ergodic nature. Our study provides strong evidence supporting that looking for multiphase ferroelectric materials can be very useful to optimize EC performance. *Published by AIP Publishing.* https://doi.org/10.1063/1.5001196

The search for alternative solid-state refrigeration materials to replace hazardous gases in conventional and cryogenic cooling devices is one of the most active fields of condensed matter and materials science.[1] Recently, electrocaloric (EC) refrigeration based on the EC effect has been considered as a promising approach for developing next generation cooling technology.[2,3] When a polar material is subject to an electric field at either an adiabatic or isothermal condition, it is accompanied by a change in either temperature, ΔT_{EC}, or entropy, ΔS_{EC}, of the material, respectively.[4] The EC effect is usually strongest near a ferroelectric-paraelectric phase transition, where the polar degrees of freedom experience significant changes.[4,5] The largest EC values have been reported for thin films, where very high electric fields can be applied due to the geometry.[6] However, for applications, the heating or cooling capacity is an important factor, which in thin films is much smaller than that in bulk materials. Therefore, bulk materials are of particular interest to develop mid- and large-scale cooling applications.[7]

Materials with the presence of a phase coexistence region are promising candidates for achieving a high EC effect even under a moderate electric field due to a small energy barrier to be overcome.[5,8] Large entropy changes and, correspondingly, a large EC effect can be obtained in these materials by electric field induced transformations of domain structures or phase transitions.[7] A typical example is the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral symmetries in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) or PbZrO$_3$-PbTiO$_3$ (PZT) material systems. For example, for PMN-PT compositions close to the MPB, a relatively high EC temperature change has been reported.[9–11] Although large EC values have been obtained in these materials, the hazardous lead content is a serious problem for industrial applications and should be omitted according to EU regulation acts.[12] Hence, the replacement of PMN-PT and PZT by environmentally friendly lead-free material systems is requested.

In this letter, we report on direct EC measurements in lead-free Ba(Sn$_x$Ti$_{1-x}$)O$_3$ (BSnT) ceramics that show excellent dielectric, piezoelectric, and electromechanical properties in the vicinity of a so-called "quasi-quadruple point" (QP), where four phases, cubic (C), tetragonal (T), rhombohedral (R), and orthorhombic (O), are merged.[8,13]

As it was shown in our previous work,[14] the aforementioned four phases merge into QP at $x = 0.105$ and $T = 28$ °C, which is accompanied by the largest value of the dielectric permittivity among all the BSnT compounds. Indirect estimations predict an improved EC response under a relatively low electric field, which was attributed to a flat energy landscape at QP, facilitating the rotation of the polarization.[14] Furthermore, the increasing Sn content reduces the ferroelectric-paraelectric transition towards room temperature and results in a cross-over to relaxor behaviour.[15] The compositions with $x = 0.14$ and $x = 0.15$ show a diffuse phase transition behaviour,[16] which leads to the extension of the high EC effect over a broad working temperature range. This is interesting for cooling applications.

Most EC studies, including previous ones,[14,17] deal with the indirect measurement method based on Maxwell's relation $\left(\frac{\partial P}{\partial T}\right)_{E,\sigma} = \left(\frac{\partial S}{\partial E}\right)_{T,\sigma}$

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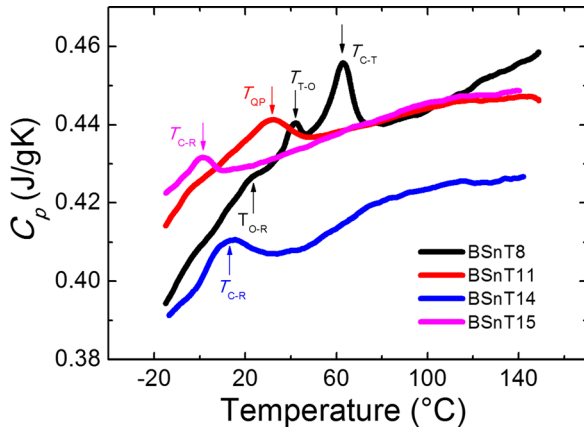
FIG. 1. Temperature dependences of the specific heat capacity, C_p, measured upon heating of Ba(Ti$_{1-x}$Sn$_x$)O$_3$ ceramics with $x = 0.08$ (BSnT8), $x = 0.11$ (BSnT11), $x = 0.14$ (BSnT14), and $x = 0.15$ (BSnT15). The arrows show the heat anomalies corresponding to the phase transitions of the ceramic systems.

$$\Delta T_{EC}^{ID} = -T \int_{E_1}^{E_2} \frac{1}{C_{E,\sigma}} \left(\frac{\partial P}{\partial T} \right)_{E,\sigma} dE, \qquad (1)$$

where T is the temperature, P is the polarization, E_1 and E_2 are the starting and final values of the applied electric field, and $C_{E,\sigma}$ is the heat capacity. However, it was shown that the EC response of multidomain ferroelectrics and non-ergodic systems, like relaxors, can be only qualitatively estimated using the indirect measurement method.[4,18,19] Therefore, direct measurements of the EC effect must be performed in order to obtain accurate and reliable EC data.[4,19–29]

In order to evaluate the reliability of the indirect EC measurements from our previous work,[14] the direct EC measurements were performed using a modified differential scanning calorimeter (Netzsch DSC 204), in which two spring loaders were built in for applying a voltage to a sample. By applying (switching) off an electric field, an exothermic (endothermic) peak was observed which is related to a heat release (absorption) by the sample. This heat exchange between the sample and the environment corresponds to the EC enthalpy change, ΔH, which can be evaluated by integration of the area under the exothermic or endothemic peaks. The EC entropy change, ΔS_{EC}, under isothermal and isobaric conditions is $\Delta S_{EC} = \frac{\Delta H}{T}$. The corresponding EC temperature change, ΔT_{EC}, can be calculated as $\Delta T_{EC} = \frac{T \Delta S_{EC}}{C}$, where C is the heat capacity.

Each temperature point was reached at a heating or cooling rate of $10\,°C/min$. Before the EC measurements were started, the sample was isothermally kept for 30 min in order to stabilize the temperature. The *dc* electric field with magnitudes of 1, 1.5, and 2 kV/mm was applied for 100 s and removed for 100 s at each measurement point. The heat capacity was measured at zero electric field using the same DSC setup, but using a standard cell.[18,20]

BSnT ceramic samples of four compositions ($x = 0.08$, 0.11, 0.14, and 0.15) were studied in this work, where Ba(Sn$_{0.11}$Ti$_{0.89}$)O$_3$ (BSnT11) is located quite close to the QP composition. The ceramic samples were fabricated using the conventional solid-state reaction method with starting materials of barium carbonate (BaCO$_3$, 99.8%), titanium dioxide (TiO$_2$, 99.8%), and tin dioxide (SnO$_2$, 99.9%). The mixtures of the aforementioned materials were then sintered at $1400\,°C$ for 4 h before being pressed into pellets.[13,14]

Figure 1 shows the temperature dependences of the specific heat capacity, C_p, which must be known to convert the enthalpy change measured by DSC into the EC temperature change, ΔT_{EC}.[20] The specific heat capacity is not constant over the studied temperature range even though it is often assumed in many works for evaluation of the EC effect. All $C_p(T)$ dependences show a peak corresponding to the ferroelectric-paraelectric phase transition. In addition to this
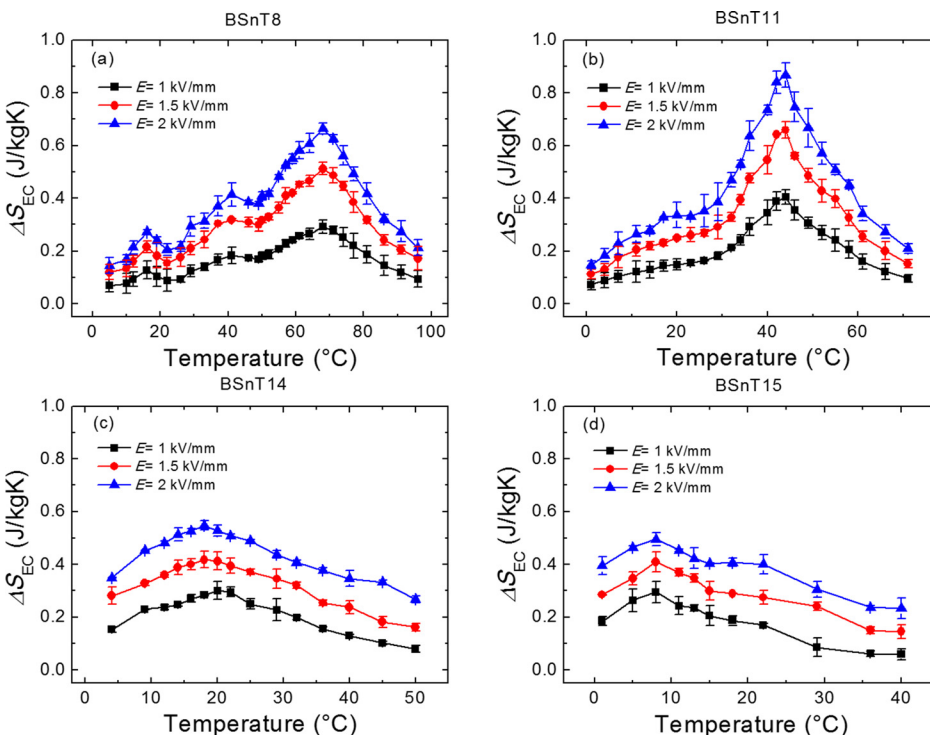

FIG. 2. Isothermal entropy change ΔS as a function of temperature in different BSnT ceramics measured by DSC: (a) x = 0.08, (b) x = 0.11, (c) x = 0.14, and (d) x = 0.15.

peak, for the composition with $x = 0.08$, other thermal anomalies can be resolved at 23 °C and 42 °C. In accordance with the phase diagram of the BSnT system, these anomalies can be attributed to the orthorhombic to rhombohedral and tetragonal to orthorhombic phase transitions, respectively.[13,14] The composition with $x = 0.11$ (BSnT11) shows only one peak in the vicinity of QP, which indicates that the ferroelectric phases with different symmetries merge in the multiphase coexistence region.

Figures 2(a)–2(d) and 3(a)–3(d) summarize the results of the direct EC measurements as a function of temperature at different electric fields ($\Delta E = 1$, 1.5, and 2 kV/mm). The insets of Figs. 3(a)–3(c) show comparisons between the direct and indirect measurements obtained for $\Delta E = 2$ kV/mm. The indirect measurement data were taken from Ref. 14. Both the EC entropy change, ΔS_{EC} [Figs. 2(a)–2(d)], and the corresponding EC temperature change, ΔT_{EC} [Figs. 3(a)–3(d)], are important to evaluate the effectiveness of EC refrigeration.[4,5] It can be seen that the variation of ΔS_{EC} is consistent with that of ΔT_{EC} since they are related via a simple relation $C\Delta T_{EC} = T\Delta S_{EC}$, where C is the heat capacity and T the temperature. All the dependences show a maximum at a few degrees above the corresponding ferroelectric-paraelectric phase transition temperature. The largest EC temperature change, $\Delta T_{EC-max} = 0.63$ K, and entropy change, $\Delta S_{EC-max} = 0.87$ J/kg·K, were observed under a field of $\Delta E = 2$ kV/mm for the BSnT11 composition at 44 °C, i.e., in the vicinity of the QP [Figs. 2(b) and 3(b)].

In general, we observed that the directly measured EC effect reaches the peak value at higher temperatures as compared to the indirect estimates from our previous work. To explain such a significant deviation in the temperature profile, we have to take into account that the direct EC effect and $P(E)$ measurements were performed with different

setups and a systematic error of the sample temperature measurements is expected. Nevertheless, we found that for BSnT8 and BSnT11 compositions, both direct measurements and indirect measurements[14] yielded the same peak magnitude of the EC effect.

As the concentration of Sn increases beyond QP, the EC temperature changes are reduced [Figs. 3(c) and 3(d)], which is accompanied by the significant broadening of the maximum of the EC effect. This is related to the diffuse phase transition behaviour of ceramics with $x \geq 0.14$ due to the appearance of polar nanoregions (PNRs) in the paraelectric phase.[16,30] For these compounds, temperature dependences of the EC properties differ from the estimation by the indirect measurement [see the inset of Fig. 3(c) for BSnT14]. Indeed, the use of Maxwell's relations for non-ergodic systems, like relaxors, has driven increasing concerns recently since they are basically not in thermal equilibrium.[4,5,18] Moreover, as relaxors are non-ergodic systems, their thermal and/or field history is of importance and may account for the observed discrepancy between the direct measurements we did and the earlier ones using the indirect approach. It turns out therefore that the maximal value of the EC effect predicted by the indirect method still shows considerable agreement with direct DSC measurement.

For the BSnT8 composition, three EC peaks corresponding to the C-to-T (68 °C), T-to-O (41 °C), and O-to-R (15 °C) phase transition were observed [see Figs. 2(a) and 3(a)]. Compared to the indirect measurements,[14] the direct measurements allow us to resolve the EC peaks associated with ferroelectric-ferroelectric phase transitions, T-to-O and O-to-R. Anomalies of the EC effect at phase transition between different ferroelectric phases have been reported for BaTiO$_3$,[31] Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$,[32] and Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ single crystals[33] and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$,[34]
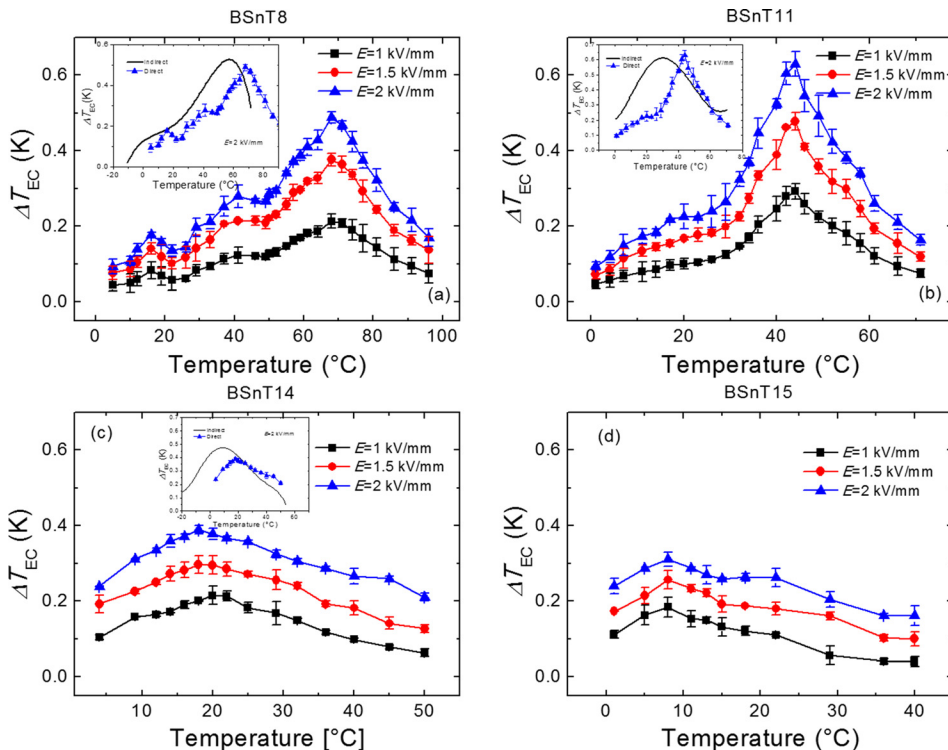

FIG. 3. EC temperature change ΔT as a function of temperature in different BSnT ceramics measured by DSC: (a) $x = 0.08$, (b) x = 0.11, (c) x = 0.14, and (d) x = 0.15. The insets show the comparisons between the direct and indirect EC measurements for $E = 2$ kV/mm. Data for the indirect EC measurements are taken from Ref. 14.

$(Na_{0.5}Bi_{0.5})TiO_3$-$(K_{0.5}Bi_{0.5})TiO_3$,[35] and $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$[19] ceramics. They were attributed to the larger configurational (polarization) disorder that occurs at interferroelectric phase transitions.[36] The magnitude and the sign of the EC effect depend on the mutual orientations of the spontaneous polarization and the applied field. In some cases, the EC effect can attain even negative values when the electric field is applied non-collinearly to the polarization direction or stabilizes the high-temperature phase.[31,32,36] In our case, the EC effect remains positive for both interferroelectric phase transitions. We also found that the ΔT_{EC} peak positions show some shifts (68 °C, 41 °C, and 15 °C) compared to the transition temperatures estimated from the dielectric permittivity measurements in our previous work (58 °C, 28 °C, and 8 °C).[14] This might be due to different characteristic time constants of different techniques.[4]

By comparison of the EC responses in the studied BSnT compositions, we have found that the largest EC temperature change for the BSnT11 sample is nearly 30% larger than the peak value of the BSnT8 ceramics. However, the dielectric permittivity (usually obtained under zero dc-field), measured in our previous work, for BSnT11 was about two times higher than that for BSnT8. That is, our EC study shows that the magnitude of dielectric permittivity is not directly related to the improvement of the EC effect in the system. Rather, one has to consider the field-dependence of the dielectric permittivity. It drastically reduces for the increasing electric field[37] and explains the non-direct relation of dielectric permittivity to the value of the EC effect. One of the key factors determining a large EC response is the latent heat, which is strongly related to the discontinuous polarization change at the phase transition and is the highest for first order phase transition.[4,38] Therefore, the BSnT14 ($x = 0.14$) and BSnT15 ($x = 0.15$) ceramics showing the diffuse phase transition behaviour exhibit smaller EC values, while the EC peaks are broader. Note that such an amplitude might be enhanced by applying a much higher electric field, allowing us to force a ferroelectric phase transition to be induced from the relaxor state.

Now, let us make further comparison between the direct [Figs. 4(a) and 4(b)] and indirect measurements [Figs. 4(c) and 4(d)] in terms of the EC temperature change and EC strength defined as $\Delta T_{EC}/\Delta E$. It is found that the indirect method [Figs. 4(c) and 4(d)] provides reasonable estimations of EC responses since it well reproduces the result obtained from the direct measurements [Figs. 4(a) and 4(b)]. Most importantly, the critical compound with $x = 0.11$ (BSnT11) shows enhanced EC properties compared to other compositions ($\Delta T_{EC\text{-max}}/\Delta E = 0.315 \times 10^{-6}$ Km/V at 44 °C), which is consistent with the main results deduced from the indirect approach. It is worth comparing the EC strength $\Delta T_{EC\text{-max}}/\Delta E$ of our BSnT11 ceramics with the results of direct EC measurements for other material systems that exhibit the MPB or phase coexistence region. So, for $0.60Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.30PbTiO_3$ single crystals, $\Delta T_{EC\text{-max}}/\Delta E = 0.65 \times 10^{-6}$ K·m/V at 140 °C,[32] for $0.60Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.30PbTiO_3$ ceramics, $\Delta T_{EC\text{-max}}/\Delta E = 0.33 \times 10^{-6}$ K·m/V at 150 °C,[39] for $0.65Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.35(Ba_{0.7}Ca_{0.3})TiO_3$, $\Delta T_{EC\text{-max}}/\Delta E = 0.165 \times 10^{-6}$ K·m/V at 65 °C,[19] for $0.82(Na_{0.5}Bi_{0.5})TiO_3$-$0.18(K_{0.5}Bi_{0.5})TiO_3$, $\Delta T_{EC\text{-max}}/\Delta E = 0.33 \times 10^{-6}$ K·m/V at 160 °C,[35] and for Li,Ca co-doped $0.94(Na_{0.5}Bi_{0.5})TiO_3$-$0.06BaTiO_3$, $\Delta T_{EC\text{-max}}/\Delta E = 0.42 \times 10^{-6}$ K·m/V at 105 °C[24] were reported. However, in comparison with the BSnT11 ceramics, most of the MPB compositions show the maximal EC effect well above room temperature, which makes them less attractive for practical cooling applications. The magnitude of the EC strength $\Delta T_{EC\text{-max}}/\Delta E$ in BSnT11 is comparable to that of other material systems with MPB, such as $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ ($\Delta T_{EC\text{-max}}/\Delta E = 0.41 \times 10^{-6}$ Km/V at 140 °C),[9] $0.65Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.35(Ba_{0.7}Ca_{0.3})TiO_3$ ($\Delta T_{EC\text{-max}}/\Delta E = 0.165 \times 10^{-6}$ Km/V at 65 °C),[19] and $0.82(Na_{0.5}Bi_{0.5})TiO_3$-$0.18(K_{0.5}Bi_{0.5})TiO_3$ ($\Delta T_{EC\text{-max}}/\Delta E = 0.33 \times 10^{-6}$ Km/V at 160 °C).[35] However, in comparison with BSnT11, most of the reported MPB compositions have their phase transition temperatures too high for practical cooling applications. Our study combining both direct and indirect measurements therefore clearly confirms
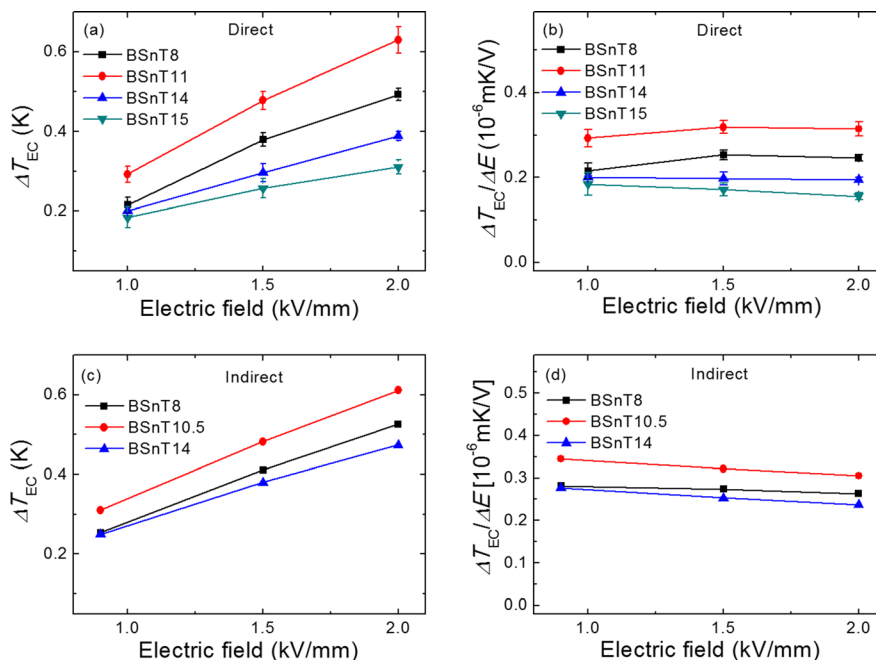

FIG. 4. Comparison of the EC temperature change ΔT and EC strength $\Delta T/\Delta E$ between the direct [(a) and (b)] and indirect measurements [(c) and (d)] for the BSnT ceramics, where $\Delta E = E_2 - E_1$ and E_1 is 0 kV/mm. Data for the indirect EC measurements are taken from Ref. 14.

that engineering multiphase coexistence in EC material systems is an effective strategy to improve their EC responses.[5,8,14]

In summary, we have carried out a comparative investigation of the EC effect in lead-free BSnT ceramics. Direct measurements using the DSC technique demonstrate that the previous indirect approach based on Maxwell's relation provides reasonable estimates of the magnitude of the EC temperature change and EC strength. However, it fails to reproduce the temperature dependences of the EC effect, especially for the compositions with diffuse phase transition behaviour. This is explained by the non-ergodic character of such a relaxor-based composition. The results of both direct and indirect measurements show that material systems with the coexistence of multiple phases can permit enhanced EC properties, which offers an effective strategy for optimizing EC performances.

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