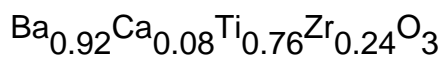


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Heat capacity and thermal expansion study of relaxor-ferroelectric $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$

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Abstract

Heat capacity and thermal expansion of the $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$ compound is measured using the methods of adiabatic calorimetry and optic-mechanical dilatometry in the temperature range 100–370 K. Three blurred anomalies on the $C_p(T)$ and $\alpha(T)$ dependencies are observed in the temperature range 200–360 K. The results of the studies are discussed together with data on the structure and dielectric properties in the framework of spherical random bond–random field model.

1. Introduction

Perovskite-like compounds attract considerable interest owing to rich diversity of their physical properties and possible applications in various technological schemes. Magnetic, dielectric, optic and electric properties of perovskite-like materials are studied extensively. Such phenomenon as relaxor behaviour, observed in doped (mixed) perovskites, is of special importance.

The first studies on relaxor ferroelectrics date back nearly 40 years [1, 2]. Recently, a new wave of interest has arisen related to their unusual physical properties and to their importance in industrial applications [3].

The main features of relaxors are connected to their structural (compositional) inhomogeneity or disorder and with the presence of polar nanodomains in a nonpolar matrix. The structural investigations and studies of the physical properties of relaxors reveal three peculiar temperatures: T_d , T_m and T_c . At temperatures above T_d , the so-called Burns temperature, the mixed compounds $\text{A}(\text{B}'\text{B}'')\text{O}_3$ have the cubic perovskite structure, where the B position is occupied by the approximately and randomly distributed B' and B'' ions. On cooling below T_d , small polar nanodomains appear, whose interactions and growth can trigger a transition into a glassy or ordered phase. If the domains become large enough, the sample will undergo a cooperative ferroelectric phase transition at T_c . On the other hand, if the nanodomains

grow but do not become large enough, they will ultimately exhibit a dynamic slowing down of their fluctuations below T_m , which is the temperature of the dielectric permittivity maximum, leading to an isotropic relaxor state with random orientation of polar domains [4].

Most relaxor ferroelectrics belong to the family of complex lead-based perovskite oxides, as does the lead magnesium niobate ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$), which is often considered as a model system. Lead-free compositions could be of great interest for environment-friendly applications (dielectric for capacitors, actuators, etc). Studies have been performed in particular on ceramics Ce-, Sn-, Hf- and Zr-doped BaTiO_3 [5–9]. It was shown that in such systems both normal ferroelectric and relaxor properties exist depending on the composition [6, 8, 9].

Based on the dielectric response, $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ solid solutions can be classified into three groups [8]. In region I ($x < 0.12$), three dielectric peaks were observed, which are due to phase transitions from a cubic paraelectric to a tetragonal ferroelectric (at T_c), and then to an orthorhombic ferroelectric (at T_1) and, finally, to a rhombohedral ferroelectric (at T_2), similar to those of pure BaTiO_3 . However, T_c of pure BaTiO_3 is shifted to a lower temperature and T_1 and T_2 to higher temperatures by the substitution of Zr ion for Ti ion. The dielectric peak at T_c is relatively sharp and the peak temperature is independent of the measuring frequencies, similar to those observed in pure BaTiO_3 . In region II ($0.12 < x < 0.25$), only one rounded dielectric peak (at T_c) with very small frequency dispersion is found in ε , corresponding to direct transformation from a cubic phase into a rhombohedral one. In region III ($x > 0.25$), the diffuse maximum of $\varepsilon(T)$ at T_m with obvious frequency dispersion is observed with further increasing Zr content, displaying a typical ferroelectric relaxor behaviour. The results of the three regions show the evolution from a normal ferroelectric to a ferroelectric relaxor with increasing Zr concentration.

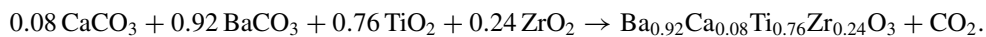
In compounds with small Ca doping, a wide boundary between zones II and III exists. There is a maximum of $\varepsilon(T)$ at T_m , but in addition a classical ferroelectric phase at $T_3 < T_m$ appears [8, 10].

X-ray diffraction study has shown that the $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$ composition of this region is rhombohedral at low temperature [11]. A transition of this type at T_3 , which occurs spontaneously (without applied electric field), was previously observed in lead-containing relaxors: PSN, PST and PMN-PT.

In this paper, we present the results of heat capacity and thermal dilatation studies on $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$ ceramics, belonging to the intermediate zone. The main aim was to clarify the behaviour of $C_p(T)$ and $\alpha(T)$ in the vicinity of T_d , T_m and T_c temperatures.

2. Sample preparation and experimental technique

The compound under investigation was obtained from CaCO_3 , BaCO_3 , TiO_2 and ZrO_2 mixture by the solid-state reaction



After calcination at 1200 °C for 15 h under oxygen, pressed pellets (8 mm in diameter) were sintered at 1400 °C for 4 h always under oxygen atmosphere [8].

Measurements of heat capacity in the temperature range 100–370 K are carried out by a method of the adiabatic calorimeter, allowing us to obtain the absolute value of integral heat capacity with a high accuracy. The mass of a ceramic sample was about 1 g. Measurements were made using the traditional method of discrete heating and in an automated regime of continuous heating at a temperature variation rate of about $10^{-1} \text{K min}^{-1}$ [12]. The accuracy of measurements depends on the method of heating and amounts to (0.1–1.0)%.

Thermal expansion measurements were performed on the same ceramic sample (thickness about 5 mm) using a quartz optic-mechanical dilatometer with a sensitivity of 1.2×10^{-6} cm. The sample was covered on the top and bottom surfaces with very thin cuprous electrodes. The electrostrictive deformation $\Delta l/l_0$ was measured in applied dc fields up to 8 kV cm^{-1} with a step about 400 V cm^{-1} .

3. Results and discussion

The results of the heat capacity measurements of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$ ceramic (BCTZ) are represented in figure 1. The deviation of experimental points relative to the smoothed curve does not exceed 0.3%. The curve describing the temperature dependence of heat capacity does not exhibit clearly manifested anomalies typical of traditional phase transitions. However, in the temperature range 200–350 K, some broad blurred anomaly in $C_p(T)$ is observed. To analyse it in more detail the anomalous and lattice contributions to the heat capacity should be separated.

The general expression for the lattice heat capacity C_L can be derived from the relation

$$C_L(T) = \frac{dE}{dT} = \frac{d}{dT} \int d\omega G(\omega)n(\omega)\hbar\omega, \quad (1)$$

where E is the internal energy of the system, $n(\omega)$ the Bose–Einstein distribution function and $G(\omega)$ the density of vibrational states. As a rule the function $G(\omega)$ for a complex composition is unknown in the entire frequency range. For this reason, we must resort to a simplified approach to obtain a description of the temperature dependence of the lattice heat capacity. In most cases, the analysis of the heat capacity to separate the lattice and anomalous contributions was carried out using a simple model describing the lattice heat capacity of the compound by a combination of the Debye and Einstein functions. In the temperature range 150–370 K, the heat capacity of our sample is already poorly sensitive to fine details of a vibration spectrum and the approximation of the lattice contribution carried out in the same way is quite justified.

The anomalous component of heat capacity $\Delta C_p = C_p - C_L$, shown in figure 2, reaches only $\sim 1.5 \text{ J mol}^{-1} \text{ K}^{-1}$ or $\sim 1.5\%$ of C_L . However, one can see three features in its behaviour near 320, 270 and 200 K.

The entropy change, associated with the anomalous behaviour of heat capacity, determined as $\Delta S = \int (\Delta C_p/T) dT$ is shown in figure 3. The small value of $\Delta S \approx 0.35 \text{ J mol}^{-1} \text{ K}^{-1}$ demonstrates clearly the displacive nature of crystal phase changes. It should be noted that for BCTZ anomalies of the heat capacity and the entropy change are much smaller than those for lead containing relaxors such as PMN. In the latter, the positional ordering of Pb ions is responsible for the main part of the entropy [13].

The results of thermal expansion study on BCTZ are presented in figure 4. Linear coefficient of thermal expansion $\alpha(T)$ shows, as heat capacity, three smeared anomalies at about 200, 270 and 320 K.

As was pointed out previously, the structural investigations and physical properties studies reveal three peculiar temperatures: T_d , T_m and T_c [4]. At Burns temperature T_d , where the dielectric permittivity starts to deviate from the Curie–Weiss law, there is anomaly in $\varepsilon(T)$ [8]. The same features were observed in PMN and other relaxors. Moreover, in PMN, there were detected also at this temperature an anomalous behaviour of soft TO mode and $R3m$ distortion in Nb-rich clusters with the appearance of polarization [14]. However the correlation length of clusters is quite small and macroscopic polarization does not appear in the whole sample.

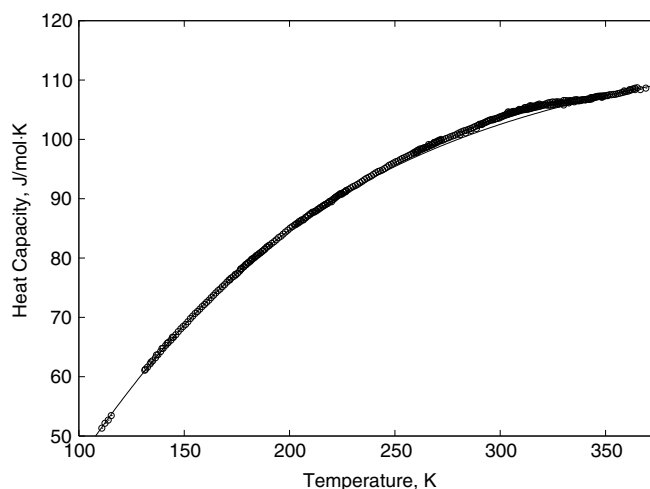


Figure 1. Temperature dependence of the heat capacity of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$. The solid line gives the lattice heat capacity approximated by the combination of the Debye and Einstein functions.

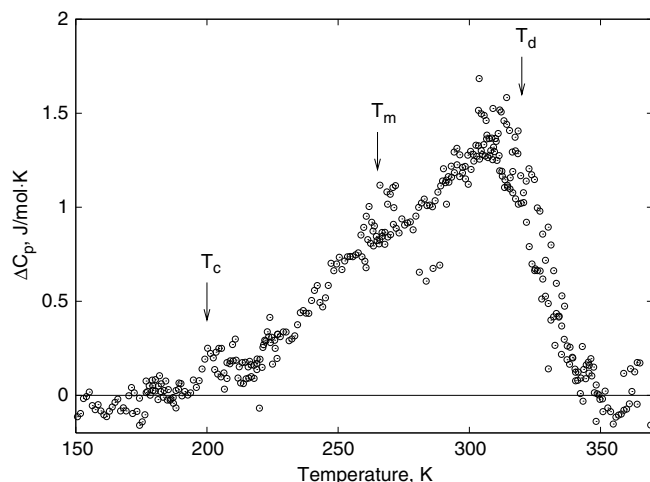


Figure 2. Anomalous component of the heat capacity of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$.

Once again we note that anomalies both in the heat capacity and in the thermal dilatation are very small and smeared in a wide temperature range that impedes determination of the temperature of abnormal contributions appearance. Deviations from regular dependences in $C_p(T)$ and $\alpha(T)$ are observed below 350–370 K, which is a little lower than the temperature (400 K) of deflection from Curie–Weiss law in the dielectric permittivity [8].

In BaTiO_3 – BaZrO_3 solid solution with increasing Zr concentration the ferroelectric long-range order prevailing in BaTiO_3 rhombohedral phase is progressively broken, and only a polar nanoregion phase is stabilized at low temperature. The local ordering in this state is rhombohedral because of the parent BaTiO_3 phase [15].

Owing to the change of phonon spectra connected with the soft-mode condensation at the Burns temperature anomalous behaviour of heat capacity and thermal expansion can be

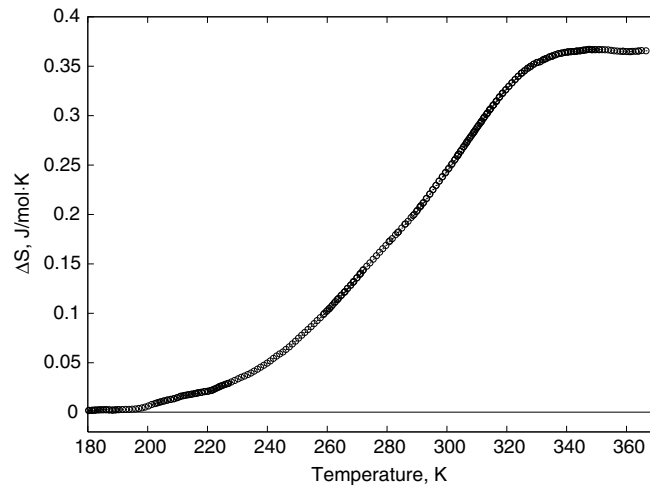


Figure 3. The anomalous entropy change of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$.

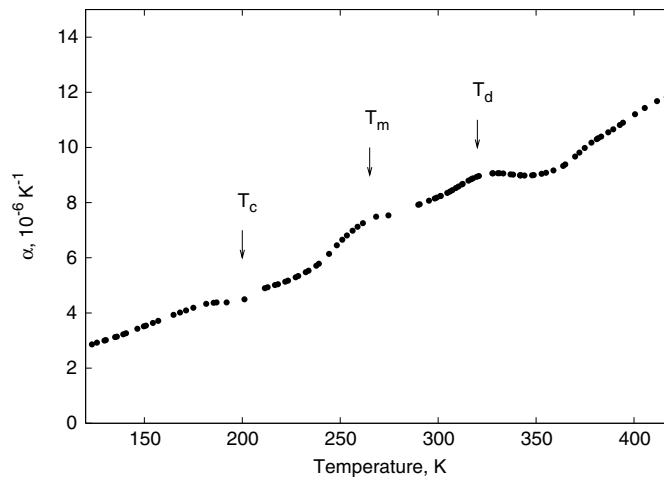


Figure 4. Thermal expansion of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.76}\text{Zr}_{0.24}\text{O}_3$.

expected and they were indeed observed in our experiments in the temperature range near 320 K.

The order parameter connected with the temperature region $T < T_d$ and responsible for the deviation from the Curie–Weiss behaviour can have different sense in different materials. For example, it can be the average square of polarization $\langle P^2 \rangle$ [4, 16].

The model of relaxors for temperatures $T < T_d$, the so-called spherical random bond–random field model (SRBRF) was proposed in [17]. This model is based on randomly competing ferroelectric and antiferroelectric interactions between the reorientable polar clusters of different size in the presence of random field.

The model Hamiltonian is given in SRBRF by [17]

$$H = -\frac{1}{2} \sum J_{ij} \vec{S}_i \vec{S}_j - \sum \vec{h}_i \vec{S}_i - g\vec{E} \sum \vec{S}_i, \quad (2)$$

where \vec{S}_i is the dipole moment of the i th polar cluster, J_{ij} the random intercluster interactions (J_0 is the mean value and J^2 the variance), \vec{E} the external electric field and \vec{h}_i the random local electric fields ($\langle h \rangle = 0$ the mean value and $\langle h^2 \rangle \equiv \Delta \neq 0$ the variance). For $J_0 < \sqrt{J^2 + \Delta}$, long-range order cannot exist and the system is in a spherical glass (SG) phase at all temperatures with a nonzero value of the order parameter $q \sim \sum_i \langle S_i \rangle^2 \sim \langle P^2 \rangle$. If $\Delta = 0$ as in magnetic spin glasses, a transition from a high-temperature paraelectric to SG phase occurs at $T_m = J/k$. For $\Delta \neq 0$ and $\Delta \ll J^2$, the sharp transition disappears, but the nonlinear susceptibility shows a maximum at $T_m \approx (\sqrt{J^2 + \Delta})/k$. For $J_0 > \sqrt{J^2 + \Delta}$, long-range order is possible and a phase transition to an inhomogeneous ferroelectric phase occurs below the critical temperature

$$T_c = \frac{J_0}{k} \left(1 - \frac{\Delta}{J_0^2 - J^2} \right). \quad (3)$$

Numerical calculations for various values of the model parameters [13] have shown that the existence and temperature variations of the q or $\langle P^2 \rangle$ parameter lead to anomalous behaviour of heat capacity at T_m . The anomaly at T_m in BCTZ really exists but is rather small to perform any quantitative analysis.

Very small anomalies of $C_p(T)$ and $\alpha(T)$ at ~ 200 K correspond to the phase transition into ferroelectric phase and correlate with the results of dielectric and structural studies [8, 10].

In the absence of external electric field in the temperature range $T_c < T < T_d$, there is no measurable remanent polarization ($\langle P \rangle = 0$); however, $\langle P^2 \rangle \neq 0$, and one can expect some features in properties which depend on P^2 such as electrostriction which is reflected in the thermal expansion. This property has provided a quantitative measure of $\langle P^2 \rangle \neq 0$ polarization for relaxor [16].

It was shown that for the cubic perovskite the thermal strain, x_{11} , is given by [16]

$$x_{11} = \frac{l_T - l_0}{l_0} = \alpha(T - T_0) + (Q_{11} + 2Q_{12})\langle P^2 \rangle, \quad (4)$$

where l_T is the sample length at T , l_0 the reference length at the reference temperature T_0 , α the linear coefficient of thermal expansion and Q_{11} and Q_{12} are electrostrictive coefficients. In the presence of polar nanoregions and $\langle P^2 \rangle \neq 0$, there are two contributions to the total thermal strain—the usual linear expansion and the contribution due to electrostriction. The latter contribution vanishes above T_d where $\langle P^2 \rangle = 0$.

Figure 5 shows the temperature dependence of the strain. Below 320 K the rate of thermal contraction reduces continuously. If we attribute this reduction to the electrostrictive consequence of an escalating $\langle P^2 \rangle$, we can estimate this value using known values of Q_{11} and Q_{12} for BaTiO₃ [18]. Figure 6 compares the calculated $\langle P^2 \rangle^{1/2}$ against P_S measured from pyroelectric depolarization [8].

In relaxor ferroelectrics, where the induced polarization reaches high values over a wide temperature range, an anomalous large electrostrictive deformation should appear. If the field dependence of the induced polarization is linear, a quadratic relation between the electric field and the deformation results,

$$\frac{\Delta l}{l_0} = Q_m P_m^2 = Q \varepsilon^2(E) E^2, \quad (5)$$

where Q_m and P_m are the electrostrictive coefficient and the induced polarization, respectively. Near the transition temperature, where dielectric nonlinearities and spontaneous polarization

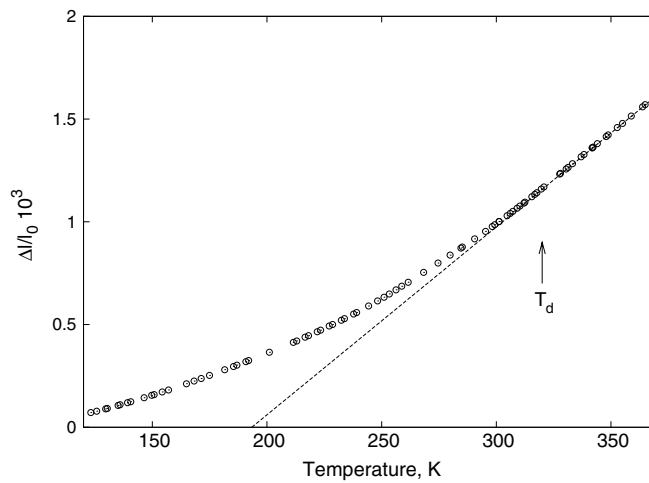


Figure 5. Thermal strain x_{11} versus temperature for ceramic sample of BCTZ.

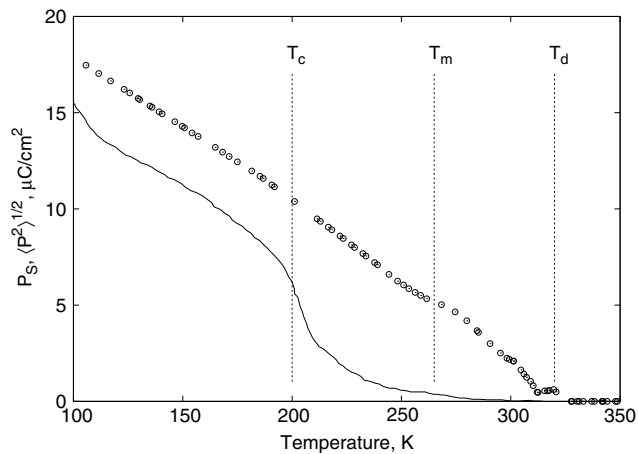


Figure 6. Calculated values of $\langle P^2 \rangle^{1/2}$ derived from thermal strain (points) data compared with pyroelectric measurements of P_S [8] (—).

arise, a linearization and finally a saturation can be found in the field dependence of the strain.

At temperature $T > T_d$, in paraelectric state, the weak dependence of strain is observed as shown in figure 7. At all studied temperatures $T < T_d$, the nonlinear dependence of electrostrictive strain versus the applied electric field was observed. The decrease in the temperature leads to enhancement of the field dependence of strain. The strain is approximately proportional to the applied field squared within the scope of the experimental error in the region $T_m < T < T_d$.

4. Conclusions

Anomalous behaviour of heat capacity and thermal dilatation were observed at all three specific temperatures characteristic for ferroelectric relaxors: at T_d , where local distortions of cubic

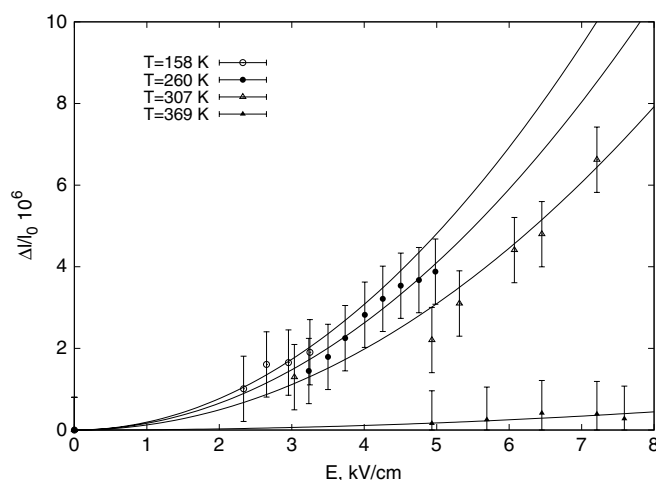


Figure 7. Electric field dependencies of deformation at different temperatures.

phase and polar nanoregions arise; at T_m —the temperature of $\varepsilon(T)$ maximum and T_c , where phase transitions into ferroelectric phase with macroscopic polarization takes place. At T_m , there are no symmetry changes and heat capacity anomaly is due to the continuous changes in $\langle P^2 \rangle$, related to the polarizations of polar nanoregions.

Acknowledgments

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