PHYSICAL REVIEW B **74**, 132101 (2006)

Absence of the heat capacity anomaly in the Pb-free relaxor $BaTi_{0.65}Zr_{0.35}O_3$

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(Received 15 July 2006; published 3 October 2006)

A relaxor ferroelectrics, $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ35), which was free from lead, was synthesized and the physicothermal properties were measured. The heat capacity was measured using a homemade adiabatic calorimeter at temperatures from 13 K to 420 K, and the dielectric constant measurements were carried out between 1 kHz and 1 MHz at temperatures from 20 K to 420 K. No anomaly was detected in the heat capacity curve for the whole temperature range covered in the present experiments, while a large and broad peak was observed in the dielectric constant curve. The dielectric constant showed the relaxor type frequency dependence. The results of the present experiments were compared with our previous studies on a typical relaxor of lead-based complex perovskite oxide, $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), which showed a large heat capacity anomaly as well as a large broad peak of dielectric constant due to formation of ferroelectric polar nanoregion in the crystal. Some differences between the two compounds, BTZ35 and PMN, were compared and the mechanism was discussed.

DOI: 10.1103/PhysRevB.74.132101 PACS number(s): 77.80.Bh, 77.84.Dy, 65.40.Ba, 82.60.Fa

I. INTRODUCTION

A ferroelectric compound, so-called relaxor, has been attracting much interest because of superior physical properties, such as giant dielectric constant, extraordinary piezoelectricity, large electromechanical coupling factors, and so on. The relaxor is characterized by a large, broad and frequency-dependent dielectric constant peak extending a wide temperature range. Due to the broad peak, Smolenskii *et al.*[1,2] initially interpreted that the ferroelectric phase transition was spread out over a wide temperature range, and they called it a diffuse phase transition. However, the x-ray and neutron diffraction studies showed that no structural change took place in a typical relaxor, $PbMg_{1/3}Nb_{2/3}O_3$ (PMN); the structure was cubic down to 5 K.[3] Burns and Dacol (Ref. 4) studied the temperature dependence of birefringence of PMN, and suggested that the polarized regions (several unit cell size) would be generated below about 620 K (Burns temperature; T_d). It has been also suggested that the direction of polarization vector of each region turns toward the eight equivalent $\langle 111 \rangle$ directions with the same probability and the polarization is canceled out as a whole. The results of x-ray and neutron diffractometry and of high resolution transmission electron microscopy suggested that the ferroelectric polar nanoregion (PNR) with the rhombohedral structure ($R3m$) should be formed in the paraelectric cubic matrix ($Pm3m$) below T_d.[5] Recently, Moriya *et al.*[6] have revealed the existence of broad anomaly in the heat capacity curves of PMN and $PbMg_{1/3}Ta_{2/3}O_3$ (PMT) by high precision adiabatic calorimetry, which should be due to the formation of PNR. The excess entropy was estimated as $\Delta S = 3.3$ J K^{-1} mol^{-1}, which is about 20% of the $R \ln 8$. Such a large entropy value indicates an order-disorder type of mechanism for the formation of PNR in PMN and PMT.

Almost all the studies on relaxors have been made on lead-based complex perovskite oxides, but nowadays lead-free compounds are highly required from the environmental point of view. Furthermore, the studies on a different type of compound should be important to clarify the mechanism of relaxors. $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ35) is a lead-free relaxor with perovskite structure, which has the same crystal structure with PMN ($Pm3m$) reported recently.[7,8] In this compound, Zr substitutes Ti in typical ferroelectric material $BaTiO_3$. With increasing the substitution of Zr for Ti, the three successive phase transitions of $BaTiO_3$ get closer to each other, and finally only one phase transition is observed for 10% substitution. By further substitution, the phase transition becomes ambiguous, and the compound of 35% substitution, $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ35), shows not a typical ferroelectric but relaxor behavior in the dielectric constant.[7,8] As the phase transition of $BaTiO_3$ is not of an order-disorder type, but of a displacive type,[9] the BTZ35 should be of a diplacive type. As mentioned above, the formation of PNR in PMN is of an order-disorder type, a comparison of the two compounds should be interesting; in general, the heat capacity anomaly is very small for a displacive phase transition, while that of an order-disorder type is very large. Recently, a report of heat capacity measurements by adiabatic calorimetry on BTZ35 has been published,[10] in which two broad anomalies are observed around 300 K and 150 K. The authors proposed that the two anomalies should be due to Burns temperature (T_d) and the peak in the dielectric constant, respectively. However, the accuracy and precision of the measurements seem not enough to confirm that. Such situation prompted the present authors to perform heat capacity measurements and to study thermodynamic properties of this lead-free compound, $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ35). From the results, the correlation between the relaxor behavior and the thermodynamic properties is discussed comparing with PMN.

II. EXPERIMENTAL

The sample of $BaTi_{0.65}Zr_{0.35}O_3$ was prepared by a conventional solid state reaction method. The starting materials of $BaCO_3$ (99.99%), TiO_2 (99.99%), and ZrO_2 (99.99%) were purchased from Rare Metallic Co., Ltd. (Japan). They were weighed out in the stoichiometric ratio and then mixed with ethanol in an alumina mortar for 2 h. The mixture was dried and heated in an electric furnace at 1473 K for 12 h. The calcined powders were ground with ethanol in an alumina mortar for 2 h and then pressed into a disk. The disk was heated at 1838 K for 20 h, and then cooled down to room temperature. The product was ground, and the powder was confirmed to be a single phase of perovskite without any impurity by x-ray diffraction analysis.

The dielectric constant measurements were carried out using a LCR meter (HP4284A) between 1 kHz and 1 MHz in the temperature range from 20 K to 420 K. For the measurements, the surface of the specimen was polished with SiC paper (No. 400, 800, 1200, and 2000), and then covered with gold by vapor deposition. The thickness and the surface area was 0.73 mm and 6.40 mm^2, respectively. The electrical leads were connected on the gold surface with platinum paste. The cooling and heating rates were about 0.01 K s^{-1}, which was small enough to neglect any thermal inhomogeneity in the specimen.

The heat capacity was measured using a homemade adiabatic calorimeter in the temperature range from 13 K to 420 K. The thermometer mounted on the calorimeter vessel was a platinum resistance thermometer (model S1059PJ5X6, Serial No. 525, Minco Products, Inc.) calibrated on the basis of the International Temperature Scale of 1990 (ITS-90). The volume and weight of calorimeter vessel was 1.930 cm^3 and 7.2376 g. The amount of the sample loaded into the calorimeter vessel was 5.2533 g (2.1151 $\times 10^{-2}$ mol). A small amount of helium gas (6.7 kPa at room temperature) was put into the calorimeter vessel for heat exchange. The accuracy of the heat capacity data was 0.1% and 0.2% at 100 K and above 300 K, respectively. The details of the apparatus and the method of measurements were described elsewhere.[6,11,12]

III. RESULTS AND DISCUSSION

The measured dielectric constant and molar heat capacity of BTZ35 are shown in Fig. 1. A large broad peak with a maximum around 200 K is clearly seen in the dielectric constant. On the low temperature side of the peak, a significant frequency dependence is observed, and the peak maximum shifts to higher temperature with increasing frequency from 1 kHz to 1 MHz, that is a typical characteristic of the relaxors.

On the other hand, no anomaly is seen in the heat capacity curve in Fig. 1. The heat capacity value increases with increasing temperature quite normally, and at room temperature, it is about 100 J K^{-1} mol^{-1}, which is properly compared to the classical limiting value of 125 J K^{-1} mol^{-1}; assuming the equipartition law, it should be $3nR$ ($n=5$, number of atoms in the formula unit; $R=$gas constant). The heat capacity curve can be analyzed more precisely by converting the heat capacity to the corresponding Debye characteristic temperature,[6] which is shown in Fig. 2, together with that of PMN. The heat capacity relates to the Debye characteristic temperature as

$$C = 3nR\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3 \int_0^{\Theta_{co}/T} \frac{x^4 e^x}{(e^x-1)^2} dx,$$

where C is the heat capacity and Θ_{D} is the Debye characteristic temperature.

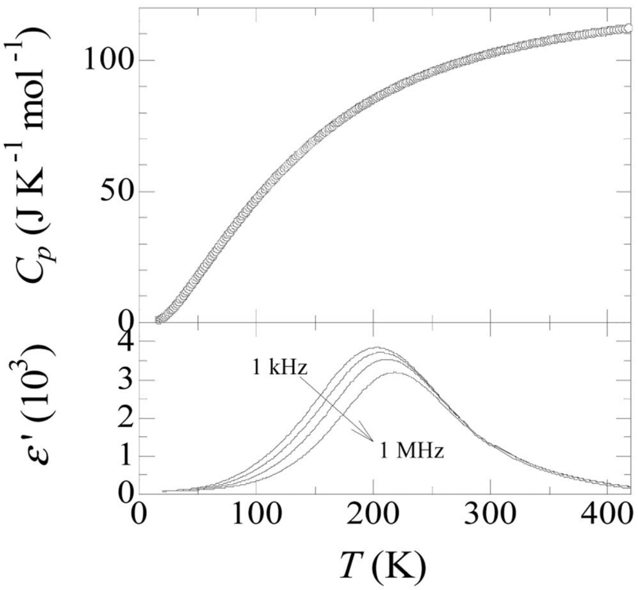

FIG. 1. Measured heat capacity C_p and real part of dielectric constant ε' of BTZ35.

As a whole, the Debye characteristic temperature of BTZ35 is larger than that of PMN. The reason of the difference should be mainly mass effect; the molar mass of BTZ35 m(BTZ) is 248.37 and that of PMN m(PMN) is 325.24, and thus the ratio of the Debye characteristic temperature should be $\Theta_{\mathrm{D}}(\mathrm{BTZ35})/\Theta_{\mathrm{D}}(\mathrm{PMN})=[m(\mathrm{PMN})/m(\mathrm{BTZ})]^{1/2}=1.11$, in which the same force constant is assumed for both compound. The difference in Fig. 2 is thus reasonable. A deep minimum is seen at about 10 K and 30 K, for PMN and

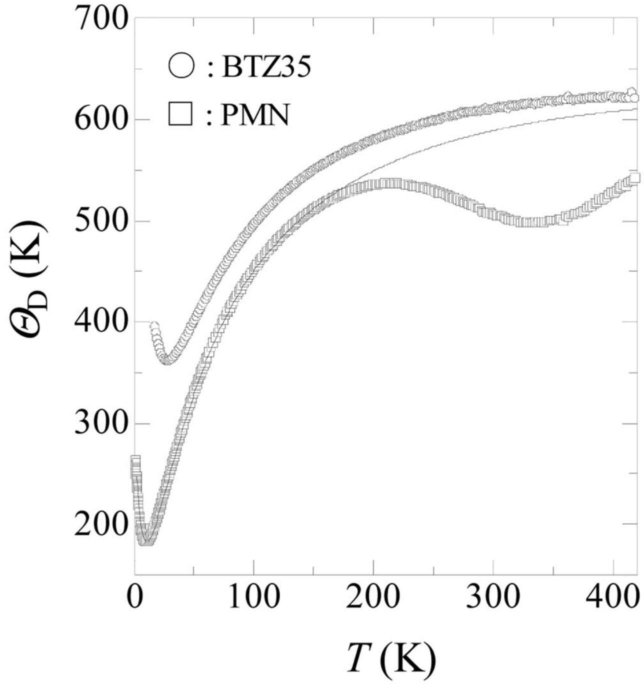

FIG. 2. Debye temperature of BTZ35 (circles) and PMN (squares) calculated from the measured heat capacity assuming 3 degrees of freedom per each atom.

BTZ35, respectively. That is commonly observed in most crystals, due to high density of states in the low frequency region of the lattice vibration spectrum.[13,14]

In the higher temperature region, a very broad hollow with a minimum at 320 K is seen in the curve of PMN, where the solid line is the normal baseline.[6] That should be the excess heat capacity due to the formation of ferroelectric polar nanoregion (PNR), corresponding to the broad peak in the dielectric constant. On the other hand, no anomaly is seen in the curve of BTZ35, which means no heat capacity anomaly is in this compound. Thus it is now concluded that no heat capacity anomaly is in BTZ35, in the present limit of experimental error.

The present result of BTZ35 is not in agreement with the recent report by Gorev *et al.*,[10] in which the heat capacity of two samples, BTZ35 and BTZ25, was given; the former showed two anomalies around 250–350 K and 150–200 K, and the latter showed one anomaly around 150–320 K in the heat capacity curves. At 350 K, the heat capacity value of BTZ35 is about 113 J K^{-1} mol^{-1}, while that of BTZ25 is 105 J K^{-1} mol^{-1}. Such big differences should be explained in terms of lattice vibration spectrum. In our experiments for different component samples,[15] a heat capacity anomaly was observed between $x=0.1$ and 0.3 in $BaTi_{1-x}Zr_xO_3$; in this compositional region, the anomaly decreased with increasing x, and finally no anomaly was observed in the sample of $x=0.35$. On the other hand, the relaxor behavior was not observed in the range of $x=0.1-0.3$, but observed for the sample of $x=0.35$.

It has been reported that the heat capacity anomaly is caused by the formation of PNR in PMN.[6] The present result that no heat capacity anomaly is in BTZ35 implies a different mechanism from that of PMN. It has been reported that the PNR growth mechanism is of order-disorder type phase transition from the result of the entropy value.[6] The observed entropy value for PMN is about 20% of the perfect ordering, and agrees with the fraction of PNR growth content reported from the neutron powder diffraction by Uesu *et al.*[16] On the other hand, BTZ35 is a solid solution compound based on $BaTiO_3$, in which the ferroelectric phase transition is of displacive type.[9] If the order-disorder mechanism is induced and some disorder is frozen in the low temperature region, heat capacity anomaly should be observed in BTZ35. On the other hand, it is well known that the entropy of a displasive type phase transition is much smaller than that of the order-disorder type phase transition.[6] Thus the heat capacity anomaly should be negligibly small when the displacive phase transition is frozen. Therefore, the relaxor behavior of BTZ35 would be attributed to the freezing of displacive-type phase transition.

The synchrotron radiation powder x-ray diffraction of BTZ35 indicates that no anharmonic feature is observed on the vibration of Ba^{2+} in the *A* site and very weak anharmonicity is detected for Ti^{4+} in the *B* site,[17] which is similar to displacive-type ferroelectric $BaTiO_3$. The study of Raman spectroscopy in BTZ35 also showed only the distortion of BO_6 octahedra around the *B* site was observable.[18] It is considered that the distortion around the *B* site plays an important role of the relaxor mechanism contrary to PMN in which the positional disorder of *A* site cation Pb^{2+} is observed.[19] The study of the high pressure Raman spectroscopy shows that the change of spectrum of BTZ35 is different from that of PMN with having a relaxor-specific spectral signature[20] and is similar to the normal ferroelectric $BaTiO_3$.[21] These also indicate that the absence of heat capacity anomaly in BTZ35 is attributed to the freezing of displacive-type phase transition. The mechanism is different from that of PMN in which the order-disorder mechanism around Pb^{2+} plays an important role.[19]

On the other hand, the recent x-ray diffraction measurements of BTZ35 performed before and after poling below δ 9.6 kV cm^{-1} shows that the splitting of 200, 222, 400 diffraction peaks are not observed,[22] which is contrary to the long-range ferroelectric ordering in PMN induced by the external electric field.[23] It also implies a deferent mechanism of the relaxor behavior of the two compounds.

IV. CONCLUSION

The relaxor ferroelectric compound, $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ35), was synthesized and the physicothermal properties were measured. The dielectric constant measured between 1 kHz and 1 MHz showed a large, broad and frequency-dependent peak extending from about 100 K to about 400 K, which is a typical characteristic of relaxors. On the other hand, no anomaly was detected in the heat capacity measured by adiabatic calorimetry between 13 K and 420 K. The results were compared with those of our previous study on the typical relaxor compound, $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), in which a broad heat capacity anomaly was observed in the same temperature range as that of the broad peak in the dielectric constant. The results of PMN showed order-disorder type of mechanism for formation of the ferroelectric polar nanoreagion (PNR) in the crystal. In the case of BTZ35, the mechanism should not be of order-disorder type, but of displacive type, because no heat capacity anomaly was detected. Further detailed study about PNR is required for this type of relaxors, comparing to the ordinary typical relaxors.

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