Vol 15 No 7, July 2006
1009-1963/2006/15(07)/1611-04

Chinese Physics

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Diffuse dielectric anomaly of $(Na_{0.5}K_{0.5}Bi)_{0.5}TiO_3$ crystal at high temperature*

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(Received 23 February 2006; revised manuscript received 8 March 2006)

This paper investigates the dielectric properties of $(Na_{0.5}K_{0.5}Bi)_{0.5}TiO_3$ crystal at intermediate frequencies (1kHz$\leq f \leq$1MHz) in the temperature range of 30–560 ℃. A pronounced high-temperature diffuse dielectric anomaly has been observed. This dielectric anomaly is shown to arise from a Debye-like dielectric dispersion that slows down following an Arrhenius law. The activation energy E_τ obtained in the fitting process is about 0.69eV. It proposes that the dielectric peak measured at low frequency above 400 ℃ is not related to the phase transition but to a space-charge relaxation.

Keywords: dielectric properties, Debye relaxation, space-charge
PACC: 7740, 7700, 7780

1. Introduction

Sodium bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) is an A-site substituted perovskite compound exhibiting strong ferroelectric properties at room temperature. Since the discovery of NBT, many of its characteristics, particularly piezoelectric properties and phase transitions, have been studied.[1−4] The findings of these investigations are partly in disagreement, and there remains considerable controversy concerning the phase structure, order–disorder and some other correlative properties.

$(Na_{1-x}K_xBi)_{0.5}TiO_3$ system, which belongs to the NBT-based material, have been reported to have a morphotropic phase boundary (MPB) in the composition range $0.1 < x < 0.2$.[5] The studies of $(Na_{1-x}K_xBi)_{0.5}TiO_3$ system were most concentrated on the ceramic form,[5,6] therefore, few characteristics of $(Na_{1-x}K_xBi)_{0.5}TiO_3$ single crystals were reported because of some difficulties in the crystal growing process.

In this work, the dielectric properties of $(Na_{0.5}K_{0.5}Bi)_{0.5}TiO_3$ (NKBT) crystal have been investigated. Focusing mainly on the temperature-dependent feature of the dielectric relaxation, we have characterized the diffuse dielectric anomaly observed in this crystal by using the Debye relaxation model.

2. Experimental procedures

The NKBT crystal was fabricated by using conventional high temperature flux method. High purity chemical powders of Bi_2O_3, TiO_2, Na_2CO_3 and K_2CO_3 were used as raw materials, with Bi_2O_3, Na_2CO_3 and K_2CO_3 as self-flux. The dimensions of NKBT crystal sample were set to 5mm×5mm×0.6 mm, and the (001) direction was chosen. The dielectric properties were measured at intermediate frequencies (1 kHz$\leq f \leq$1 MHz) by Agilent 4294 A impedance analyser in the temperature range of 30–560 ℃ with the heating rate of 2 ℃/min.

3. Results and discussion

Figures 1 and 2 show the temperature dependence of dielectric constant and dielectric loss in NKBT crystal at various measuring frequencies. In these figures, the dielectric curves exhibit intense frequency dependence behaviour. The dielectric curves show only one peak at about 300 ℃ by using high frequencies ($f \geq$100 kHz), however, at frequencies below 100kHz, a diffuse second maximum can be observed in the temperature range of 400–500 ℃. Similar dielectric behaviours have been reported in NBT crystal.[2] As the sequence of phase transition for NBT from room

*Project supported by the National Nature Science Foundation of China (Grant No 50572056).
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temperature rhombohedral (below 255 ℃) to one of tetragonal (400–500℃) and then cubic (above 540 ℃), had been established,[7] the second dielectric peak above 500 ℃ in pure NBT crystal was ever thought to be an implication of tetragonal to cubic phase transition.

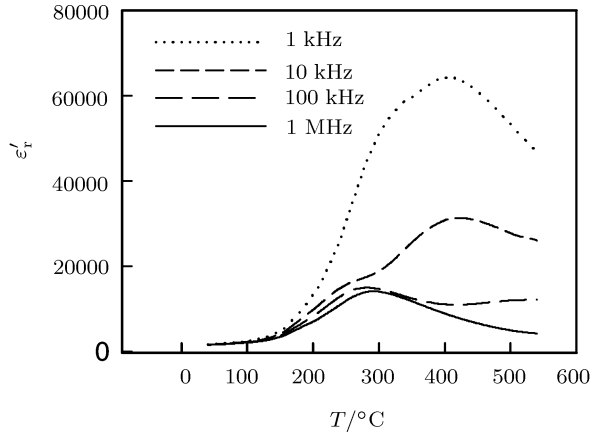


Fig.1. The temperature dependence of dielectric constant of NKBT crystal at various measuring frequencies.

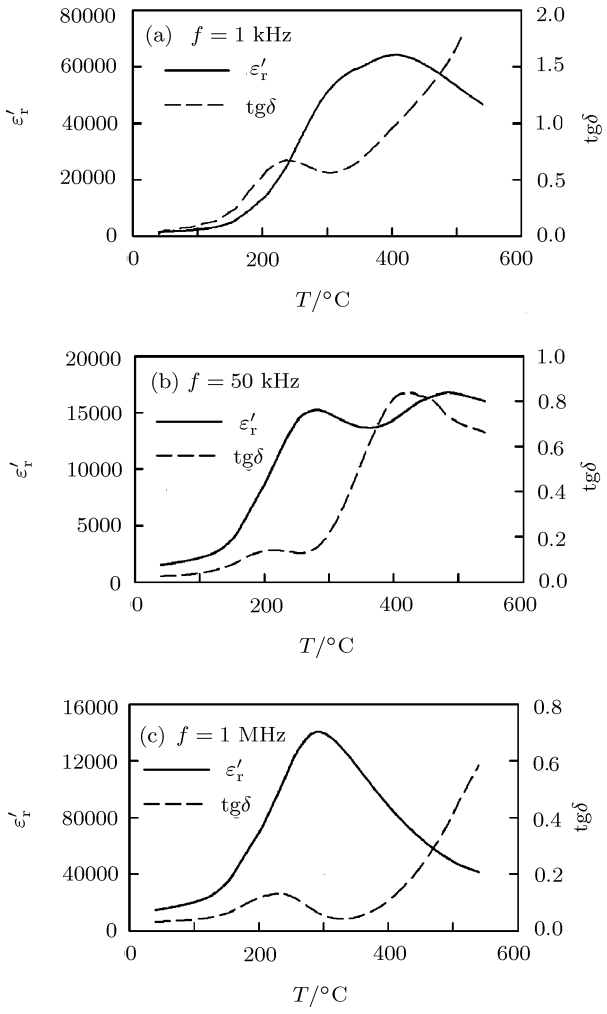


Fig.2. The temperature dependence of dielectric loss of NKBT crystal at selected measuring frequencies.

But for NKBT, most of the previous studies were mainly concentrated on ceramic form, and the second dielectric peak had not been found in this composition. According to Elkechai's results,[5] the dielectric peak at about 340 ℃ in NKBT ceramic had been confirmed to result from a tetragonal–cubic phase transition. It seems that no more phase transition can be related to the present founding of the second dielectric peak at higher temperature. Thus, in this study, the Curie temperature of NKBT crystal should be about 300 ℃ according to the high frequency results, and another contribution should be purposed to explain the second dielectric peak.

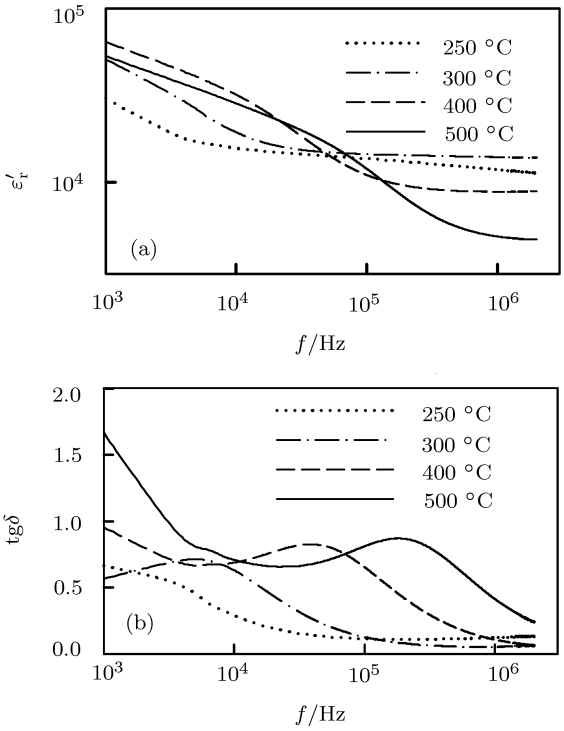


Fig.3. The frequency dependence of dielectric constant (a) and dielectric loss (b) at various temperatures.

In our opinion, although the diffuse dielectric anomalies in NBT-based crystal look like the behaviour of the diffuse phase transition, it is different in origin from the dielectric anomaly by the phase transition observed in the relaxor such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$.[8,9] Figure 3 shows the frequency dependence of dielectric constant and dielectric loss at various temperatures. Above the temperature 300 ℃, a dielectric loss peak can be observed and the peak shifts to higher frequencies as the temperature is increased. This is typical of a thermally activated Debye relaxation in the fre-

quency space.

To get a more quantitative insight in these results, we carried out a data analysis in the frequency space. The real and the imaginary part of dielectric constants can be described by the Debye relaxation formula

$$\varepsilon^* = \varepsilon' - \mathrm{j}\,\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_\mathrm{s} - \varepsilon_\infty}{1 + \mathrm{j}\,\varpi\tau}. \qquad (1)$$

Concerning the Debye relaxation alone, we know that the adjustable parameters are the relaxation step $\Delta\varepsilon = \varepsilon_\mathrm{S} - \varepsilon_\infty$ and the relaxation time τ. Thus, all the fits are reliable by using the nearly monodispersive Debye law. Figure 4 shows the fitted Cole–Cole plot based on the dielectric data for temperature 400 ℃. The Cole–Cole plot is best fitted with the experimental data in most frequency range. The deviation of experimental data from the theoretic result at low frequencies (f < 30 kHz) can be explained by the influence of increased conductivity in high temperature range.

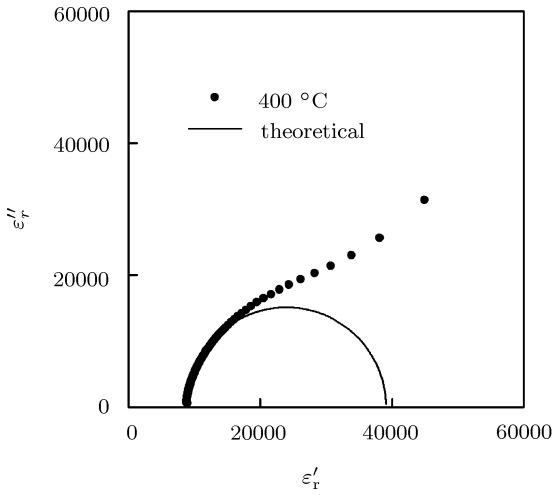


Fig.4. The fitted Cole–Cole plot based on the dielectric data for temperature 400 ℃.

The variation of the relaxation time was mainly concerned according to the previous studies,[10,11] which may be described by a thermally activated Arrhenius law,

$$\tau = \tau_0 \exp(E_\tau / k_\mathrm{B} T), \qquad (2)$$

where τ_0 is the relaxation time at infinite temperature, E_τ is the activation energy for the dielectric relaxation, k_B is the Boltzmann constant, and T is the absolute temperature. Figure 5 shows the linear relationship between the log scale of relaxation time and the inverse temperature. The activation energy E_τ obtained in the fitting process is about 0.69eV for this NKBT crystal in the temperature range of 300–560 ℃.

For NBT-based crystals, Jones et al had proved that Bi^{3+} may show a 22%–35% valency deficiency from its ideal value of 3.0, which can give rise to a displacement of the cation in order to satisfy its own stereochemical preference. Moreover, we propose that the oxygen vacancies may be easier to be engendered in these crystals as the large quantity of valency deficiency for Bi^{3+}. As space-charge dipoles are strongly influenced by lattice defects, the diffuse dielectric anomaly in NKBT crystal has to be related to the space-charge relaxation.[10–12] Therefore, the relaxing thermal motion of increased lattice defects especially oxygen vacancies is suggested to be the origin of the diffuse dielectric anomaly at high temperature, and the Curie temperature of NKBT crystal is determined to be about 300 ℃ according to the high frequency results.

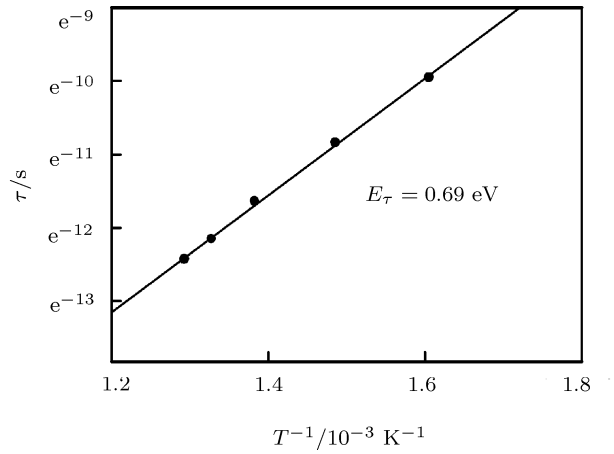


Fig.5. The relationship between the log scale of relaxation time and the inverse temperature.

4. Conclusion

The dielectric properties of $(Na_{0.5}K_{0.5}Bi)_{0.5}TiO_3$ crystal have been investigated at intermediate frequencies (1 kHz≤ f ≤1 MHz) in the temperature range of 30–560 ℃. A pronounced high-temperature diffuse dielectric anomaly has been observed. This dielectric anomaly is shown to arise from a Debye-like dielectric dispersion that slows down following an Arrhenius law. The activation energy E_τ obtained in the fitting process is about 0.69 eV. We propose that the dielectric peak measured at low frequency above 300 ℃ is not related to the phase transition but to a space-charge relaxation.

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