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Pseudo-relaxor behavior in $Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$ ceramics

Pengfei Liang, Yanyan Li, Xiaolian Chao, Zupei Yang *

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, Shaanxi, PR China

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ABSTRACT

High temperature dielectric behaviors have been explored in $Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$ ceramics. The broad dielectric peaks could be fine fitted by the modified Curie–Weiss law and the Vogel–Fulcher relationship. Based on the universal dielectric response law and Maxwell–Wagner relaxation, the occurrence of the polarization mechanism transition from the grain boundary response to the electrode one with temperature is clearly evidenced in the low frequency range. It is likely to propose that the apparent relaxor-like behavior is related to an extrinsic effect instead of ferroelectricity.

1. Introduction

$Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$ (NBCTO) is isostructural with $CaCu_3Ti_4O_{12}$ (CCTO) and retains centrosymmetric and cubic symmetry (space group $Im\overline{3}$) down to 4 K [1]. The giant permittivity ε_r ($\sim$11,000) and relatively low dielectric loss were observed at near room temperature for NBCTO ceramics from radio frequency by Yang et al. [2–4]. According to the impedance spectroscopy, it has been proved that NBCTO ceramics consist of semiconducting grains and insulating grain boundaries. The giant dielectric response could be explained by an internal barrier layer capacitance (IBLC) effect. In addition to the giant dielectric constant owing to the extrinsic effect, NBCTO ceramics also exhibit relatively high bulk intrinsic dielectric constant (about 260) at 10 K [1,3,4]. Based on the low-temperature measurement and infrared spectroscopy, the high intrinsic dielectric constant is closely linked to the occurrence of an incipient ferroelectricity in NBCTO [1,4]. Concurrently, for CCTO ceramics, Lunkenheimer et al. have revealed that the temperature dependence of dielectric constant in the infrared region resembles the soft-phonon behavior that is typical for incipient ferroelectric, not for ferroelectrics [5,6].

Besides the incipient ferroelectricity based on the bulk intrinsic response, high-temperature dielectric peaks with frequency dispersion was also observed in CCTO ceramics. Some previous works attributed this dielectric anomaly to a characteristic of the relaxor ferroelectric on the basis of the intrinsic effect [7–9]. However, this interpretation is in contradiction with previous results [2–4] and has been challenged by the fact that the occurrence of structural phase transition were not observed for CCTO in a wide temperature range [10–14]. Reversely, considering the extrinsic effect, the relaxor-like anomaly is attributed to the combined effect of the dipolar and MW relaxation [11]. In addition, this dielectric behavior is proposed to be an artifact induced mainly by a non-ohmic sample-electrode contact impedance [10,13,14]. Therefore, there exist some discrepancies between several models in the available literatures and a number of questions need to be addressed. For example, is the high temperature dielectric anomaly an extrinsic or an intrinsic effect? Could it be called a diffuse transition? Furthermore, to the best of our knowledge, the high temperature dielectric behaviors in NBCTO have not been reported.

In this paper, we conducted a systematical study on the high temperature dielectric anomaly of NBCTO ceramics. Based on the extrinsic and intrinsic effect, the relevant underlying mechanisms resulting in the high temperature dielectric anomaly were discussed in detail.

2. Experimental procedure

$Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$ (NBCTO) polycrystalline bulk samples were prepared by solid-state reaction [2]. Stoichiometric amounts of Bi_2O_3 (99.9%), TiO_2 (99.99%), Na_2CO_3 (99.8%), and CuO (99%) reagents were mixed by ball milling in alcohol for 10 h using agate balls. After drying, the mixed powders were calcined at 850 °C for 10 h in air and then pressed into disk pellets with a diameter of 15 mm under 100 MPa pressure, finally sintered at 1000 °C for 7.5 h

* Corresponding author. Tel.: +86 29 81530 718; fax: +86 29 81530 702.
E-mail address: yangzp@snnu.edu.cn (Z. Yang).

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in air. After being polished and pasted by silver paste on both sides, the ceramic samples were then treated at 840 °C for 30 min to form the electrodes for electrical measurements. Dielectric dispersion and complex impedance were measured by Agilent 4294A (Palo Alto, CA) impedance analyzer in the frequency range of 100 Hz–1 MHz and over the temperature range from 30 °C to 360 °C. Temperature dependences of dielectric constant were measured on the LCR meter (Agilent E4980A) from ambient temperature to 500 °C at different frequencies.

3. Results and discussion

Fig. 1(a)displays the temperature dependences of dielectric constant in NBCTO ceramics at various frequencies. A series of dielectric constant peaks in the temperature range of 100–400 °C shift to higher temperature and decrease in amplitude with increasing frequencies. Further increasing the temperature after 400 °C, a monotonous increase trend in dielectric constant is observed irrespective of the measurement frequency, which is attributed to the space charge polarization at higher temperatures [15,16]. We primarily focus on these observed broad dielectric peaks. At first glance, it seems that the NBCTO ceramic exhibits more of the characteristic behaviors of a ferroelectric relaxor, which is usually characterized by a diffuse phase transition, and a strong relaxational dispersion in dielectric constant and dielectric loss. As for relaxor ferroelectrics, the dielectric maximum is defined as a dynamic freezing or glasslike transition temperature, T_m. The strong frequency dispersive dielectric constant on the low-temperature side of T_m is correlated with the slowing down of dipolar fluctuations within the polar nanoclusters [8].

The relaxation behavior in relaxor ferroelectrics was widely interpreted on the basis of polar nanoregions (PNRs) which are induced by the local distortion of the crystal structure [17–21]. Uchino and Nomura [22] have suggested a modified Curie–Weiss law to describe the dielectric constant of a relaxor ferroelectric in the paraelectric phase, which is expressed as:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)^{\gamma}}{C} \quad (1)$$

where ε_m is the maximum value of dielectric constant, ε is the dielectric constant at temperature T,T_m is the temperature at the peak of the dielectric constant, C is the Curie constant, and γ is the diffusion coefficient ranging from 1 (a normal ferroelectric) to 2 (an ideal relaxor ferroelectric). According to Eq. (1), the plot of log $(1/\varepsilon-1/\varepsilon_m)$ as a function of $\log(T-T_m)$ for NBCTO ceramics at 1 kHz in the temperature range of ~250–350 °C is shown in Fig. 1(b). A linear relationship is obtained for NBCTO ceramic. The slope of the fitting curves is used to determine the γ value, which is 1.76. Furthermore, it is well known that the frequency dependence of the T_m in the relaxor ferroelectrics can be described by the Vogel–Fulcher (VF) law [23,24],

$$f=f_0\exp\left[-\frac{E_a}{K_B}(T_m-T_{VF})\right] \quad (2)$$

where f is the measurement frequency, f_0 is the pre-exponential factor, E_a is the activation energy describing the relaxation process, T_m is the absolute temperature at which the dielectric permittivity reaches the maximum, T_{VF} is the freezing temperature, and K_B is the Boltzmann constant. In the relaxor ferroelectrics, T_{VF} is believed to be a freezing temperature whereupon the dynamic behavior induced by the thermal agitation is no longer sufficient to reorient the polar nanodomains. Fig. 1(c) displays the plot of f as a function of T_m. It can be seen that the experimental data is well fitted with the VF equation. The parameters obtained by fitting are $f_0 = 2.46\times10^7$ Hz, $E_a = 0.20$ eV, and $T_{VF} = 290.07$ K, which are physically reasonable. These results indicated that NBCTO ceramic belongs to the relaxor ferroelectric.

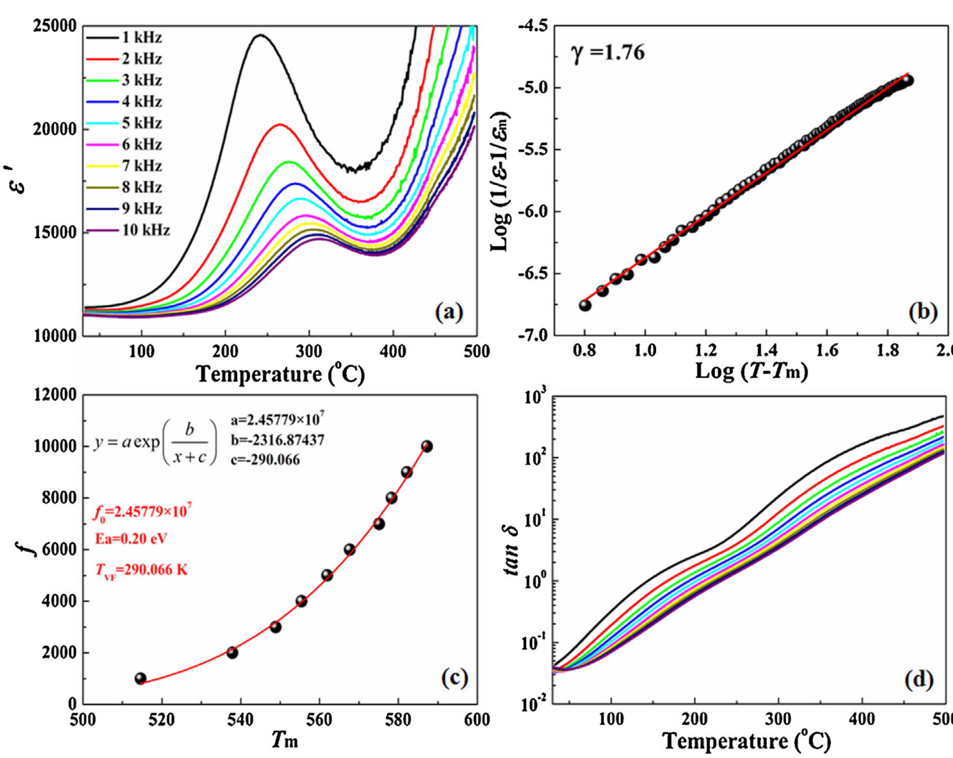

Fig. 1. (a) Temperature dependences of dielectric constant of NBCTO ceramics at various frequencies, (b) $\log(1/\varepsilon-1/\varepsilon_m)$ as a function of $\log(T-T_m)$ for NBCTO ceramics at 1 kHz in the temperature range of ~250–350 °C (symbols: experimental data; solid line: fitting to the modified Curie–Weiss law), (c) the real permittivity maxima T_m as a function of frequency (points) and the VF fitting curve and (d) temperature dependences of dielectric loss of NBCTO ceramics at various frequencies.