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High-temperature dielectric properties of $TbFeO_3$ ceramics

Da Zhang, Qiuju Li*, Chunchang Wang, Nan Zhang, Haibo Li

Laboratory of Dielectric Functional Materials, School of Physics and Material Science, Anhui University, Hefei 230039, China

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Abstract

$TbFeO_3$ ceramics were prepared via conventional solid-state reaction route. By means of the complex dielectric permittivity, electric modulus, and impedance analysis, the high-temperature dielectric properties of $TbFeO_3$ were investigated in the temperature range from 300 to 1073 K and frequency range of 10^2–10^7 Hz. Rich dielectric phenomena, including three dielectric responses (R1–R3), a relaxor-like dielectric anomaly and negative capacitance were found in the order of ascending temperature. The low-temperature relaxation (R1) near room temperature is caused by the surface-layer effect. The high-temperature relaxations R2 and R3 were argued to be related to the dipolar and Maxwell–Wagner relaxation, The anomaly is confirmed to be caused by the negative capacitance effect.

Keywords: Ceramics; Dielectric anomaly; Maxwell–Wagner relaxation; Negative capacitance

1. Introduction

In the trend towards miniaturization, colossal dielectric constant (CDC) materials are going to play an important role. As a typical representative of CDC materials, $CaCu_3Ti_4O_{12}$ (CCTO) had been widely investigated during the past 15 years [1–5]. Apart form the stunning CDC behavior in the temperature range below room temperature (RT), CCTO also shows a relaxor-like behavior in the temperature range above RT. Numerous experimental work indicated that the high-temperature relaxor-like dielectric anomaly is unrelated to ferroelectric transition and is almost a common dielectric phenomenon for oxides [6–10]. This anomaly is now called pseudo-relaxor behavior [11]. Li and coauthors attributed the behavior to be an artificial phenomenon resulting from negative capacitance as the investigated sample is highly leaky at high temperatures [12]. Our recent work pointed out that the anomaly is composed of two close relaxations with the low-temperature one being the dipolar relaxation and the high-temperature one being the MW relaxation. Both relaxations are related to the hopping motion of oxygen vacancies [6,7].

Recently, investigation on the low-temperature (100–300 K) dielectric properties of $TbFeO_3$ (TFO) revealed that the sample shows CDC behavior similar to that found in CCTO [13]. It is expected that TFO might exhibit relaxor-like behavior at high temperatures. In the present work, the dielectric properties of TFO in the temperature range from 300 to 1073 K were investigated. Three dielectric relaxations and an dielectric anomaly along with negative capacitance effect were observed. The mechanisms of these relaxation and anomaly were discussed.

2. Experimental

TFO ceramic samples were prepared by the conventional solid state reaction method using high purity (4 N grade) Tb_4O_7 and Fe_2O_3 powders as described in our previous paper [13]. Dielectric properties were measured using a Wayne Kerr 6500B precise impedance analyzer. Annealing treatments were performed in flowing (200 ml/min) oxygen and nitrogen (both with purity > 99.999%). Electrodes were made by printing silver paste on both sides of the disk-type samples and then fired at 1073 K for 2 h in order to remove the polymeric component.

*Corresponding author. Tel.: +86 551 63861902; fax: +86 551 65846849.
E-mail address: liqj@mail.ustc.edu.cn (Q. Li).

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3. Results and discussion

Fig. 1(a) and (b) shows, respectively, the typical temperature dependence of dielectric constant $\varepsilon'(T)$ and dielectric loss tangent, $\tan\delta(T)$($\tan\delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary part of the complex permittivity ε^*) for $TbFeO_3$. From Fig. 1(a), we can see that $\varepsilon'(T)$ exhibits an obvious stepwise increase around 500 K and a pronounced relaxor-like dielectric anomaly around 800 K followed by negative capacitance effect. In the $\tan\delta(T)$ curves [see Fig. 1(b)], a set of thermally activated relaxation peaks, humps, and sharp peaks correspond to the stepwise increase, anomaly, and negative capacitance, respectively, were observed. When the temperature rises higher than 500 K, the $\tan\delta(T)$ curve shows lager value and increases with increasing temperature causing remarkable background. This implies that the conductivity is notable in this temperature range. In order to get more information of the dielectric phenomena, we applied the dielectric function of electric modulus M^*, which is defined as $M^* = 1/\varepsilon^*$ and considered as "good dielectric function" that can provide information about relaxation in the absence of a well-defined peak in $\tan\delta(T)$[14,15].

Fig. 2 shows the temperature dependence of the imaginary part of electric modulus for TFO at various frequencies. We

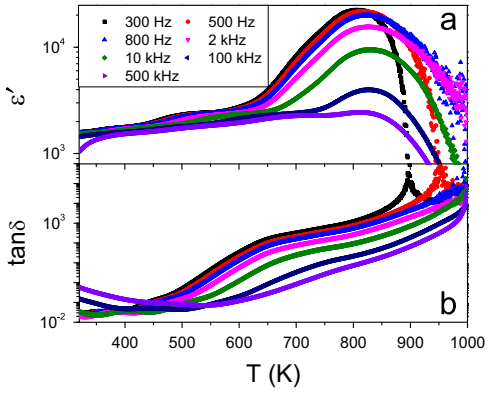

Fig. 1. Temperature dependence of ε' (a) and $\tan\delta$ (b) of TFO measured at various frequencies.

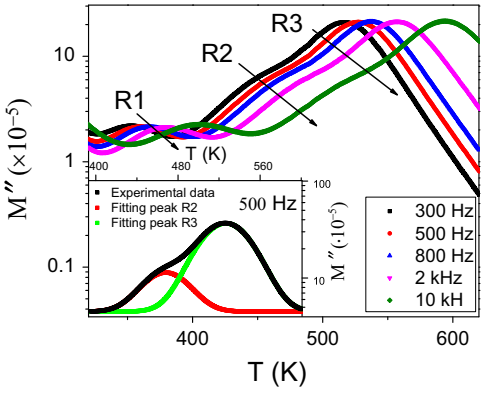

Fig. 2. Temperature dependence of $M''(T)$ measured at various frequencies. The inset shows the fitting result of R2 and R3 peaks recorded at 500 Hz.

can clearly see that the $M''(T)$ curves show two distinct sets of relaxation peaks and a set of humps between them. This finding indicates that there are three relaxations in TFO in the tested temperature range. For simplicity, these relaxations were designed as R1, R2, and R3 in the order of ascending temperature. To calculated the relaxation parameters, the accurate peak position is need. Since the position of the hump is strongly affected by the peak of R3, two Debye peaks were applied to fit the hump and the high-temperature peak in order to deduce the accurate positions of R2 and R3. As an illustration, the inset of Fig. 2 displays the fitting result to the experimental data recorded at 500 Hz. Based on the fitting result, the peak positions of R2 and R3 can be obtained.

Fig. 3 presents the measuring frequency f versus the reciprocal of the peak temperature $1000/T_p$. The obtained data for the three relaxations fall on straight lines in the half-logarithmic scale indicating that these relaxations follow the Arrhenius law:

$$f = f_0 \exp(E_a/k_B T_p) \quad (1)$$

where f_0 is the preexponential factor, E_a is the activation energy for relaxation, k_B is the Boltzmann constant. The values of E_a and f_0 were calculated to be 0.59 eV and 6.69×10^{13} Hz for R1, 1.08 eV and 2.81×10^{14} Hz for R2, and 1.19 eV and 1.1×10^{14} Hz for R3. We note the relaxation parameters ($E_a = 0.59$ eV and $f_0 = 6.69 \times 10^{13}$ Hz) of R1 are the same as those ($E_a = 0.59$ eV and $f_0 = 6.78 \times 10^{13}$ Hz) of the relaxation around room temperature in our previous report [13]. This relaxation was clarified to be a Maxwell–Wagner relaxation caused by the surface-layer effect and will not be further discussed in the following part.

We now turn our attention to R2 and R3. It is well known that oxygen vacancies as native point defects are unavoidable in perovskite oxides. The activation energy around 1.0 eV is typical value for relaxation related to the hopping motion of oxygen vacancies in various perovskites [16–20]. To identify the relationship between oxygen vacancies and the observed relaxations, the sample of TFO was treated by the following processes: (1) annealing in O_2 at 1073 K for 2 h to decrease the oxygen vacancies content; (2) annealing in N_2 at 1073 K for 2 h to increase the oxygen vacancies content. Fig. 4 displays the comparison of the temperature dependence of electric modulus recorded at 10 kHz before and after being annealed in

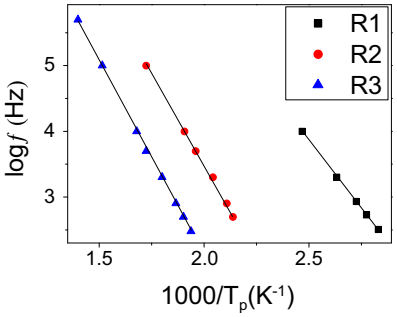

Fig. 3. The Arrhenius plots of the three relaxations.