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Evolvement of dielectric relaxation of barium stannate titanate ceramics

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Abstract

In barium stannate titanate (BTS) ceramics, low frequency dielectric relaxation was observed at temperatures far below room temperature. Curve fitting of the temperature dependence of dielectric constant was done according to empirical equations. Several models were employed to study the thermal activated relaxation. The inflexions of frequency difference of dielectric permittivity were compared with the phase transition region for the various compositions of barium stannate titanate ceramics.

Keywords: Dielectric relaxation; Barium stannate titanate

1. Introduction

After the pioneer work of Smolensky in 1970 [1], relaxor ferroelectrics (RFE) has attracted much attention because of its potential applications, such as high capacitance capacitor, hysteresis free actuator and high performance sensor. Setter [2,3] proved that the B-site disorder should contribute to the diffused phase transition behavior of relaxor ferroelectric ceramic lead scandium titanate (PST). Yao et al. [4] assumed that the transition of macro domain to micro domain dominates the dielectric behavior of RFE ceramic lanthanum-doped lead zirconate titanate (PLZT). Burns and Dacol [5] and Viehland et al. [6] treated RFE as a glassy polarization phase. Cheng [7–10] put forward the "new glass model" and the breathing model of polar region for RFE. Cross [11,12] proposed the superparaelectric theory after reviewing the experimental and theoretical history of RFE.

Barium stannate titanate (BTS) is a solid solution system of barium titanate and barium stannate. This material is one of the earliest prototypes of diffused phase transition study [1]. Similar to barium zirconate titanate and barium hafnate titanate [13], the dielectric behavior of BTS changes from normal ferroelectrics to RFE with increasing tin substitution. Although the present authors have explained the relaxor behavior of BTS ceramics under the supposition of polar nanoregions [14], the variation details of the evolvement is not known yet. In the present study, dielectric properties of several compositions of BTS ceramics were studied. Different kinds of mathematical approaches were employed to evaluate the evolvement of relaxor behavior.

2. Experiment

Ceramics BTS20 ($Ba(Sn_{0.20}Ti_{0.80})O_3$), BTS225 ($Ba(Sn_{0.225}Ti_{0.775})O_3$), BTS25 ($Ba(Sn_{0.25}Ti_{0.75})O_3$), BTS275 ($Ba(Sn_{0.275}Ti_{0.725})O_3$) and BTS30 ($Ba(Sn_{0.30}Ti_{0.70})O_3$) were prepared by solid state reaction. The size of the sample pallet is 10 mm in diameter and about 1 mm in thickness. The temperature dependence of dielectric constant was measured via a computer controlled system, including a high precision LCR meter (HP 4284A, Hewlett-Packard Inc.) and an environmental box with its temperature range form liquid nitrogen to 250 °C.

3. Results and discussion

3.1. Temperature dependence of dielectric constant

The dielectric constants with temperature of BTS20, BTS225, BTS25, BTS275 and BTS30 samples were shown

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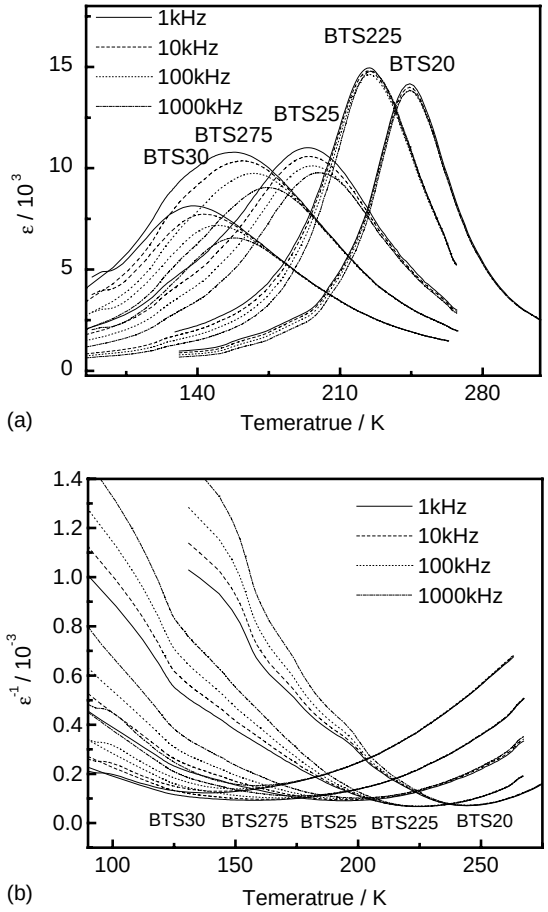

Fig. 1. Temperature dependence of dielectric constant (a) and reciprocal dielectric constant (b) of barium stannate titanate ceramics.

in Fig. 1a. With the increasing tin composition, the dielectric peaks of these samples shift to lower temperature along with increasing diffuseness, and the temperature differences among the peaks of different frequency become larger. In other words, the relaxor behavior is stronger for the higher tin substitution samples. As indicated in Fig. 1, BTS20 is likely a ferroelectrics with diffused phase transition, and BTS275 and BTS30 are RFEs, and others are mediacies between the above two ones. Depicted by Fig. 1b, when temperature is above that of dielectric maxima, the relationships between reciprocal dielectric constant and temperature deviate from linear relationship, which is predicted by Curie–Weiss law for normal ferroelectric ceramics.

3.2. Empirical equations

To evaluate the evolvement of relaxor behavior of BTS ceramics, several empirical laws were employed. The simplest one is the temperature span of dielectric peaks between the lowest and highest frequencies. Here, we check the value of ΔT_m:

$$\Delta T_m = T_{m\,(1\,MHz)} - T_{m\,(1\,kHz)} \quad (1)$$

where T_m is the temperature of dielectric maximum.

Table 1
Results of empirical equations

	Sample				
	BTS20	BTS225	BTS25	BTS275	BTS30
ΔT_m (K)	0.0	1.0	5.8	17.6	18.5
δ (K^2)	23.1	22.7	32.9	38.4	41.9
γ	1.86	2.02	2.13	2.24	1.99
C' (K^γ)	7×10^6	2×10^7	4×10^7	1×10^8	3×10^7

Smolensky [1] had proposed a quadratic relationship of temperature dependence of the dielectric constant above T_m for RFE:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m}\left(1 + \frac{(T - T_m)^2}{2\delta^2}\right) \quad (2)$$

where parameter δ is a measure of diffuseness, and ε and ε_m are the dielectric constant and its maximum, respectively.

Martirena and Burfoot [15] suggested the variable power law to describe the temperature dependence of ε. The law is rewritten to:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_m)^\gamma}{C'} \quad (3)$$

where C' and γ are constants.

We have tried data fitting with the above three empirical equations, and the results were listed in Table 1. The value of ΔT_m is zero for BTS20 and increases to 18.5 for BTS30. This indicates that phase transition of BTS20 is not frequency dispersive, and that of BTS30 is strongly frequency dispersive. The fitting of quadratic relationship is fairly good for BTS225, BTS25 and BTS30, and the value of δ increased with tin composition. The value of γ increased with tin composition except for that of BTS30. This irregularity may be due to the instability of fitting results. We have tried to lower the complexity of data fitting to improve the stability, e.g., use linear fitting of $\ln((1/\varepsilon) - (1/\varepsilon_m))$ and $\ln(T - T_m)$ for data fitting of Eq. (3), but the irregularity still appear. This is a shortcoming shared by empirical data fitting, especially for the complex ones. Fig. 2 shows the double logarithm

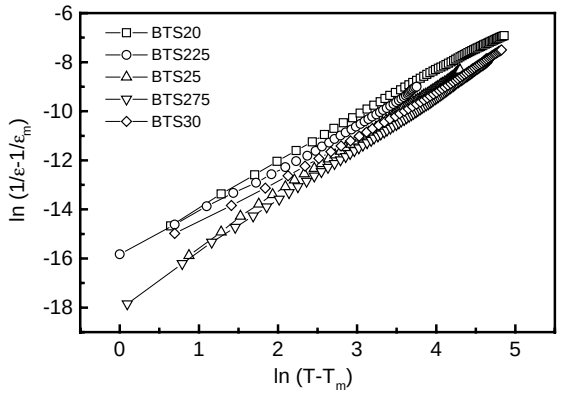

Fig. 2. Double logarithm data fitting of variable power law of barium stannate titanate ceramics.

data fitting for all the compositions. Anyway, these results suggest that the relaxor behavior is stronger for the sample with higher tin composition.

3.3. Model fitting

For BTS25, BTS275 and BTS30, the relationships between frequency and the temperature of dielectric maxima are analyzed with three models, i.e., the well known Debye's theory, the "new glass model" [7,8] and the "glass model" [6], which are expressed as Eqs. (4)–(6), respectively. These equations may describe the relaxor behavior of polar regions or clusters of unsymmetrical lattice cells.

$$\omega = \omega_0 \exp\left(\frac{E_a}{k_b T}\right) \tag{4}$$

$$\omega = \omega_0 \exp\left(\frac{E_a}{k_b T}\right)^p \tag{5}$$

$$\omega = \omega_0 \exp\left(\frac{E_a}{k_b (T - T_f)}\right) \tag{6}$$

where ω and ω_0 are relaxation frequency at temperature T and temperature high enough, respectively. The E_a is activating energy of polar region and k_b the Boltzman constant. T_f is the freezing temperature and p a power parameter.

The data fitting results are shown in Table 2. The value of ω_0 is too high to be practical for the Debye's model, while the other two models have reasonable ω_0 values. This is in agreement with Cheng's results on lead magnoniobate ceramics [13]. For the new glass model, the value of p is as high as 60.5 in BTS25, which indicates a weak relaxor behavior in this composition. In BTS275 and BTS30, the p is about 8 or 7, which indicate fairly strong relaxor behaviors. For the glass model, the freezing temperature decreases with increasing tin composition. In a word, the above results suggest that the relaxor behavior is strong in BTS275 and BTS30 (Fig. 3).

Table 2
Results of model fitting

		Sample		
		BTS25	BTS275	BTS30
Debye's model	ω_0 (Hz)	2×10^{103}	9×10^{33}	3×10^{29}
	E_a (eV)	3.82	0.94	0.69
New glass model	ω_0 (Hz)	3×10^{7}	1×10^{9}	8×10^{8}
	E_a (eV)	0.017	0.019	0.017
	p	60.9	8.03	7.03
Glass model	ω_0 (Hz)	1×10^{9}	8×10^{11}	2×10^{11}
	E_a (eV)	0.0041	0.047	0.042
	T_f (K)	189	128	110

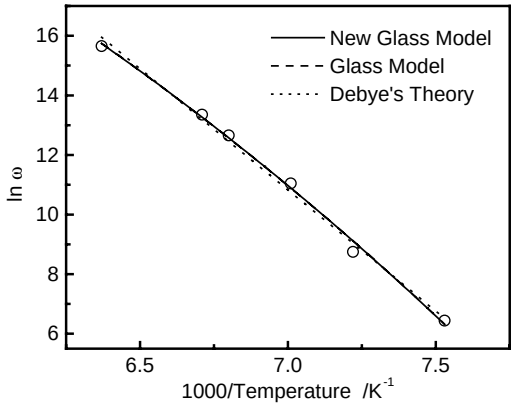

Fig. 3. Model fitting of BTS30 ceramics.

3.4. Comparison of frequency difference of dielectric permittivity (FDDP) with phase transition

The present author proposed a parameter FDDP, which is defined as $1 - (\varepsilon_{1\,\mathrm{MHz}}/\varepsilon_{1\,\mathrm{kHz}})$ for relaxor behavior studies [14]. A material exhibits strong relaxor behavior only if the FDDP inflexion is at the temperature close to that of dielectric peak. In the present study, we can evaluate the relaxor behavior of BTS ceramics by comparing the FDDP inflexion with the phase transition region, which is defined by the full-width at half-maxima (FWHM) value of the dielectric peaks at 1 kHz. Fig. 4 shows the FDDP curves of BTS ceramics. Fig. 5 is the comparison of FDDP inflexion with phase transition region of BTS ceramics. For BTS275 and BTS30, the inflexions are very close to the dielectric maxima, thus these two materials exhibit strong relaxor behavior. For BTS225 and BTS25, the inflexions are comparable away from the center of dielectric maxima, therefore the relaxor behavior is relatively weak. For BTS20, the inflexion is out of the phase transition region, and consequently this material doesn't shows relaxor behavior.

The above discussions demonstrate that relaxor behavior corresponds to the comparison of the FDDP inflexion

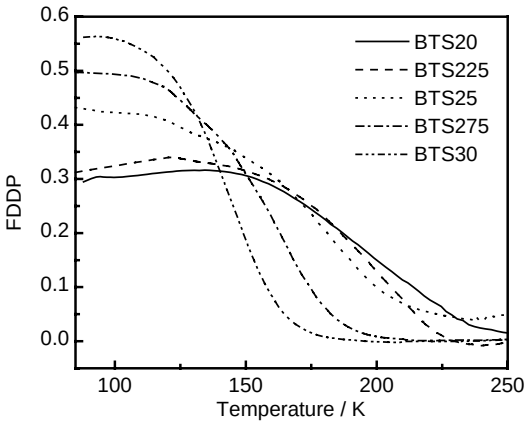

Fig. 4. FDDP with temperature of barium stannate titanate ceramics.

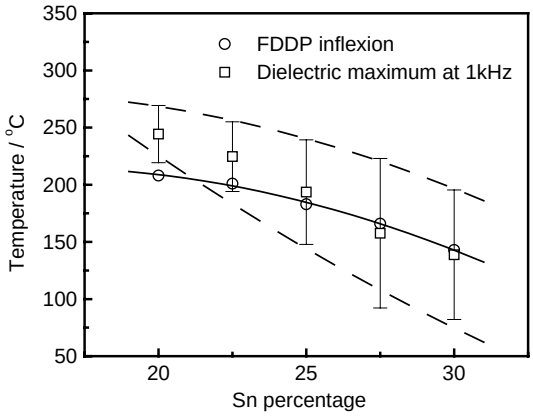

Fig. 5. FDDP inflexion compared with phase transition region of barium stannate titanate ceramics. The area inside the two dash lines are phase transition region described by the dielectric maxima and the FWHM of the dielectric peaks.

with the phase transition region in barium stannate titanate ceramics. This correspondence is the evidence that the relaxation behavior is originated from polar region. With tin percentage increased, the size of the polar region becomes smaller and the response to external disturbance becomes quicker. Thus, the freezing of polar region moves to lower temperature as well as the inflexion of FDDP. This is in agreement with the decreased T_f value of the glass model.

4. Conclusion

In barium stannate titanate ceramics, low frequency dielectric relaxation was observed at temperatures far below room temperature. The empirical equations and models suggested that the relaxation behavior is stronger for higher tin composition. Inflexions of FDDP are close to the dielectric maxima for samples with strong relaxation behavior, and vice versa.

Acknowledgements

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