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Dielectric properties of barium stannate titanate ceramics under bias field

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Abstract

The biased dielectric properties of several barium stannate titanate ceramics were reported in the present study. The reversible dielectric nonlinearities (RDNs) were investigated both in ferroelectric and paraelectric phases. The increased lateral dielectric constant was illustrated with the anisotropy model in ferroelectric phase. The field dependence of dielectric constant was analysed by thermodynamic models in paraelectric phase.

Keywords: Barium stannate titanate; Reversible dielectric nonlinearity

1. Introduction

Barium stannate titanate 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 [2], the crystallographic phase structures evolve from tetragonal, orthorhombic, rhombohedral to cubic with the increasing tin composition at room temperature.

Much attention has been focused on the electrical field tunable materials due to their potential applications as phase shifter [3–8]. However, we cannot well solve the material problem for this purpose partially because the field tuning mechanism is not clearly known yet. In the present study, we are going to study the reversible dielectric nonlinearity (RDN), which is a measure of field tuning ability of reversible dielectric constant (small signal dielectric constant).

2. Experiment

BTS10 ($Ba(Sn_{0.10}Ti_{0.90})O_3$), BTS20 ($Ba(Sn_{0.20}Ti_{0.80})O_3$) and BTS30 ($Ba(Sn_{0.30}Ti_{0.70})O_3$) ceramics were prepared by solid state reaction approaches. The geometry of the sample pallet is 10 mm in diameter and about 1 mm in thickness. A computer controlled system, which is composing of a LCR meter (TH2816, Tonghui Electronic Instrument Inc.), a high voltage source (SRS PS350, Stanford Research System Inc.), an environmental box (Delta Design 9023, Delta Design Inc.) and a voltage protection circuit, was employed to measure the dielectric nonlinear properties of the ceramics. The temperature dependence of dielectric constant was measured via another 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 and tunability

The dielectric constants with temperature of BTS10, BTS20 and BTS30 samples were shown in Fig. 1. The dielectric maxima of these samples move to lower temperature with the increasing tin composition.

Electric field dependence of dielectric constant could be measured by the automated measurement system at various temperatures. Thus, we could draw three-dimensional surfaces of $\varepsilon - E - T$ or $tg\delta - E - T$. Fig. 2a and b are

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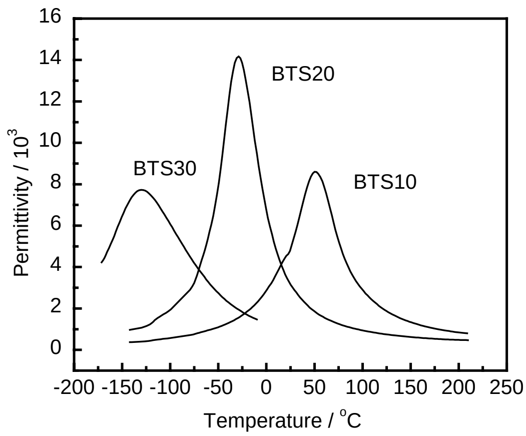

Fig. 1. Dielectric constants with temperature of BTS10, BTS20 and BTS30 at 10 kHz.

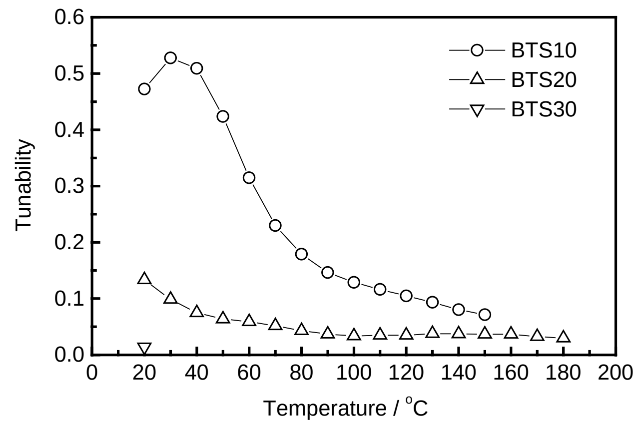

Fig. 3. Tunability with temperature at 10 kV/cm of BTS10, BTS20 and BTS30. The frequency of signal field is 10 kHz.

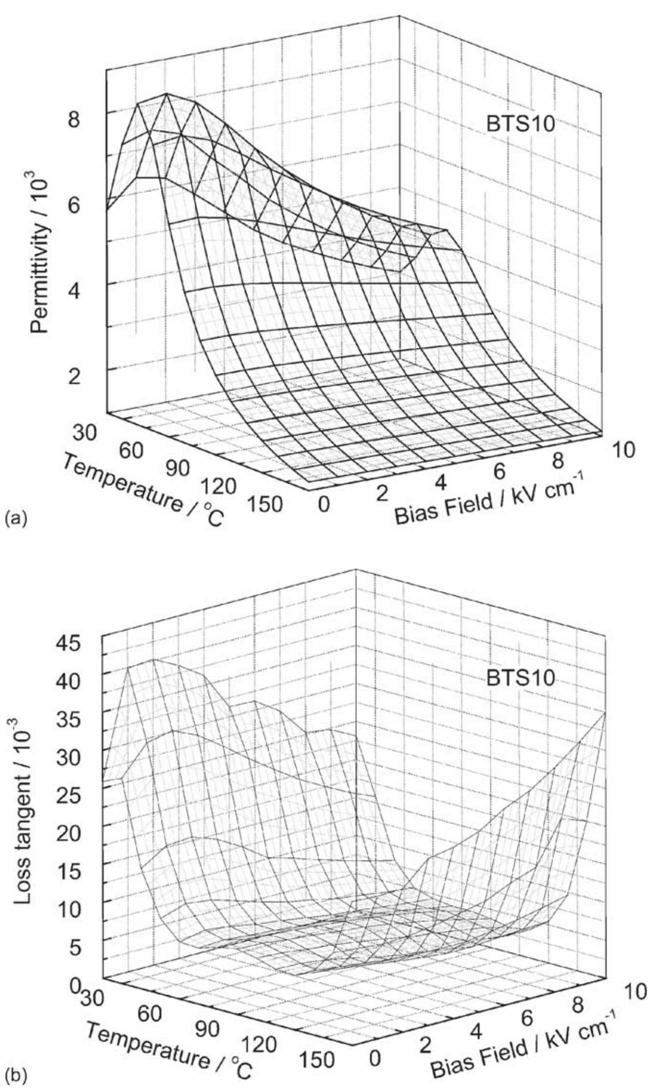

Fig. 2. $\epsilon - E - T$ (a), $tg\delta - E - T$ (b) surfaces of BTS10 ceramics. The frequency of signal field is 10 kHz.

surfaces of the dielectric constant and dielectric loss tangent of BTS10 ceramics, respectively.

Ordinarily, the RDN is quantitated by tunability, which is defined as the reduction of reversible dielectric constant under bias field with respect to the original one, i.e., it can be expressed as:

$$T_E = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \quad (1)$$

where $\varepsilon(0)$ and $\varepsilon(E)$ is the reversible dielectric constant under zero and E bias fields, respectively. Fig. 3 shows the tunabilities with temperature of BTS10, BTS20 and BTS30 samples. The tunability of BTS10 exhibit a maximum at about 30 °C, which is a little bit lower than its Curie temperature. For both BTS10 and BTS20 samples, the tunabilities decrease with temperature at their paraelectric phase. The tunability of BTS30 is neglectable even at room temperature because its Curie temperature is far away from room temperature.

3.2. Reversible dielectric nonlinearity in ferroelectric phase

In ferroelectric phase, RDN originated from two mechanisms, i.e., intrinsic and extrinsic ones. For single domain ferroelectric crystal, only the former one exists. We can express the RDN with the phenomenological thermodynamic theories. This is the same as that of paraelectric phase formally, which will be mention in the next section. For multiple domain ferroelectrics, we must consider the effect of the latter one, which is corresponding to the existence of ferroelectric domains. The relative models are anisotropy, clamping effect and vibration of domain wall. Then, we will show some experimental evidences for anisotropy model of RDN.

Here, anisotropy refers to that the dielectric constant is different along different crystal axis of single crystal. Based on the model of anisotropy, direct current bias field will drive 90° domain wall to move. This will change the reversible dielectric constant of the volume where the domain wall swept

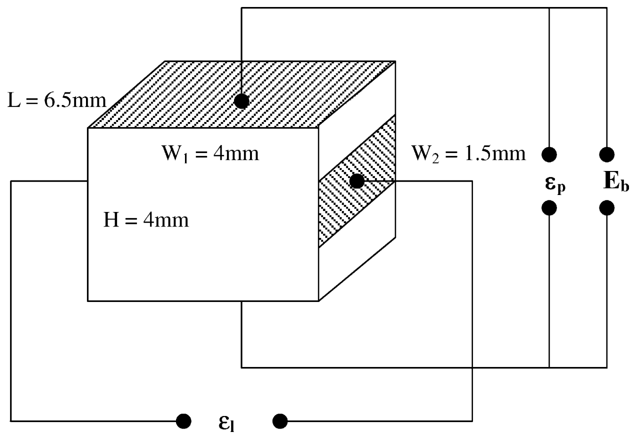

Fig. 4. Schematic drawing of the sample for lateral dielectric constant measurement.

over. The dielectric constant parallel to the field will decrease and the lateral one will increase. Uchida and Ikeda [9] explained the decrease of dielectric constant of BT and PZT ceramics along parallel direction by anisotropic model. Marutake and Ikeda [10] predicted that the dielectric constant of BT along lateral direction might increase with bias field.

Fig. 4 illustrates the structure of the sample used in the present study. Fig. 5 shows that the lateral dielectric constant of BTS10 ceramics in its ferroelectric state, which is measured along lateral direction, increase with bias field, i.e., the tunability is negative. This result is a positive experimental evidence of anisotropy model, which is consistent with that of Uchida and Marutake, but it is contradictive to that of Diamond [11] and Zhang et al. [12], where they have observed the lateral dielectric constant decrease with increasing bias field. This argument may have two originations. First, the anisotropy model may overestimate the volume ratio of domains who are reoriented by 90° in certain materials, and this may lead to the mis-estimation. Second, there are two pairs of perpendicular electrodes, and the bias field and the signal field disturb with each other inevitably. Thus, the precise dependence of dielectric constant with bias field is unavailable.

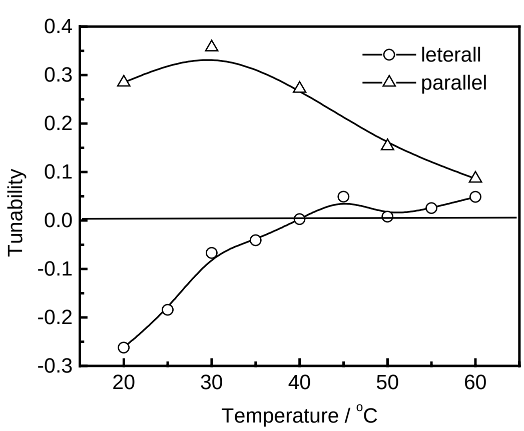

Fig. 5. Parallel and lateral tunabilities of BTS10 ceramics. The frequency of signal field is 10 kHz.

3.3. Reversible dielectric nonlinearity in paraelectric phase

Basically speaking, only intrinsic mechanism of RDN contributes in paraelectric phase. Starting from the definition of Helmholtz free energy, Johnson [13] derived an expression of ac dielectric constant with electric field. With analogizing, he gave a compact approximation of the relationship between differential dielectric constant and electric field (Here, the expression was rewritten with SI unit instead of CGS unit.):

$$\varepsilon(E) = \frac{\varepsilon(0)}{(1+3\beta\varepsilon(0)^3E^2)^{1/3}} \tag{2}$$

where β is a parameter related to the coefficient of the free energy. This expression is also appropriate for RDN because reversible dielectric constant is equal to differential dielectric constant in paraelectrics.

With weak field approximation, the reversible dielectric constant can be deduced from Gibbs free energy [14]:

$$\varepsilon(E) \approx \frac{\partial P}{\partial E} = \frac{1}{\alpha} - \frac{3\beta}{\alpha^4}E^2 = \varepsilon(0) + \Delta\varepsilon \tag{3}$$

where α and β are coefficients of the free energy.

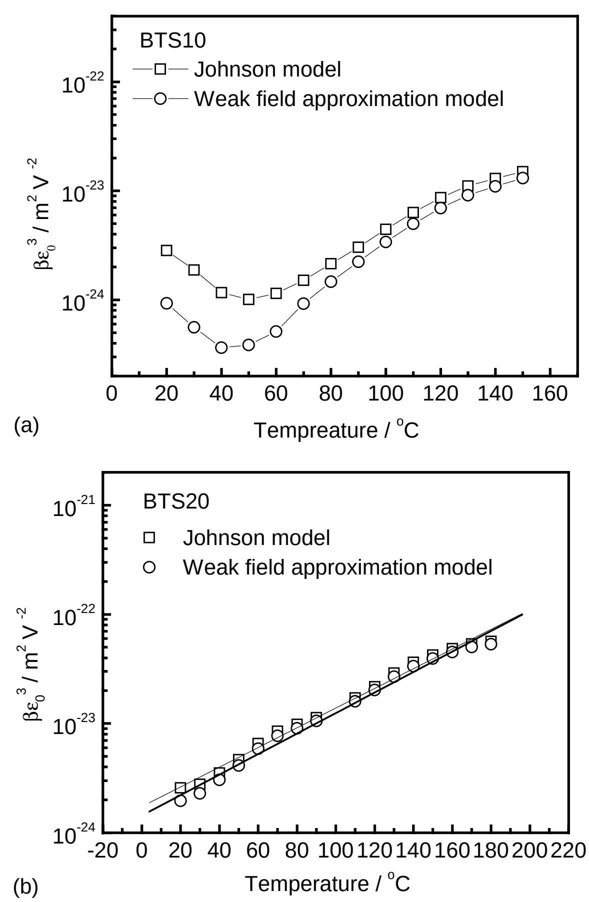

Fig. 6. Inharmonic factor β with temperature of BTS10 (a), and BTS20 (b).

The data fitting of both the above two equations show good agreement with experimental results. By fitting the experimental data of BTS10 and BTS20 with Eqs. (2) and (3), we obtained the value of β with temperature as shown in Fig. 6. The β values obtained are strongly temperature dependent and are close to each other for the two models. The β parameters of BTS10 show minima at 50 °C and for Eq. (2) and 40 °C for Eq. (3). The log(β) increases linearly with temperature for BTS20, and the slope is 0.00902 for Eq. (2) and 0.00939 for Eq. (3). These values are comparable with that reported by Liou and Chiou [15].

4. Conclusion

The reversible dielectric nonlinearities of several barium stannate titanate ceramics were investigated both in ferroelectric and paraelectric phases. The increased lateral dielectric constant in ferroelectric phase is a positive evidence of the anisotropy model. The field dependence of dielectric constant in paraelectric is analysed by the Johnson's model and the weak field approximation model. The fitting results suggest that the β values are strongly temperature dependent.

Acknowledgements

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