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Dielectric relaxation behavior in barium stannate titanate ferroelectric ceramics with diffused phase transition

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The temperature dependence of dielectric permittivity was investigated for two ferroelectric ceramic compositions in a barium stannate titanate solid solution system. The dielectric relaxation behavior was observed in these ferroelectrics with diffused phase transition. In view of the polar nanoregion, the relationship between relaxor ferroelectric and ferroelectrics with a diffused phase transition was explored. The results suggest that, in barium stannate titanate, the relaxor ferroelectric dielectric behavior is universal in the diffused phase transition region, but it only appears when the experimental frequency is close to the relaxation frequency of polar nanoregion at that temperature.

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Since the 1970's, ferroelectrics with diffused phase transition (DPTs) have attracted much interest due to their physical mechanism of diffuse-type phase transition.¹⁻⁴ Smolensky¹ proposed that the broadened phase transition originates from the composition fluctuation of the microscopic "kangzic region." Isupov² explained some problems of ferroelectrics with DPTs in view of the polar region.

Relaxor ferroelectrics (RFEs) have many potential applications, such as a high capacitance capacitor, hysteresis free actuator, and high performance sensor. Setter^{5,6} proposed that the B-site disorder should contribute to the DPT behavior of the RFE ceramic lead scandium titanate (PST). Yao⁷ proved that the macrodomain to microdomain transition dominates the dielectric behavior of RFE ceramic lanthanum doped lead zirconate titanate (PLZT). Burns⁸ and Viehland⁹ treated RFE as a glassy polarization phase. Cheng¹⁰⁻¹³ put forward the "new glass model" and the breathing model of polar region for RFE. Cross^{14,15} reviewed the experimental and theoretical history of RFE.

Although numerous work has been done on ferroelectrics with DPTs and RFEs, the relationship between them is not clear, e.g., all RFEs have DPTs, but not all ferroelectrics with DPTs are believed to be RFEs. To clarify this uncertainty, barium stannate titanate, which is a prototype of ferroelectrics with DPTs, was selected as the research object. Barium stannate titanate is a binary solid solution system of nonferroelectric barium stannate and ferroelectric barium titanate, and both of the two end compositions are of perovskite structure. When $x \leq 0.30$, the Curie temperature of $\text{Ba}(\text{Sn}_x\text{Ti}_{1-x})\text{O}_3$ declines about 8 K for every 1 at. % of titanium substitution by tin. This can be phenomenologically illustrated as that nonferroelectric barium stannate dilutes the ferroelectricity of barium titanate and thus makes the spontaneous polarization less stable. With a tin additive, composition fluctuates in the polar nanoregion (PNR) whose size decreases with increasing tin content and eventually goes down to zero.

A conventional solid reaction route was employed to

synthesize barium stannate titanate ceramics. The sample pallets, about 10 mm in diameter and 1 mm in thickness, were put into a self-made ambient temperature box for the temperature dependence measurement of dielectric properties with a HP4284A LCR meter (Hewlett Packard Corp., California).

Dielectric properties of sample $\text{BaSn}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (BTS20) and $\text{BaSn}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (BTS30) are shown in Fig. 1. There are permittivity peaks for both samples corresponding to their ferroelectric to paraelectric phase transition. For BTS20, the dielectric maxima of the experimental frequencies are the same at about 245 K. The phase transition region is diffused, the full width of half maximum (FWHM) extends to about

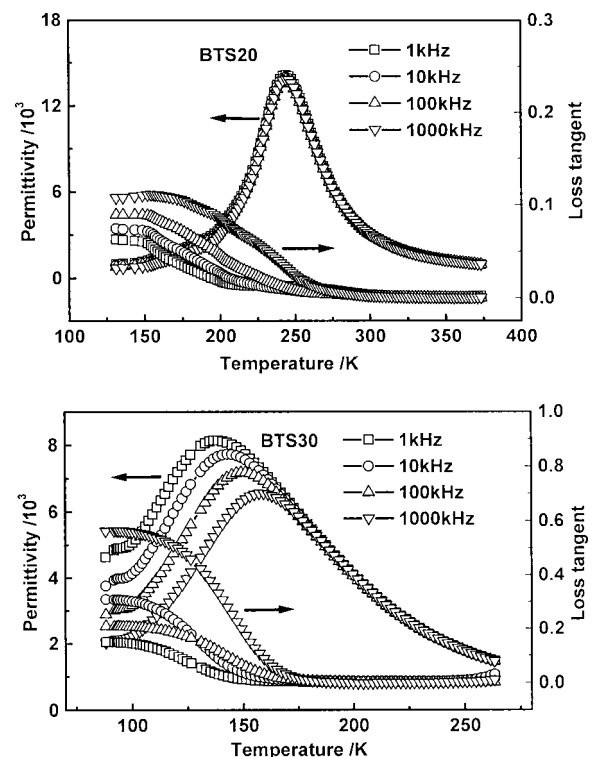


FIG. 1. Temperature dependence of dielectric properties for BTS ceramic samples: (a) BTS20 and (b) BTS30.

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TABLE I. Curve fitting results for BTS20 and BTS30.

Sample	T_m (K)	$1/\epsilon_m$ (10^{-5})	γ	C' ($10^5 K^{\gamma}$)
BTS20	244.25	7	1.40	9.55
BTS30	128.85 (1 kHz)	12	1.97	267

50 K (from 220 K to 270 K). For BTS30, a typical RFE behavior appears. The dielectric maximum shifted to higher temperature for a higher frequency. The phase transition is also diffused, the FWHM, which is about 100 K (for 1 kHz, from 90 K to 190 K), is even wider than that of BTS20. Though the compositions of these two samples are close to each other, their dielectric behavior is somewhat different: One for ferroelectrics with DPTs and another for RFEs. The present authors have studied the BTS system systematically,¹⁶ and found that it is a continuous solid solution system, i.e., the structure and properties are changing successively. So, it seems impossible that there is any abrupt microstructural change in the composition span between BTS20 and BTS30.

Martirena¹⁷ and Uchino¹⁸ suggested the variable power law, which is rewritten to Eq. (1). It describes the paraelectric side dielectric permittivity of ferroelectrics with DPTs. In Eq. (1), ϵ and ϵ_m are the permittivity and its maximum, respectively, T is the temperature, T_m is the temperature of ϵ_m , and C' and γ are constants. It is believed that the power factor γ close to 1 suggests normal ferroelectrics, while close to 2 suggests relaxor ferroelectrics. Curve fitting results for BTS20 and BTS30 samples were shown in Table I. The γ values for the two samples are 1.40 and 1.97, respectively. These results suggest that BTS30 is most probably a RFE and BTS20 is a mediacy between normal ferroelectrics and a RFE.

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_m} + \frac{(T - T_m)^\gamma}{C'} \quad (1)$$

The frequency difference of dielectric permittivity (FDDP), defined as $1 - \epsilon_{1M}/\epsilon_{1k}$, is introduced to describe the extent of the dielectric dispersion. Figure 2 shows temperature dependency of the FDDP for BTS20 and BTS30

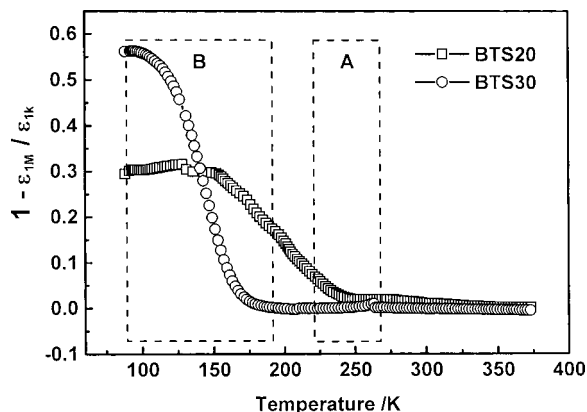


FIG. 2. Frequency difference of dielectric permittivity for BTS20 and BTS30 samples. (The dashed line rectangle A indicates temperature range defined by the FWHM of BTS20 permittivity peak, and rectangle B indicates that of BTS30).

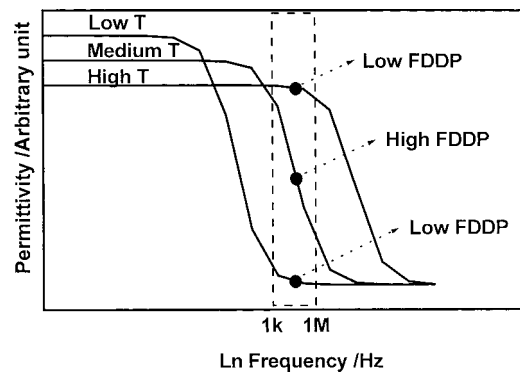


FIG. 3. Schematic drawing for frequency dependence of certain relaxation polarization mechanism at different temperatures.

samples. The dashed line in rectangle A of Fig. 2 indicates the temperature range of the phase transition for BTS20, defined by the FWHM of BTS20 permittivity peak, and rectangle B indicates that of BTS30. The FDDP of BTS20 shows a high plateau before 150 K, and declines to almost zero after 240 K. The FDDP for BTS30 shows a rapid decrease from 100 K to 170 K, which is located in rectangle B of Fig. 2. These phenomena indicate that some kinds of relaxation polarizations exist in both samples. Figure 3 is a schematic drawing of the frequency dependence of certain relaxations at different temperatures. For the specified 1 kHz–1 MHz frequency range (such as the dashed line rectangle in Fig. 3), the FDDP is high at a medium temperature, but low at both high and low temperatures.

If we attribute the polarization relaxation to the polar region,^{1,2,11,14,19,20} which is better called the PNR due to its nanosized geometry, the relationship between ferroelectrics with DPTs and RFEs can be reasonably defined. Because the structure and properties change successively in this solid solution system, it is reasonable to assume that the size and response of the PNR also change successively with increasing tin substitution. In BTS30, the PNR is more sensitive to external excitation than the BTS20 due to its smaller size and quicker response. This leads to higher a PNR relaxation frequency. For BTS30, the rapid decrease of the FDDP meets with rectangle B, which represents a phase transition, accidentally. This means that the relaxation frequency of the PNR is close to the experimental frequencies at that temperature and it makes the material be a RFE. For BTS20, the FDDP decrease is located apart from rectangle A, only a slight permittivity difference exists. And, when the temperature increased to its phase transition region, the FDDP decreases to zero. This implies that the relaxation frequency of the PNR move to a higher value, thus BTS20 is a ferroelectrics with DPTs. A reasonable inference is that BTS20 may act as a RFE with an adequately high experimental frequency. So, we can consider BTS20 as a potential RFE. This suggests that all ferroelectrics with DPTs may be RFEs or potential RFEs, depending on the relaxation frequency of the PNR.

In barium stannate titanate, if the FDDP decrease meets with a phase transition, the ferroelectrics will be RFE; if not, it may only demonstrate DPTs. In other words, in this solid solution system, the relaxation dielectric behavior is universal in the phase transition region, but it can be observed only

when the experimental frequency is close to the relaxation frequency of the PNR at that temperature.

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