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Nonlinear dielectric properties of barium strontium titanate ceramics

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Abstract

In barium strontium titanate ($Ba_xSr_{1-x}TiO_3$) ceramics, obvious tunabilities of both dielectric permittivity and loss tangent under external DC bias field were observed. The temperature and frequency dependences of nonlinear dielectric properties were studied. Polarizing process was carried out to evaluate the influence of domain reorientation on dielectric nonlinearity in the ferroelectric polycrystalline samples. The nonlinear variation of dielectric properties under external DC bias field was tentatively explained.

Keywords: Polar nanoregion; DC bias field; Dielectric nonlinearity; Barium strontium titanate

1. Introduction

Barium strontium titanate($Ba_xSr_{1-x}TiO_3$) is a solid solution family composed of barium titanate and strontium titanate with its curie temperature covering over a wide range. When strontium atoms were introduced to A site in perovskite barium titanate matrix to replace barium atoms, the phase transition temperature of paraelectric to ferroelectric decreases and the phase transition behavior changes from sharp to diffuse. Although numerous works [1–5] have been done on structure, property and application problems of that system, the behavior and mechanism of dielectric nonlinearity under DC bias field could not be well understood yet. DC bias field will decrease dielectric permittivity and loss tangent of $Ba_xSr_{1-x}TiO_3$ ceramics, and the percentage of reduction called dielectric tunability [3], hereafter designated as tunability.

Johnson [6] had derived a relationship between permittivity and external DC bias field from the Helmholts free energy. This was verified well in paraelectric phase region of barium titanate and strontium titanate. Uchida et al. [7] proposed an intuitive model for ferroelectic domain reorientation in PZT ceramics. They believed it is the 90° domain reorientation that causes dielectric nonlinearity. Alert [8] found transient 90° domain wall plays an important role on permittivity tunability under bias field in PZT. Confused by the contradictive results deduced from domain reorientation model, Diamond [9] supposed that the local area composition of $Ba_xSr_{1-x}TiO_3$ ceramics obeys gaussian distribution, thereafter, the origin of dielectric nonlinearity is attributed to bias field induced phase transition from nonferroelectric to ferroelectric.

Another kind of interpretation of dielectric nonlinearity is related to polar nanoregion. The concept of polar nanoregion is more precise than that of polarmicroregion (PMR) because of their nanometer scale. Polar nanoregion defined as nanometer scale region with parallel oriented spontaneous polarization, where they consists of each other acting as a giant dipole with slow relaxation frequency [10–12]. The polar nanoregion is susceptive to environmental disturbance and apt to redirect to external field vector even under weak signal level. Dielectric nonlinearity can be manifestly under-

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stood under the assumption that polar nanoregion losses its susceptibility while merging into micro domain or macro domain if applied external bias field is strong enough.

2. Experimental

$Ba_xSr_{1-x}TiO_3$ ceramics $Ba_{0.8}Sr_{0.2}TiO_3$ (designated as BST8 hereafter) was used as the selected material. Usual solid reaction route was employed to prepare ceramics. Reagent grade barium carbonate, strontium carbonate and titania were used as starting materials. Stochiometric proportioning raw materials were ground by zirconia ball for twice time with a 1000–1100 °C calcination introduced between the twice grinding. Twelve mm diameter green pallets were fired at 1400–1500 °C for 2 h followed by silver electrode painting. The ceramic prepared is dense(relative density $>$ 95%) and the average grain size is about 10–30 µn. XRD results indicate that only pure perovskite structure exists for both calcinated and fired bodies [13]. Polarizing process was carried out by cooling from above curie temperature to room temperature with 10 kV cm^{-1} electric field applied on sample pallet, and depolarizing was carried out by thermal annealing these pallets at 300 °C for 1 h.

A computer controlled system, including HP 4284 high precision LCR meter(Hewllet Packard Corp. USA), environmental box with its temperature range form liquid nitrogen to 250 °C, was used to measure temperature and frequency dependence of dielectric properties. Another computer controlled system, including TH2816 LCR meter(Tonghui Electronic Instrument Corp. China), SRS PS350 high voltage generator(Stanford Research System Corp. USA.), Delta Design 9023 environmental box(Delta Design Corp. USA), self-designed high voltage protection circuit, and IEEE 488 bus(IEEE standard) for interconnection, was employed to evaluate the dielectric nonlinear properties of BST8 ceramics.

The concept dielectric permittivity used here denotes incremental permittivity, which is quite different from the differential permittivity derived from P–E loop. It is measured and calculated under small signal level (1 V rms) at 1 kHz frequency by LCR meter in the present study.

3. Results

Fig. 1 shows the temperature dependence of dielectric properties of BST8 sample under zero bias field. During the temperature span of 0–100 °C, a slightly diffused ferroelectric to paraelectric phase transition peak was observed. Dielectric permittivity frequency dispersion is very weak. The temperature of dielectric maximum and loss tangent maximum locates at about 56 and 49 °C, respectively.

A temperature range of 20–100 °C, covering ferroelectric, transition and paraelectric phase region of BST8 ceramics, was chosen to study bias field induced dielectric nonlinearity. Based on the experimental data, 3-dimensional curved surfaces of both dielectric permittivity and loss tangent were plotted according to their bias field and temperature dependence as shown in Fig. 2.

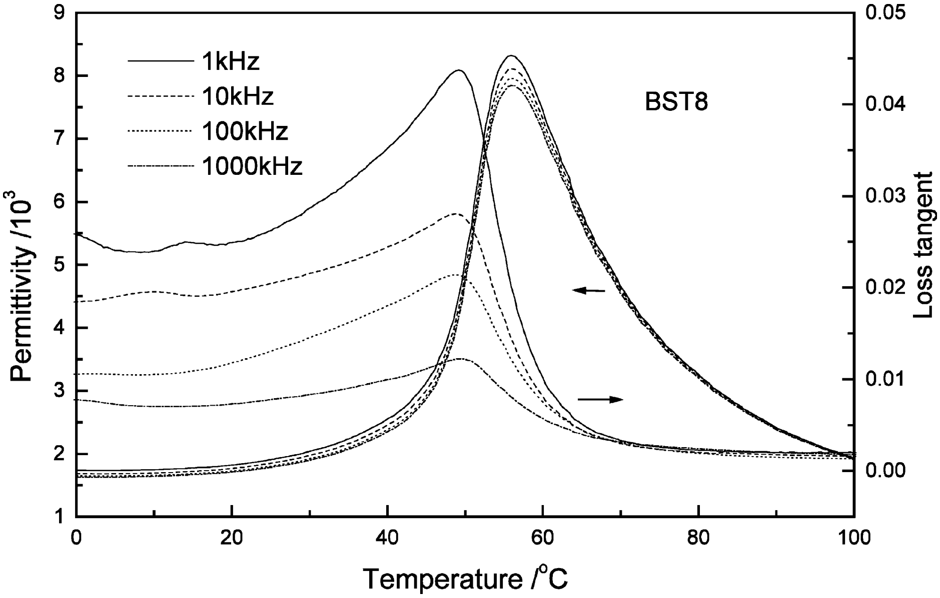
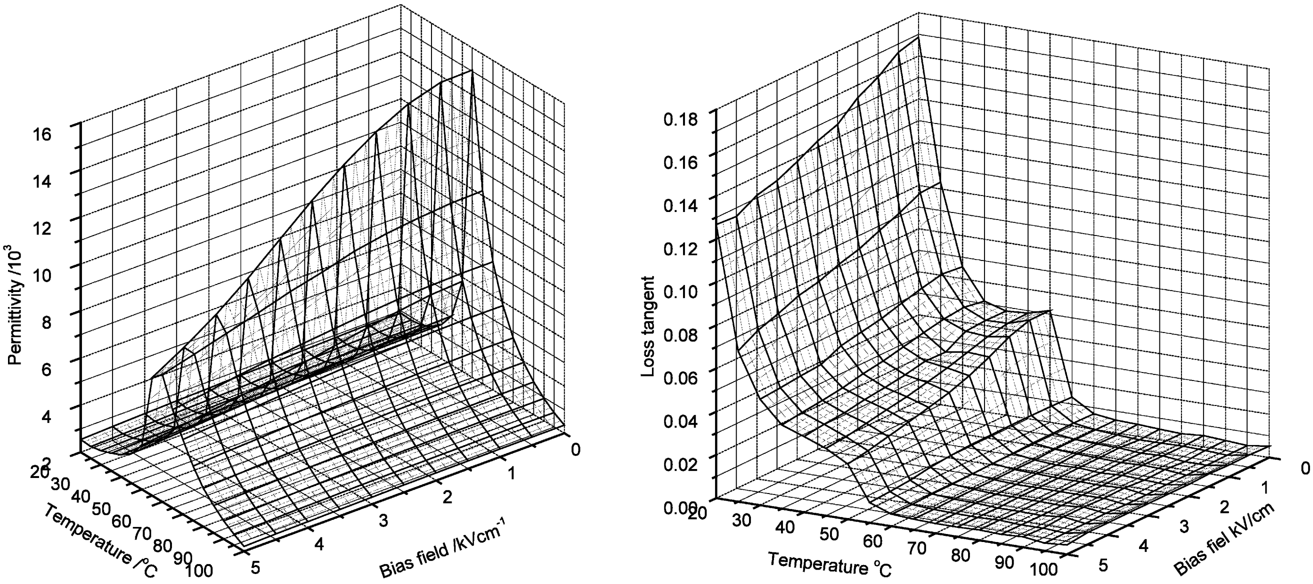


Fig. 1. Temperature dependence of dielectric properties of BST8 sample under zero bias field. (a), Dielectric permittivity; (b), Loss tangent.



a) Dielectric permittivity

b) Loss tangent

Fig. 2. Temperature and bias field dependence of dielectric permittivity and loss tangent.

Fig. 3 shows the temperature dependence of dielectric permittivity tunability under 5 kV cm^{-1} bias field. It's interesting that the peak of tunability appears closely at the temperature of dielectric maximum. This hints there is some kind of relationship between dielectric nonlinearity and ferroelectricity in nature. The dielectric permittivity tunability is a little stronger in ferroelectric side than that of paraelectric side.

Fig. 4 shows frequency dependence of normalized permittivity tunability. With frequency increasing, permittivity tunability decreases apparently in ferroelectric region(25 °C) while it increases for a little bit in transition region(55 °C) and almost keeps constant in paraelectric region(85 °C).

To investigate the relationship between dielectric nonlinearity and domain structure in ferroelectric polycrystalline samples, polarized and depolarized samples were used as representatives of uniformly oriented and randomly oriented domain structure, respectively. As shown in Fig. 5, the polarized sample shows much lesser

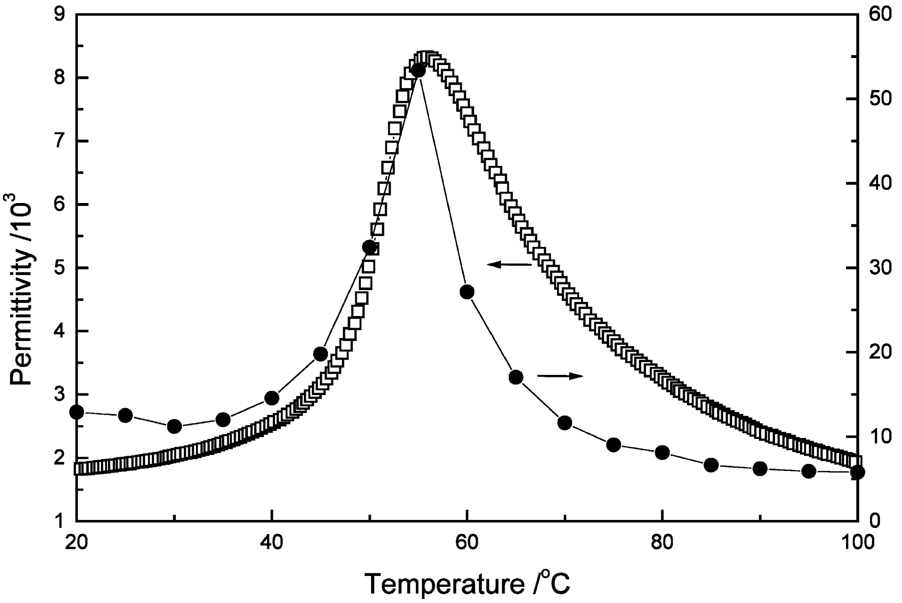


Fig. 3. Temperature dependence of dielectric permittivity tunability under 5 kV cm^{-1} bias field.

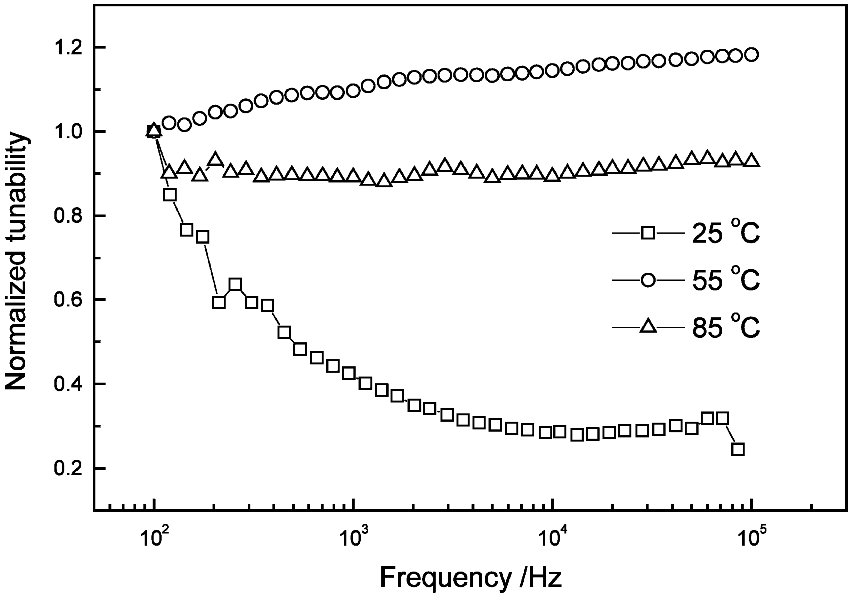


Fig. 4. Frequency dependence of permittivity tunability under 3 kV cm^{-1}.

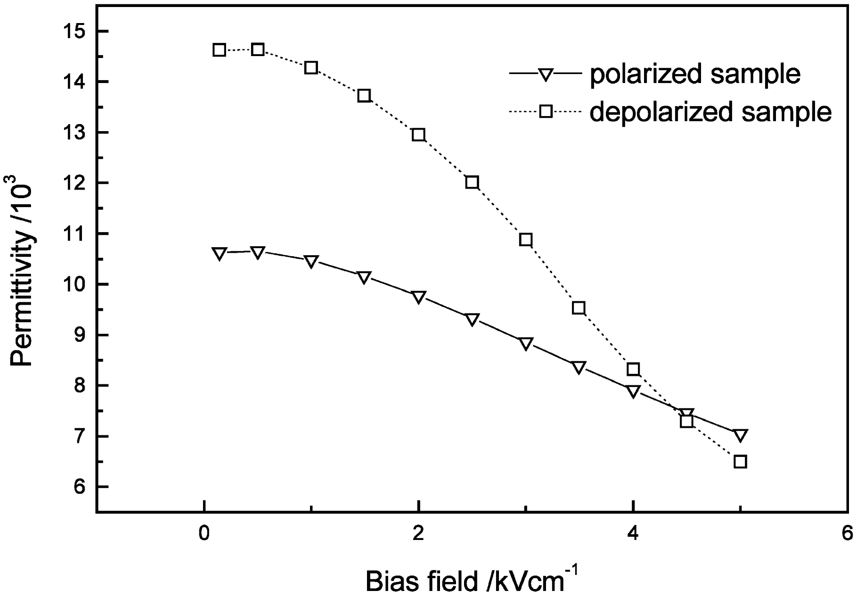


Fig. 5. Dielectric nonlinearity of polarized and depolarized samples.

tunability than that of the polarized one under bias field at 55 °C, which is close to its dielectric maximum temperature.

4. Discussion

Based on the above experimental results, dielectric nonlinearity phenomena can be interpreted from the view of polar nanoregion (see Section 1). In this work, temperature range covering ferroelectric, transition and paraelectric phase region was selected. In ferroelectric region, where ordinary ferroelectric domain exists, both permittivity and its tunability are relatively lower. The strong frequency dependence of dielectric nonlinearity reveals some kind of slow relaxation mechanism. With increasing temperature, ordinary ferroelectric domains break into numerous polar nanoregions and nanosized ferroelectric domains in transition region due to thermal activation. The permittivity and its tunability reach their maximum, because polar nanoregion is susceptive to weak signal field and apt to merge into ferroelectric domain under DC bias field, respectively. Polarizing field will change the distribution of domain orientation and polar nanoregion, thus affect the permittivity tunability of sample. In the paraelectric region, polar nanoregions are distributed isolating from each other among paraelectric matrix. Both permittivity and its tunability decrease. The near-constant tunability in Fig. 4 indicates the relaxation frequency of polar nanoregion at this temperature is far from the frequency range used here.

5. Conclusion

Nonlinear dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics were studied in ferroelectric, transition and paraelectric regions. Tentative explanations were given from view of polar nanoregion.

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