Analysis of the dielectric characteristics for polycrystalline $Ba_{0.65}Sr_{0.35}TiO_3$ (II) – d.c. field dependence with a modified bias equation

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The effect of direct-current (d.c.) biasing on the dielectric properties of $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) with various grain sizes (0.87 μm to 5.43 μm) have been studied in the paraelectric state. The leakage current of BST samples is proportional to the biasing field. Specimens with larger grains exhibit higher leakage current under biasing. The bias equation used in the literature to predict the d.c. field dependence of permittivity is modified by introducing a bias exponent parameter β. This modified bias equation gives a better fit to the experimental results both in this study and in the literature. Similar trends of α (representing the distribution of relaxation times), β, and the variance of lattice distortion with grain sizes suggests that β is a material parameter. It is concluded that the temperature dependence, the frequency response and d.c. field effect for the dielectric characteristics of $Ba_{0.65}Sr_{0.35}TiO_3$ are all suppressed by the transition broadening.
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1. Introduction

Ferroelectric barium strontium titanate (BST) is of great interest for many practical applications. The dielectric characteristics of polycrystalline BST depend strongly both on its microstructure and the environment during usage. The effects of d.c. field on the dielectric behavior of BST have been reported [1, 2] and applied in various devices such as tunable capacitors [3] and microwave phase shifters [4, 5]. However, only a few studies [3, 6, 7] have been conducted on the d.c. field related properties of paraelectric BST, especially the BST system with various grain sizes. The non-linearity of dielectric permittivity with d.c. biasing field in the paraelectric state is believed to originate from the anharmonic interaction of Ti ions in the perovskite cubic structure. Johnson [2] started from Devonshire's theory and proposed a bias equation to correlate the dielectric constant and d.c. field. Outzourhit *et al.* [3] fitted this phenomenological equation to their experimental data and argued that deviations from the theoretical prediction were attributed to the dielectric dispersion caused by non-uniform grain sizes. In our previous work [7], it was observed that the d.c. effect is suppressed for BST with finer grains due to the smaller dielectric constant caused by transition broadening.

In this study, the d.c. field dependence of dielectric constant and dielectric loss for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes are investigated in the paraelectric state. Dopants MgO and MnO_2 are used to obtain uniform grained, low-loss dielectrics [8, 9]. Samples with various grain sizes are obtained by varying sintering temperatures and times. The purpose is to analyze the

frequency response and d.c. effect for $Ba_{0.65}Sr_{0.35}TiO_3$ and to find the correlation between these characteristics and the grain size. The frequency response, reported previously [10], was analyzed with two power laws which are obtained from the Cole–Cole expression at low frequencies. The d.c. field dependence of the dielectric permittivity is analyzed with a modified bias equation which is proposed in this study.

2. Experimental procedures

The $Ba_{0.65}Sr_{0.35}TiO_3$ polycrystalline samples with various grain sizes were prepared by the conventional solid state reaction method with commercial powders of $BaCo_3$, $SrCo_3$, TiO_2, MnO_2, and MgO. Powder mixtures containing additives of 1.0 mol % MgO and 0.05 mol % MnO_2 were calcined at 1100 °C for 2 h in air and pressed to form disk-shaped samples at 180 MPa. Samples with various grain sizes were prepared with a fast-firing, two-stage, sintering profile described previously [7]. Phase identification and average grain size were analyzed by powder X-ray diffraction and scanning electron microscopy (SEM) examination, respectively. Lattice distortion in polycrystalline BST is calculated by the X-ray diffraction peak broadening of a single peak profile. For dielectric characteristic measurement, the bulk sample was polished to 0.4 mm in thickness before making electrodes. The current–voltage curve was obtained with an HP4140 pA meter (Hewlett Packard). The capacitance and tangent loss were measured with an HP4275A LCR meter (Hewlett Packard). A 200 V d.c.

power supply was connected to the LCR meter as the external d.c. bias for fields up to $5000 \, V \, cm^{-1}$. The measuring frequency range in this study is from $10 \, kHz$ to $4 \, MHz$.

3. Results and discussion

When the electrical signal passes through dielectrics, the transmitted information is deteriorated by leakage currents, especially when a d.c. field is applied. Therefore, it is crucial to understand the d.c. field dependence of leakage current. The current densities for each samples at various applied d.c. fields are shown in Fig. 1. A larger leakage current for $Ba_{0.65}Sr_{0.35}TiO_3$ is observed for samples with larger grams. Dopants MgO and MnO_2 used in this study are known to serve as grain growth inhibitors barium titanate because they segregate preferentially at grain surfaces. However, there is a small fraction of these dopants which may dissolve in the grains and become p-type acceptors [11, 12]. Lewis *et al.* [11] calculated the surface defect energies for $BaTiO_3$ with various dopants, such as Mg and Mn. They reported some accompanied oxygen defects with the acceptors substituting on Ti sites. Recently, Langhammer *et al.* [13] found that the defect concentration in Mn-doped $BaTiO_3$ increased as more Mn was added. In this study, samples with larger grains were obtained with longer sintering time or higher sintering temperature, the acceptor-type dopants were believed to dissolve more into the grains, thus more oxygen defects were produced due to valence charge compensation. The *I–V* characteristics for barium titanate have been explained by the space charge limited currents (SCLC) theory [14] for polycrystalline insulators. This states that strongly defective surfaces of the crystalline grains provide a source of deep trap states in insulators where the trapped charge carriers are excited by the applied voltage. Therefore, $Ba_{0.65}Sr_{0.35}TiO_3$ with larger grains has more defects and consequently yield larger leakage current, as shown in Fig. 1. The SCLC theory suggests that below an onset voltage, an ohmic current flows. At higher voltages, the current transfers to a rapidly increasing behavior of the form of $I - V^{\alpha}$ where α is in the range of 1.2 to 2.0 [14]. It is seen in Fig. 1, that the current density is linearly dependent on the applied field. The d.c. resistivities are then calculated and summarized in Table I. Resistivity decreases with the increase of grain size due to the increase of defects.

Considering the frequency response of an electrically tunable capacitor, an equivalent circuit model containing a d.c. resistor and a voltage-variable capacitor in parallel combination can be applied adequately. Both the d.c.
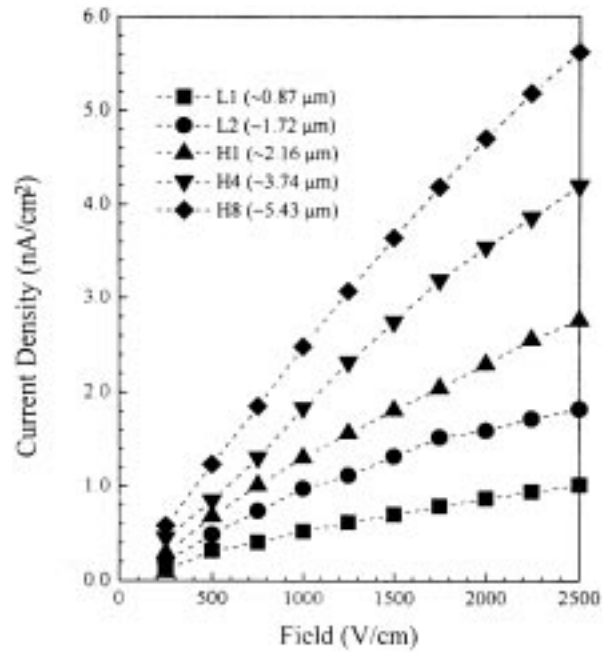

Figure 1 Leakage current density as a function of d.c. field for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes.

resistance as well as the capacitance are d.c. field dependent under d.c. biasing.

$$R(V) = V/I(V) \qquad (1)$$

$$C(V) = C_0[\varepsilon'(V) - j\varepsilon''(V)] \qquad (2)$$

where C_0 is the geometrical capacitance of the capacitor and the relative permittivity $\varepsilon(V) = \varepsilon'(V) - j\varepsilon''(V)$ has its real and imaginary parts which are both d.c. field dependent. The current–voltage characteristics $I(V)$ for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes exhibit ohmic behavior, as illustrated in Fig. 1. Assuming that the onset of *I–V* behavior-transformation (SCLC theory) is not reached by the d.c. field applied when a.c. measurements are being carried out, the resistance of these samples is then constant with field. The real part of the relative permittivity can be calculated by the measured capacitance. As for the measured dielectric loss $\tan\delta$, it contains two terms, one for the imaginary permittivity, the other for loss due to the leakage current. Therefore at some specific measuring frequency ω, the voltage variable loss tangent can be expressed as:

$$\tan\delta(V) = \frac{\varepsilon''(V)}{\varepsilon'(V)} + \frac{1}{\omega R \varepsilon'(V) C_0} \qquad (3)$$

The first term on the right hand side of Equation 3 is the intrinsic loss of the dielectrics, and the second term is the

T A B L E I Dielectric constant, dielectric loss, and resistivity for MgO and MnO_2 doped $Ba_{0.65}Sr_{0.35}TiO_3$ with various average grain sizes*

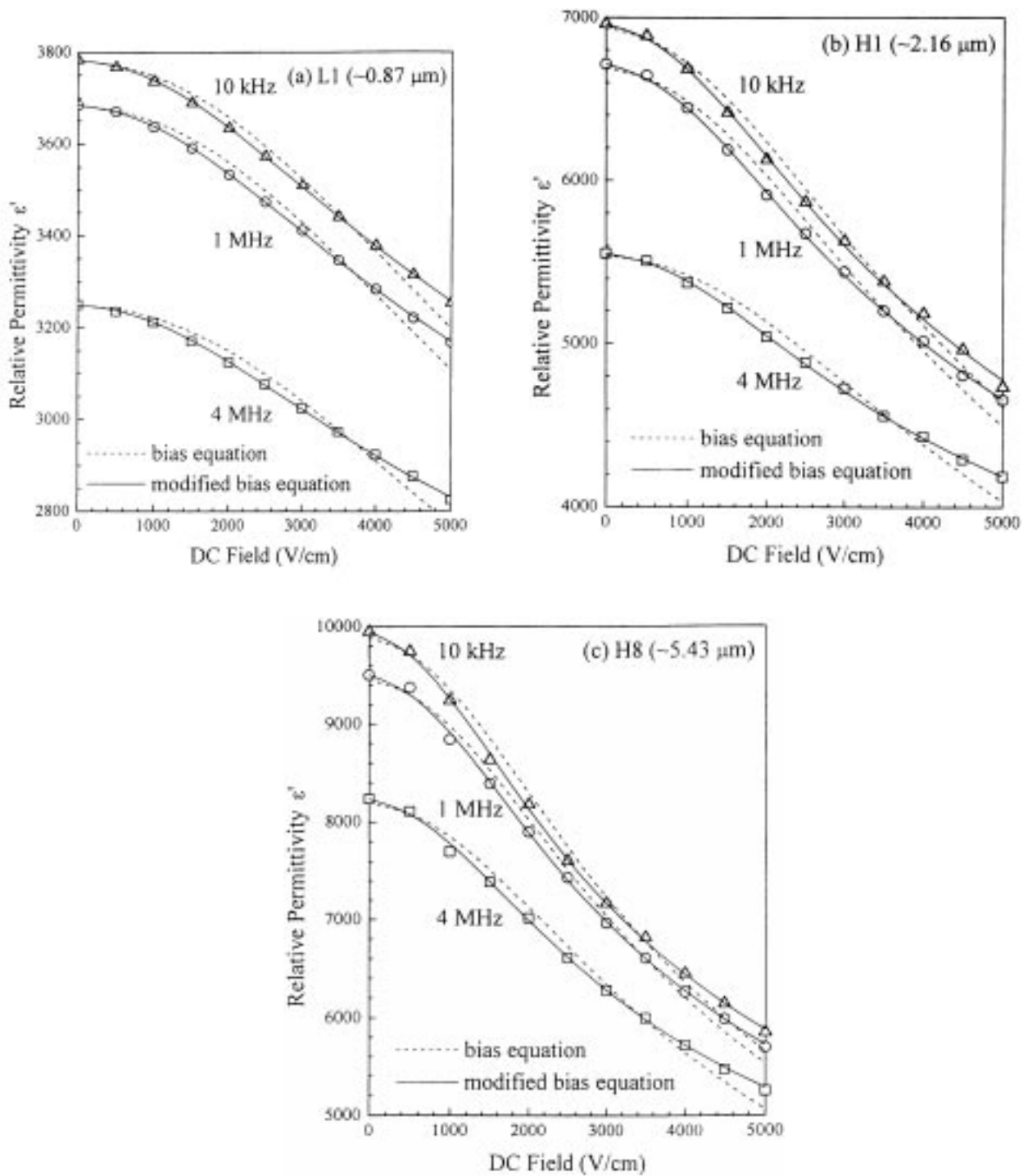| Specimen (grain size (µm))	Dielectric constant		Dielectric loss		d.c. resistivity (GΩ cm)
	10 kHz	4 MHz	10 kHz	4 kHz	
L1(0.87)	3783	3251	0.0115	0.1241	2477
L2(1.72)	5269	4801	0.0132	0.1200	1376
H1(2.16)	6959	5557	0.0288	0.2063	907.2
H4(3.74)	9808	7915	0.0134	0.2992	597.5
H8(5.43)	9947	8233	0.0168	0.3733	444.7

*Data of the dielectric properties were reported in previous work [10].

Figure 2 Relative permittivity ε'' as a function of d.c. biasing field for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes (a) L1, (b) H1 and (c) H8. Curves are fitted with the bias equation and the modified bias equation. Note that the modified equation gives better fits than the original one.

conduction loss. With the resistivity and dielectric constant listed in Table I, the conduction losses for the $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes are estimated to be less than 10^{-7} for all frequency and field ranges in this study. Hence, the conduction loss term can be neglected so that the imaginary permittivity ε'' is approximately the product of dielectric constant and tangent loss.

A bias equation on the basis of Devonshire's theory to correlate the relative permittivity ε' and applying d.c. field E is proposed phenomenologically [2]:

$$\varepsilon'(E) = \frac{\varepsilon'(0)}{(1 + AE^2)^{1/3}} \qquad (4)$$

where $\varepsilon'(0)$ is the initial permittivity under zero d.c. biasing. The field coefficient A represents the strength of the d.c. field effect. The value of A equals $a\varepsilon'^3$ where a is the anharmonic coefficient. As the anharmonic interaction becomes stronger, a larger value of A yields a larger value of field coefficient and thus the d.c. field is more effective to reduce the permittivity. Johnson claimed that some deviations due to polycrystallinity can be absorbed in the field coefficient A. Therefore Equation 4 can be applied with validity to the polycrystalline barium strontium titanate system. As for the imaginary part of dielectric permittivity, Johnson proposed another bias equation based on a RC series circuit:

$$\varepsilon''(E) = \frac{\varepsilon''(0)}{\left(1 + AE^2\right)^{2/3}} \qquad (5)$$

Recently, Outzourhit *et al.* [3] investigated the d.c. field dependence of the dielectric constant of $Ba_{0.1}Sr_{0.9}TiO_3$ ceramics prepared by the wet method and the solid state method. They found that good fitting of this bias equation to the experimental results can only be made separately in low and high field ranges. For the BST system in this study, it is found that the suppression of the d.c. field effect by the grain size is remarkable [10]. The validity of the bias equation was questioned when there is a transition broadening. In Outzourhit's work, the bias equation did not fit the experimental data, presumably due to the diffuseness of the transition of $Ba_{0.1}Sr_{0.9}TiO_3$ with grain sizes of about 1 μm and 10 μm.

Attempts to employ the bias equation for the dielectric characteristics of $Ba_{0.65}Sr_{0.35}TiO_3$ in this study (shown in Fig. 1 of Liou and Chiou [10]), reveal some controversies such as: (a) the bias equation does not predict well the dielectric behavior under d.c. biasing though the best fitted field coefficient A is chosen, (b) if the field coefficient is calculated by Equation 4, it is no longer a constant with field, and (c) the field coefficient is frequency dependent. Since the bias equation was explained adequately for single crystal or ceramics with high crystallization [2], it is argued that the controversies were attributed to the various microstructures of the polycrystalline ceramics, especially the grain size. It was reported previously that there are various distributions of Curie temperatures occurring in the $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes [10]. This implies that each grain has its own initial permittivity $\varepsilon'(0)$ which is different from each other. Thus, the dielectric behavior under d.c. field changes profoundly due to the grain size effect. To realize the d.c effect by a distribution of $\varepsilon'(0)$ in polycrystallites, the denominator of the bias equation is modified by introducing a bias exponent β:

$$\varepsilon'(E) = \frac{\varepsilon'(0)}{\left(1 + BE^2\right)^{\frac{1-\beta}{3}}} \qquad (6)$$

The bias exponent β ranges from 0 to 1 and represents the order of suppression of the d.c. field effect. The related field coefficient B is supposed to be field independent and represents the strength of the d.c. field effect. The fittings of bias equation and modified bias equation for samples L1, H1, and H4 at 10 kHz, 1 MHz and 4 MHz are shown in Fig. 2a to c for comparison. For the fitting of the modified bias equation, a two-parameter least square method was employed. The initial values of the two parameters, B and β, were calculated by solving two equations constructed by two experimental data, $\varepsilon(E_1)$ and $\varepsilon(E_2)$. The optimum β was obtained by the least squares method with the calculated B. The optimum B was then obtained by the least squares method with the optimum β. As shown in Fig 2a to c, the magnitude predicted by the bias equation in all samples is too high in the low field region and too low in the high field region. This is why Outzourhit *et al.* fitted their results with the bias equation separately in high field and low field regions. Meanwhile, less deviation of the modified bias equation
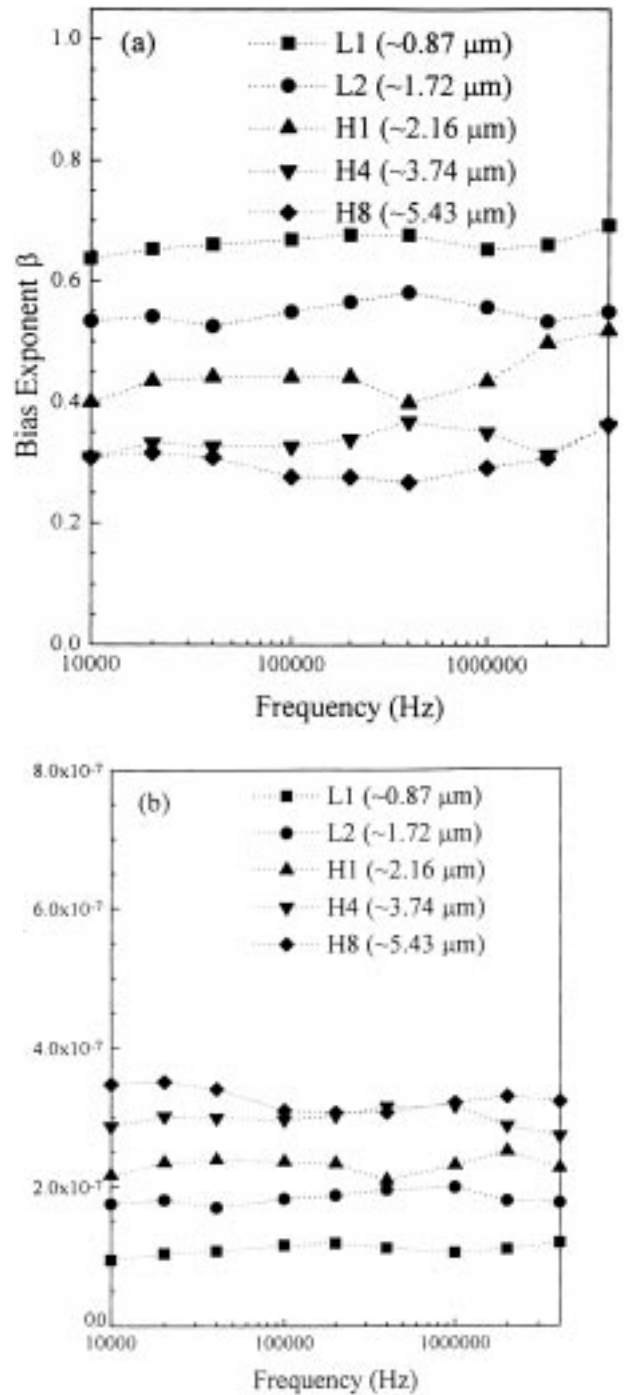
Figure 3 (a) Bias exponent β and (b) field coefficient B of permittivity ε' as a function of frequency for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes.

($< 0.6\%$) is observed at d.c. fields up to $5000\,V\,cm^{-1}$. With the fittings to the dielectric characteristics shown in Fig. 1 of [10], the bias exponents β and field coefficients B for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes at different frequencies are shown in Fig. 3a and b, respectively. No apparent frequency dependence of β and B suggest that these two parameters are material parameters. The increase of β and the decrease of B with the decrease of grain size is clearly seen. Larger β and smaller B make the denominator in the modified bias equation (Equation 6) closer to one, thus the reduction of dielectric constant by the d.c. field is suppressed. This suppression is presumably due to the broad distribution of Curie temperatures in polycrystalline materials.
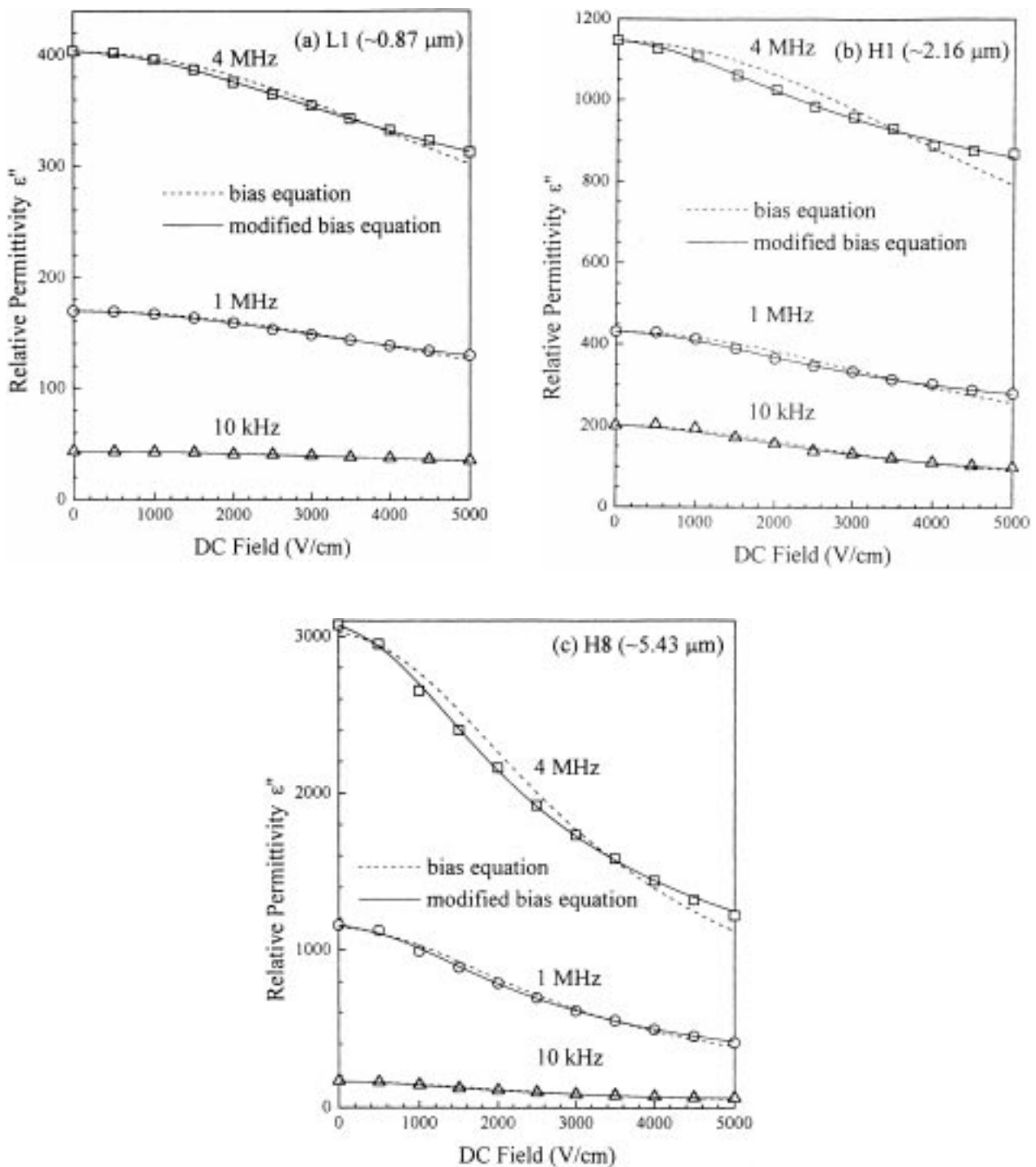
Figure 4 Relative permittivity ε'' as a function of d.c. biasing field for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes (a) L1, (b) H1 and (c) H8. Curves are fitted with the bias equation and the modified bias equation. Note that the modified equation gives better fits than the original one.

Equation 5 is modified in a similar way as:

$$\varepsilon''(E) = \frac{\varepsilon''(0)}{(1 + BE^2)^{\frac{2(1-\beta)}{3}}} \quad (7)$$

Fig. 4 shows the fittings with the bias equation (Equation 5) and the modified bias equation (Equation 7). The modified equation gives a better fit, as in the case of $\varepsilon'(E)$. As reported previously, dopants contribute to the split of dipolar relaxation, and the losses at frequencies below 100 kHz are higher than those predicted by the approximated power law [10]. It is noted in Fig. 4 that the behavior of the dielectric loss ε'' at 10 kHz is also in agreement with the prediction of the modified bias equation. As shown in Fig. 5, the bias exponent β

increases and the field coefficient B decreases with the increase of grain size. Similar trends of $\varepsilon'(E)$ and $\varepsilon''(E)$ are observed, β ranges from 0.27 to 0.70 for ε' and from 0.29 to 0.70 for ε''. Although the bias field coefficients for both ε' and ε'' are also comparable, more fluctuations of β and B for ε'' at different frequencies are observed in Fig. 5. The calculation of the imaginary permittivity ε'' is based on Equation 3 neglecting the second term as the leakage current is very small. There are differences between the β and B in Fig. 3 and those in Fig. 5. It is believed that fitting data with Equation 6 (Fig. 3) gives more accurate β and B values, since the contribution of conduction loss and dopant-related relaxation to ε'' are neglected in Equation 7 (Fig. 5).

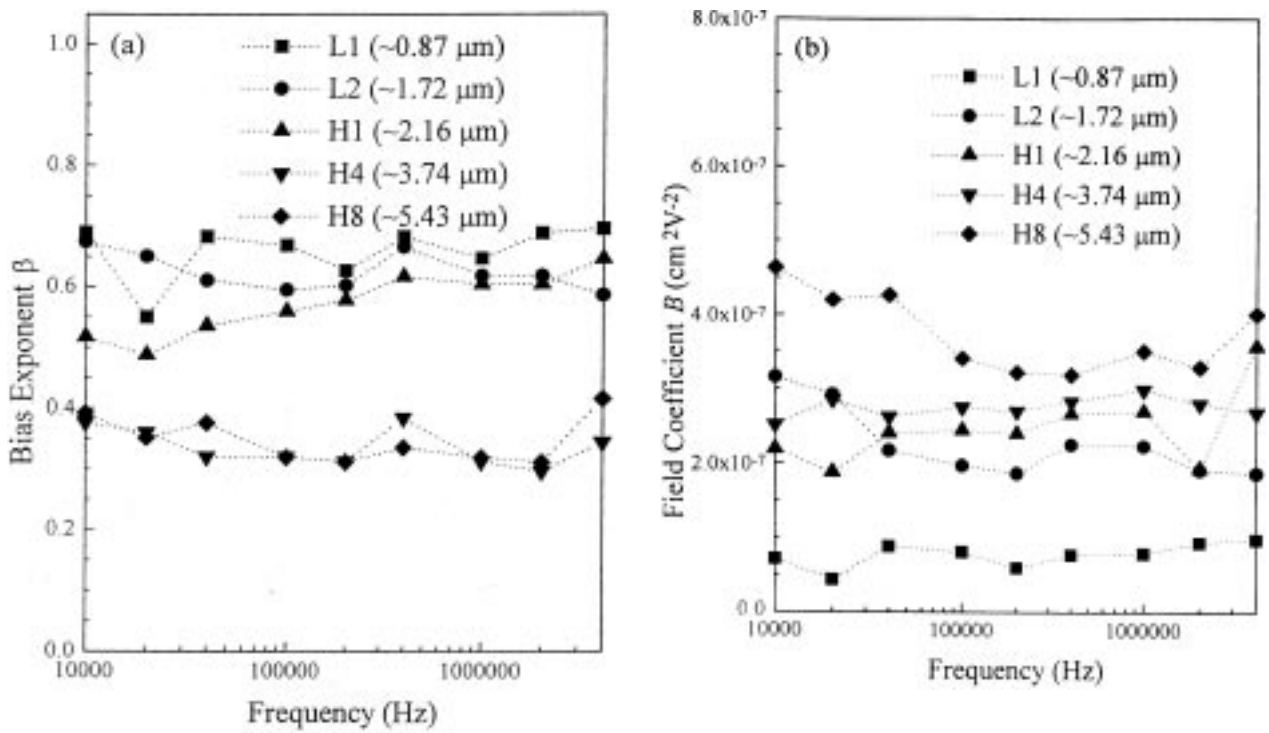Using the modified bias equation proposed in this

Figure 5 (a) Bias exponent β and (b) field coefficient B of permittivity ε' as a function of frequency for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes.

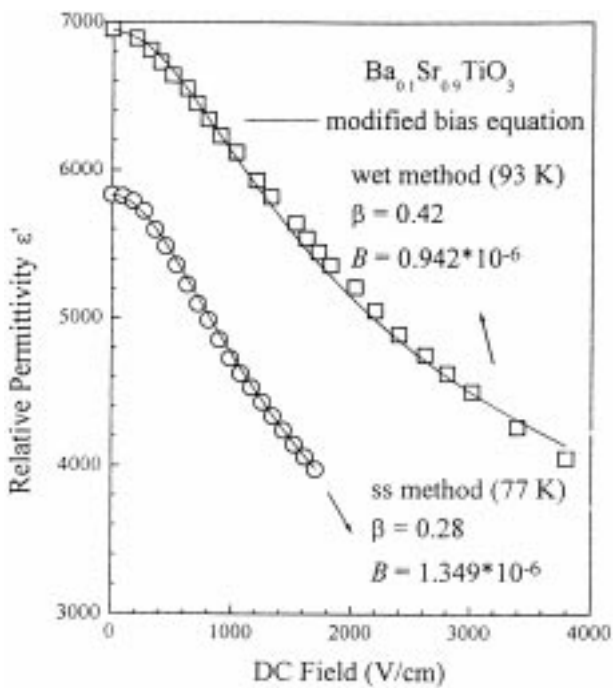*Figure 6* Cure fitting with the modified bias equation for the permittivity ε'. $Ba_{0.1}Sr_{0.9}TiO_3$ prepared by wet and solid state methods (data obtained from Outzourhit *et al.* [15]).

Figure 7 Grain size dependence of variance of lattice distortion and the suppressing parameters α, β for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes.

study, the fittings of Outzourhit's results are shown in Fig. 6. The bias exponent β is 0.42 for $Ba_{0.1}Sr_{0.9}TiO_3$ prepared by the wet method and is 0.28 for that prepared by the solid state method (ss method). The grain sizes of Outzourhit's samples are about 1 µm (wet method) and 10 µm (ss method), respectively. Outzourhit also showed that samples prepared by the wet method had broader Curie peaks than those prepared by the solid state method. The larger value of bias exponent is explained by the broader transition distribution in the sample prepared by the wet method.
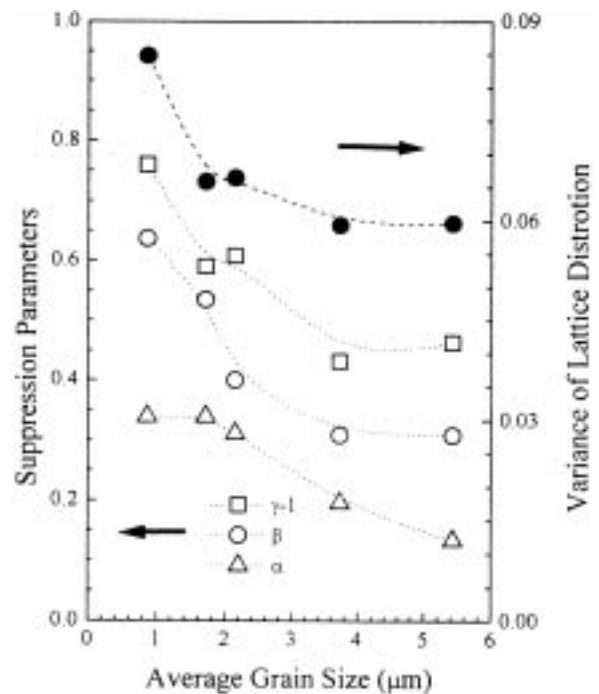
One may argue that an equation with two fitting parameters always gives better fits than one with only one fitting parameter. This is true with regard to the mathematics. The bias exponent β varies, the trend of modified bias equation intrinsically, i.e., different β values determine different function forms of Equations 6 and 7. Together with the frequency independence of β, as shown in Figs 3a and 5a, these features suggest that β is a material parameter. Perhaps the bias coefficient B plays a tuning role during the fitting procedure. Nevertheless, once these two parameters are

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properly chosen, the dielectric behavior can be predicted well with the initial value ($\varepsilon'(0)$ or $\varepsilon''(0)$) known. The modified bias equation is then useful for applications. Furthermore, from the same trends of the tilt parameter α [10], critical exponent γ [10] and bias exponent β for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes, the variance of β is also believed to be due to the ferroelectric to paraelectric transition broadening. These parameters are called ''suppression parameters'' to represent the suppression order of temperature dependence, frequency response and d.c. field effect. Fig. 7 exhibits the grain size dependence of these parameters. In this figure the lattice distortion is obtained from the X-ray analysis at room temperature, γ is obtained at 10 kHz, β is obtained at $10\,^{\circ}C$ and 10 kHz, and α is obtained at $10\,^{\circ}C$. All these four parameters decrease as grain size increases.

4. Conclusions

1. A decrease of the dielectric constant for $Ba_{0.65}Sr_{0.35}TiO_3$ with the increase of d.c. biasing field is observed. A modified bias equation with a bias exponent β, is proposed to predict the dielectric behavior under d.c. biasing. It is found that the fits are better than the original bias equation for $Ba_{0.65}Sr_{0.35}TiO_3$ with various grain sizes. Once the parameters in the modified bias equation are properly chosen, the dielectric behavior under the d.c. field can be predicted accurately with the initial value ($\varepsilon'(0)$ or $\varepsilon''(0)$) known.

2. Frequency independence of the bias exponent β suggests that it is a material parameter. The increase of β with the decrease of grain size indicates that the suppression of the d.c. field effect occurs in polycrystalline $Ba_{0.65}Sr_{0.35}TiO_3$.

3. The grain size dependence of suppression parameters α, β and γ obtained from the dielectric characteristics of frequency response, d.c. field effect and temperature dependence, show the same trend with the variance of lattice distortion for polycrystalline $Ba_{0.65}Sr_{0.35}TiO_3$.

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