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Xiaoyong Wei, Yujun Feng, and Xi Yao

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Slow relaxation of field-induced piezoelectric resonance in paraelectric barium stannate titanate

Xiaoyong Wei,[a)] Yujun Feng, and Xi Yao
Electronic Materials Research Laboratory, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

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A kind of slow relaxation of field-induced piezoelectric resonance is observed in paraelectric barium stannate titanate ceramics. The piezoelectric resonance peaks vanish in several minutes when bias field is either applied or removed. These phenomena may be universal for dielectrics and can be explained by a model of slow dipoles composed of injected homocharges. With this model, the authors predict a negative piezoelectric modulus of d_{33} when just the bias field is removed, and verify it by experimental results. © *2004 American Institute of Physics.*
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Much attention has been focused on electrical field tunable materials due to their potential application as phase shifters.[1–6] Van Keuls *et al.* have obtained phase shifts beyond 360° at 16 GHz with barium strontium titanate thin films.[4] Although technical research is in progress, various details of the material interior when an electrical field is applied are not known yet. Recently, Li *et al.* pointed out that both a rapid effect and slow effect, which are induced by the electrical field, exist in dielectrics, and the influence of the slow effect cannot be ignored.[7] The present authors have observed several slow effects in ceramics. This letter reports the slow relaxation of field-induced piezoelectric resonance in paraelectric barium stannate titanate.

BTS20 ($BaTi_{0.80}Sn_{0.20}O_3$) ceramic was prepared by solid state reaction. Sample pallets were cut into 10 mm in diameter and 0.3 mm in thickness. Silver electrodes were coated fully (10 mm in diameter) on one side of the pallet and partially (6 mm in diameter) in the center on the other side to prevent electrical breakthrough along the edge. A Direct current field was generated by a high voltage source (SRS 350, Stanford Research Systems). An impedance analyzer (HP4192A, Hewlett Packard) was employed to measure the field-induced piezoelectric resonance of the samples. A protective circuit was placed between the source and the analyzer to prevent the devices from any high voltage damage.

The Curie temperature of the ferroelectric BTS20 ceramics is about −30 °C.[8] Thus it is in paraelectric phase at room temperature. When an electrical field is applied to these paraelectrics, we observe an electrostriction effect, which arises from the field-induced polarization of the material. When we apply a small sine alternating current field in addition to a strong direct current bias field, we observe a biased electrostriction effect, i.e., a field-induced piezoelectric effect. Figure 1(a) shows an impedance spectrum of the field-induced piezoelectric resonance of BTS20 in the frequency range of 365–380 kHz. The temperature is 20 °C. The bias voltage is 1000 V. The level of the sine signal field is 1 V. Numbers 1–11 in Fig. 1(a) indicate the sequence of measurement. The time between each is about 43 s. From Fig. 1(a), we can see that the 1000 V bias field does induce piezoelectric resonance in BTS20 ceramics, although the planar electromechanical coupling factor k_p is only about 0.1.

By applying and removing bias voltage, a series of interesting phenomena appear for longer measurements. First,

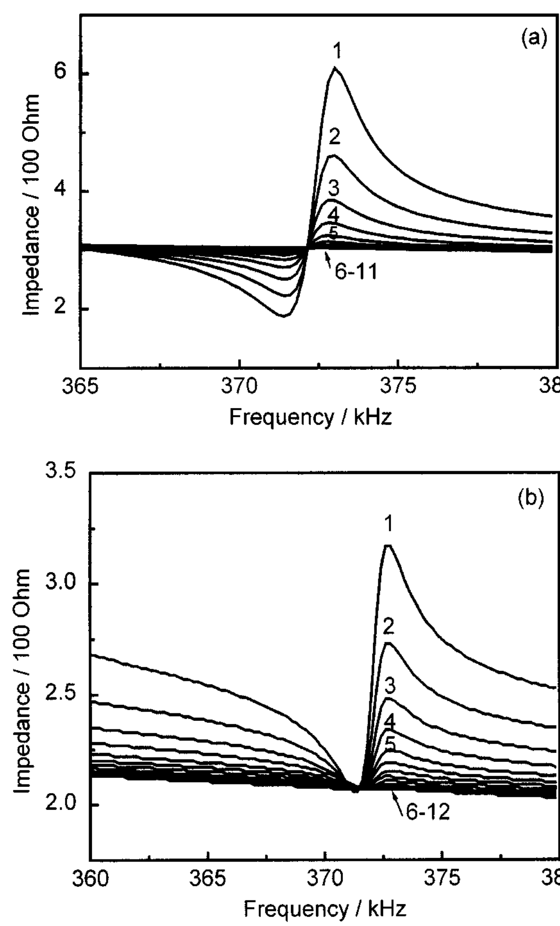

FIG. 1. Impedance spectrum of BTS20 at 20 °C when 1000 V voltage was applied (a) and when 1000 V voltage was removed (b). Numbers 1–12 indicate the sequence of measurement. The time between two adjacent measurements is 43 (a) and 40 s (b), respectively.

[a)]Electronic mail: wdy@mail.xjtu.edu.cn

TABLE I. Resonance data for both applying and removing bias voltage. (f_r, f_a in kHz; Z_r, Z_a in Ω.)

Sequence No.		1	2	3	4	5	6	7	8	9	10	11	12
Bias voltage applied	f_r	371.4	371.4	371.4	371.4	371.4	371.4	371.5	371.5	371.5	371.6	⋯	
	Z_r	187	222	250	270	283	291	296	300	301	302	303	
	f_a	373.0	373.0	372.8	372.8	372.8	372.8	372.7	372.8	372.8	372.7	⋯	
	Z_a	609	461	385	346	324	314	308	304	303	303	303	
Bias voltage removed	f_r	371.3	371.3	371.3	371.4	371.5	371.5	371.4	371.4	371.4	371.6	371.5	⋯
	Z_r	206	207	208	208	208	208	208	208	208	207	207	207
	f_a	372.7	372.7	372.7	372.7	372.8	372.7	372.9	372.7	372.8	372.9	372.8	⋯
	Z_a	317	273	248	234	225	219	215	213	211	209	208	207

when applying the bias, the field-induced resonance peaks vanish within 11 times measurements, i.e., within about 430 s. Second, as depicted in Fig. 1(b), resonance peaks reappear when the bias is removed. Next, these resonance peaks that reappeared vanish again within 12 times measurements, i.e., within about 440 s.

Ignoring dissipation, we assign f_r and f_a as the resonance frequency and antiresonance frequency that correspond to the minimum impedance Z_r and maximum impedance Z_a, respectively. Resonance data for both applying and removing the bias voltage are shown in Table I. Obviously, k_p or Δf is not appropriate for indicating the strength of field-induced piezoelectricity, because they remain almost constant even when the resonance peaks vanish. Here we choose another parameter, R, to represent the strength of induced piezoelectricity.

$$R=\frac{Z_a-Z_r}{Z_a+Z_r}. \tag{1}$$

Li *et al.* have proposed an equation to describe a random relaxation mechanism in dielectrics when bias field is applied:[7]

$$\frac{Q(t)}{Q(0)}=1-r\exp\left(-\frac{t}{\tau}\right), \tag{2}$$

where Q is a relaxation parameter. Let $Q=R+1$ and $Q(0)=1$, then Eq. (2) can be rewritten as

$$\lg(R)=\frac{1}{2.303}\left(\ln(-r)-\frac{1}{\tau}t\right). \tag{3}$$

Then we can derive relaxation time τ from the slope of $\lg(R)$ for time t. Figure 2 shows the relationship of $\lg(R)$ vs t at different temperatures. Upon removing the bias voltage, $\lg(R)$ decreases linearly over time at 20, 40, and 60 °C, respectively. Upon applying bias voltage, the variation is somewhat complex, i.e., $\lg(R)$ decreases first, then approaches zero, and then increases to a constant value. This procedure is accelerated by elevated temperatures. To unify the expressions, we chose another parameter, R', to substitute for R. R' is defined as $R'=R+R_0$ when R decreases over time and $R'=R_0-R$ when R increases over time. Constant R_0 is equal to the eventually stabilized R value. Therefore relaxation time τ can be calculated from the slope of $\lg(R')$ for time t. The τ values are listed in Table II. The relaxation time at higher temperature is shorter than that at lower temperature. Moreover, it is different for different bias field strengths. This kind of slow relaxation of induced piezoelectricity mentioned above is also observed in other

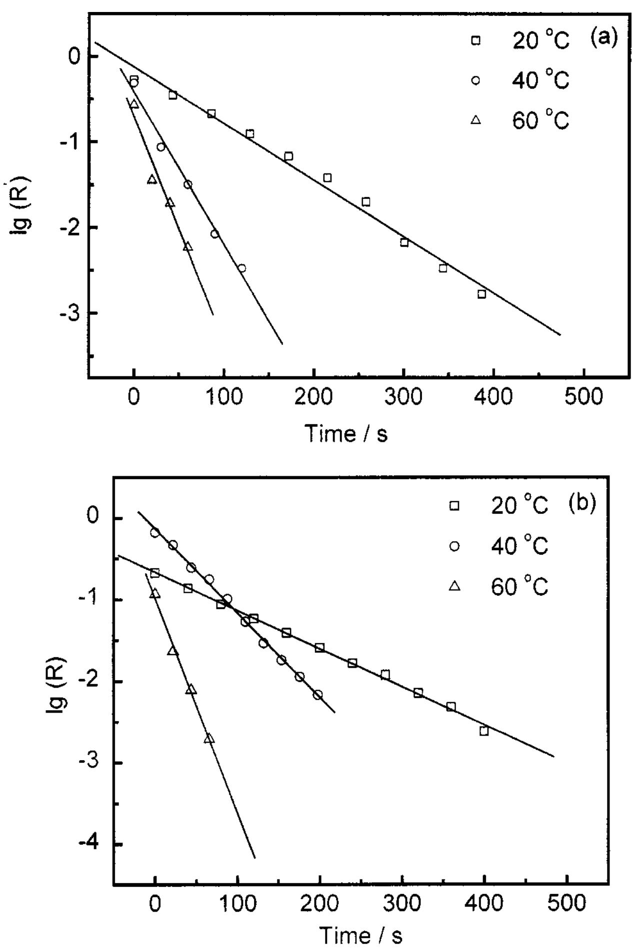

FIG. 2. $\lg(R)$ vs time at different temperatures when 1000 V bias voltage was applied (a) and when 1000 V bias voltage was removed (b).

TABLE II. Relaxation time for both applying and removing bias voltage.

	Bias voltage applied			Bias voltage removed		
Temperature (°C)	20	40	60	20	40	60
Relaxation time (s)	71	24	17	93	42	16

paraelectric material, such as $BaTi_{0.70}Sn_{0.30}O_3$ ceramics. However, this is not true for ferroelectric material $BaTi_{0.90}Sn_{0.10}O_3$ ceramics.

To explain what we have observed, we now focus attention on slow dipoles induced by the bias field, which is comprised of either lattice defects or space charge. Daniels proposed the barium vacancy model in barium titanate ceramics.[9] There are combined defects, i.e., defect dipoles, in crystals. Gemant[10] proved the existence of both heterocharges and homocharges, which constitute space charge dipoles, in electrets.[11] Considering the dense insulating body of BTS20 ceramics, the probability of defect dipoles and heterocharge dipoles can be ignored. Homocharges, which are injected onto the material surface by electrodes in a strong external field, are the most probable origin of slow dipoles.

When the bias field is applied, field-induced polarization builds up promptly, and the homocharged slow dipole builds up in dielectrics gradually. The direction of the slow dipole is antiparallel to that of field-induced polarization, thus the effect of slow dipoles cancels, smears out, or even inverts the original polarization. Therefore field-induced piezoelectricity may vanish gradually and eventually reappear. Similarly, the slow dipole degrades gradually when the bias field is removed. Thus field-induced piezoelectricity may vanish gradually.

With this model of slow dipoles, all the phenomena mentioned above can be well explained. The temperature and field strength dependence of induced piezoelectricity can be easily understood by the space charge dipole. For ferroelectric material $BaTi_{0.90}Sn_{0.10}O_3$ ceramics, ferroelectric spontaneous polarization is strong enough to maintain piezoelectricity, thus no relaxation was observed.

To verify this model, we measured the d_{33} value of the BTS20 sample when just the bias field was removed after having been applied for a long time. According to this model, the slow dipoles, which are antiparallel to the bias field, still exist at the time, thus the apparent piezoelectric modulus d_{33} should be negative. Experimental results of the d_{33} value, which is measured by Berlincourt approach, proved this prediction. As shown in Fig. 3, d_{33} is less than zero.

The logarithm value of $-d_{33}$ decreases linearly over time and the relaxation time is 189 s. This is in qualitative agreement with the degradation of parameter $\lg(R)$. In Fig. 1(b), the baselines of the resonance peaks decrease over time, which agrees with the time dependence of the capacitance measurement. This reveals that the internal field built up by the slow dipoles lowers the dielectric constant in the same way the external bias field does.

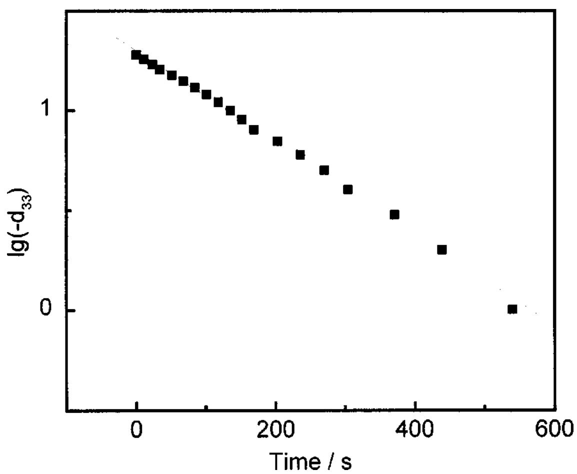

FIG. 3. Piezoelectric modulus d_{33} when the bias field was removed.

This letter introduced slow relaxation of the induced piezoelectricity of paraelectric BTS20 ceramics. The authors explained the phenomenon with the model of slow space charge dipoles, and predicted a negative piezoelectric modulus d_{33}, which was proved by experimental results.

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