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Isothermal relaxation of field-biased barium stannate titanate

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The isothermal time dependences of the dielectric constant and the discharging current of barium stannate titanate ceramics after application or removal of a step field were investigated in both ferroelectric and paraelectric temperature regions. The experimental results exhibited a substantial difference for these two phases. For the ferroelectric phase, the relaxation of the dielectric constant is weak and the discharging current obeys Hammon's model. While for the paraelectric phase, the relaxation is relatively strong and the discharging current obeys the complex exponential decay model. The relaxation of the field-induced piezoelectric resonance indicated the first relaxation observed in a paraelectric phase sample corresponding to homocharges. The authors proposed that the transportation of homocharges is the microscopic origin of the strong relaxation observed in the paraelectric phase. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2032607]

As we know, the dielectric constant of ferroelectrics is field dependent and it can be controlled by adjusting the field strength. Many kinds of devices can be developed with this feature, such as a dielectric amplifier, parametric device, and microwave ferroelectric phase shifter. The mechanism of the dielectric nonlinearity is lacking the comprehensive understanding up to date,[1–3] little is known regarding the tuning dynamics. Therefore, more attention should be given to the bias field related studies.

For highly insulating ferroelectric ceramics, the dielectric responses often show strong time dependences. For example, after application or removal of a step field, it is not safe to estimate the real time value of either the charging current, the discharging current, or the dielectric constant. The study of the isothermal current and dielectric relaxation behavior are of both technical and theoretical importance, and may be helpful in understanding the field tuning mechanism.

Isothermal measurements, experimental techniques frequently used to study the low frequency dielectric constant, distribution of active energy, and distribution of space charge in various insulators,[4–6] include polarization (charging) and depolarization (discharging) current measurement after application or removal of a step field while a constant temperature is kept. The best advantage of isothermal study is that it is capable of providing direct experimental observation of the relaxation function, which is essential for a dielectric property study. There are mainly three kinds of proposed empirical models of the relaxation function. They are: the Hamon's method analysis,[7] the exponential decay function, and the Kohlrausch-Willams-Watts function.[8]

In the present work, the authors investigated the isothermal time dependence of the dielectric constant and the current of barium stannate titanate ceramics after a step field in both the ferroelectric and paraelectric temperatures regions. The experimental results exhibited a substantial difference for these two phases. For the ferroelectric phase, the relaxation of the dielectric constant is weak and the discharging current obeys the Hammon model. While for the paraelectric phase, the relaxation is relatively strong and the discharging current obeys a complex exponential decay model. These different isothermal relaxation behaviors originate from their different microstructure. The relaxation of the field induced piezoelectric resonance also reflects this fact.

Barium stannate titanate is a solid solution system of barium titanate and barium stannate. Although this material is one of the earliest prototypes of diffused phase transition studies, it riveted many research interests recently due to its abnormal dielectric properties and strong dielectric nonlinearity for the application in tunable microwave electronics. $BaTi_{0.80}Sn_{0.20}O_3$ (BTS20) ceramic was prepared by a solid state reaction. Sample pallets were cut into the size of 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 LCR meter (TH2816, Tonghui) and a picoammeter (6485, Keithlay) were employed to measure the time-dependent dielectric constant and current of the samples, respectively, and experimental data were recorded by using computer programs. Step field was generated by a high voltage source (SRS350, Stanford Research System) artificially. The rise time is several seconds, which is negligible compared with the thousands of seconds of recording time. A protection circuit was introduced between the source and the meters to prevent any high voltage damage to the devices. The sample was put into a temperature chamber (Delta9023, Delta Design) for the purpose of temperature control. An impedance analyzer (HP4192, Hewllet-Packard) was used to measure the field induced piezoelectric resonance.

As the Curie temperature of BTS20 is about −30 °C,[9] we chose two temperature points −60 and 20 °C in order to retain the ferroelectric and paraelectric phases, respectively. The isothermal relaxation of the dielectric constant after application and removal of a step field (1 kV/mm) is shown in Fig. 1. As we can see, the dielectric relaxation of ferroelectric phase (BTS@−60 °C) is weak after either the application or the removal of a bias field. Quantitatively, the percentage of the relaxation (slow) tunability with respect to the total one is only 4.2% after the field application. While in the paraelectric phase (BTS@20 °C), the relaxation is relatively

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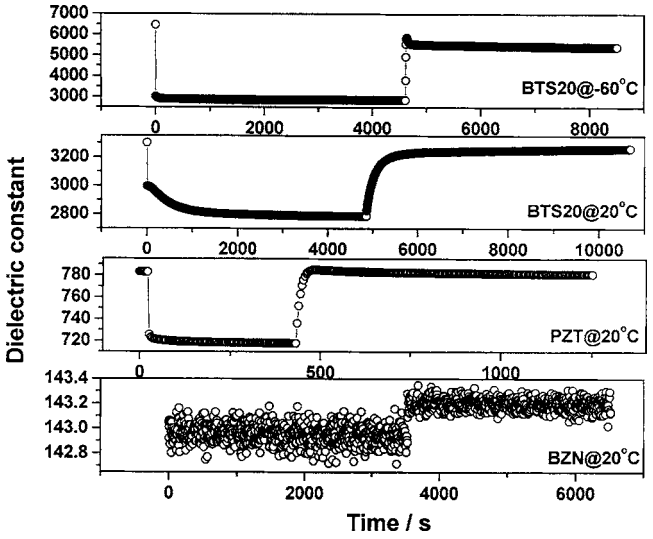

FIG. 1. Time dependence of the dielectric constant (10 kHz) after the application and removal of a bias field 1 kV/mm.

strong and the corresponding percentage is about 40.7%. This figure means nearly half of the field tunability of the paraelectric sample is contributed by slow effects! The technical meaning is: If this perplexing phenomenon is inevitable, paraelectrics should have to give its place to ferroelectrics as candidate materials of tunable microwave components because of a lack of stability. For further comparison, we measured the same time dependences of lead zirconate titanate (PZT) and bismuth zinc niobate (BZN) ceramic samples. PZT is in its ferroelectric phase at room temperature, and the relaxation is weak also. The percentage of the relaxation tunability is about 12.3%. BZN is a linear dielectrics with negligible tunability even under a strong bias field of 1 kV/mm. For all ferroelectric and paraelectric samples mentioned earlier, there are asymmetries in the dielectric constant after the removal of the bias field. Repeated cycling holds a similar variation of the dielectric constant although the absolute value may be slightly different.

Time dependences of the discharging current after the removal of a bias field of 1 kV/mm are shown in Fig. 2. Charging currents are not presented because of the noisy

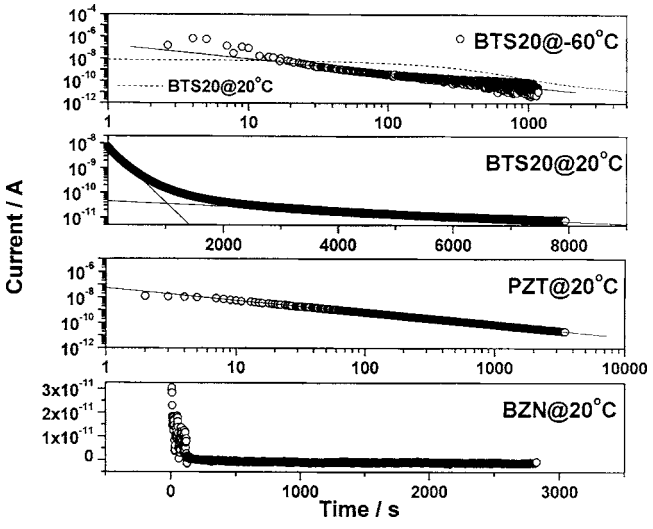

FIG. 2. Time dependence of the discharging current after the removal of a bias field 1 kV/mm.

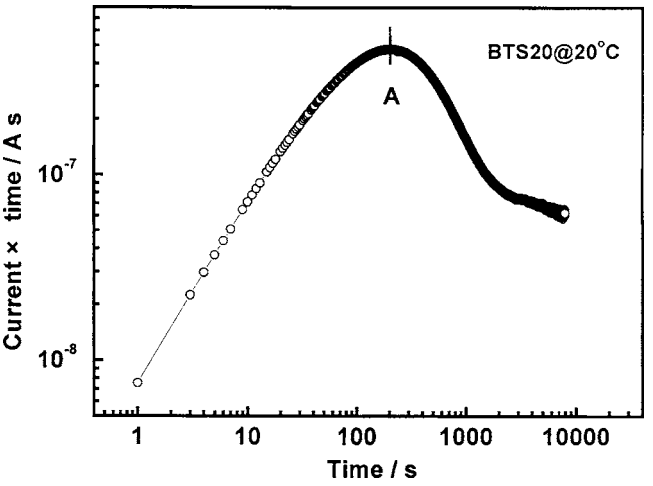

FIG. 3. Differential time domain spectrum of the discharging current of BTS20@20 °C.

conductance matrix part. The isothermal discharging current of the ferroelectric (BTS@−60°C) sample roughly exhibits a straight line in a double logarithm plot of the current and time. In other words, the relaxation function obeys the Hammon's analysis, the universal dielectric relaxation law in solids,[7] and the fitting result is

$$I(t) = 1.86 \times 10^{-7} t^{-1.27} (A). \quad (1)$$

To our surprise, for the paraelectric phase, the discharging current of the BTS sample did not obey the Hammon analysis any longer, and it did not obey either the exponential decay function or the Kohlrausch-Willams-Watts function. As shown in the top plot of Fig. 2, the dashed line (discharging current of BTS20@−20°C) is not a straight line in double logarithm coordinates. Fortunately, we can find an empirical fitting law as that shown in the second plot of Fig. 2. It is a combination of two straight lines in a single logarithm plot, i.e., a complex exponential decay function. The best fitting result is

$$I(t) = 7.04 \times 10^{-9} e^{-t/195} + 4.50 \times 10^{-11} e^{-t/4294} (A). \quad (2)$$

For PZT@20 °C sample, the discharging current exhibits well the straight line fitting in the double logarithm plot with a power index of −0.97. For the BZN sample, the current decays too fast to fitting with any known relaxation function.

Equation (2) hints that two relaxation mechanisms existed in the paraelectric BTS sample. We name them as relaxation A and relaxation B with their relaxation time of 195 and 4294 s, respectively. To examine the validity of the earlier data fitting, we take another mathematical treatment to deal with the current relaxation data, such as fast Fourier transform and differential time domain spectrum.[10] The former one is a common data processing tool and the latter one is rather specified for time domain relaxation studies, which take the current multiplied by time as a function of time. The locations of the function maxima are equal to the intrinsic relaxation times.[10] The plot of BTS@20 °C is shown in Fig. 3. The position of peak A is 200, which suggests that there is a relaxation process with a relaxation time of 200 s. This result agrees well with the earlier relaxation A (195 s) described in Eq. (2). Relaxation B cannot be picked up from Fig. 3 because of the low resolution at the long time end.

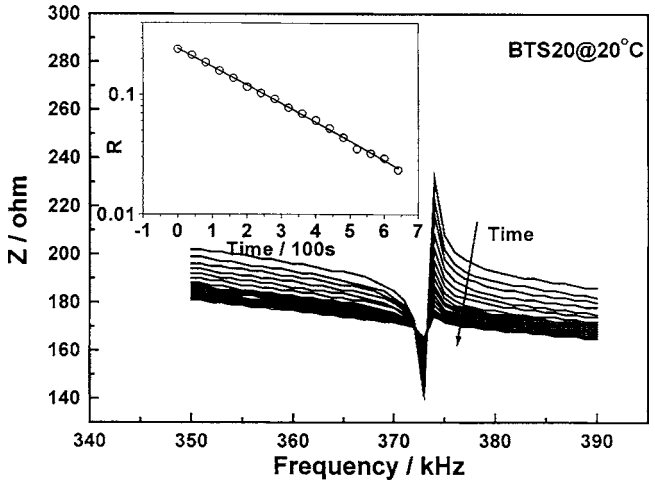

FIG. 4. Relaxation of the piezoelectric resonance of BTS20@20 °C after the removal of the bias field of 1 kV/mm.

Although one relaxation process with a relaxation time of about 200 s was confirmed up until now, its microscopic origin is not known yet. Is it space charge or something else? To answer this question, another interesting isothermal relaxation phenomenon of BTS20 should be mentioned, which is the relaxation of the field induced piezoelectric resonance as shown in Fig. 4. The present authors attributed it to the injection and decay of homocharges in the ceramics,[11] where we define parameter R as a measure of resonance strength. The straight line of $\log R$ with the time in the inlet of Fig. 4 indicates a relaxation time of 281 s, which is longer than the measured relaxation time of 93 s under the 3.3 kV/mm bias field[11] and is comparable to relaxation A (about 200 s). This agreement supports the argument, namely that the first relaxation process of paraelectric BTS20 is related to the injection and decay of the homocharges. Consequently, the strong dielectric relaxation of paraelectric BTS20 is attributed to the same origin. Injected homocharges are apt to decrease electrostatic energy within the sample, thus the material becomes electrically "stiffer" which leads to a dielectric constant decrease. And the transportation of the homocharges results in an external relaxation current. Relaxation B observed in the paraelectric BTS20 sample has a longer relaxation time as well as a higher activation energy. It may be linked to the movement of the other defect structure, which needs further discussion.

But why does the ferroelectric phase not exhibit such strong relaxation effects? Jiménez *et al.*[12] had mentioned that in aurivillius-type structure materials, defects are accumulated and frozen at domain walls. In the paraelectric temperature region, domains disappear, and those defects are de-iced. The present authors agree with this point. In the ferroelectric phase, injected homocharges are easily caught and are accumulated at domain walls. They can seldom move, thus they contribute almost nothing to the dielectric constant and current. The field tunability is mainly contributed by the reorientation of ferroelectric domains (fast) and the current obeys the universal dielectric relaxation law—the Hammon model, which corresponds to a distribution of the relaxation time. In the paraelectric phase, the temperature is higher than the Curie point and there is no ferroelectric domain. Driven by a bias field, the homocharges are relatively easy to move. This mechanism contributes much to the dielectric constant and current. The field tunability is contributed either by the response of the polar nanoregions (fast) or by the transportation of the homocharges (slow) and the relaxation current obeys the exponential decay law, which corresponds to a single relaxation time.

In summary, the isothermal relaxation of the dielectric constant and discharging current of BTS20 ceramic samples were investigated. The relaxation behavior of the ferroelectric and paraelectric phase is substantially different. The author proposes that the transportation of the homocharges is the microscopic origin of the strong relaxation observed in the paraelectric phase.

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