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Abnormal *C–V* curve and clockwise hysteresis loop in ferroelectric barium stannate titanate ceramics

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Abstract

Reversible hysteresis loop, defined as integral of small signal dielectric constant with electrical field, represents the contribution of the reversible part of polarization. In barium stannate titanate ceramics, field dependence of small signal dielectric constant was abnormal. The subsequent mathematical integral showed an abnormal clockwise hysteresis loop in the temperature range of 10–40 °C. The ferroelectric hysteresis loop measured by Sawyer–Tower circuit showed slim-waist or pinched shape. This phenomenon may reveal abnormal domain switching mechanism and is believed to be related with the strong interaction between point defects and domain walls.

Keywords: Barium stannate titanate; *C–V* curve; Clockwise hysteresis loop; Slim-waist or pinched hysteresis loop

1. Introduction

For non-linear dielectrics, the dielectric constant is field dependent and we can control the dielectric constant by adjusting field strength. With this feature, many kinds of devices can be developed, such as dielectric amplifier, parametric device, microwave frequency multiplier [1,2], switching circuit snubber [3,4], especially the microwave ferroelectric phase shifter used in phased array antenna developed in recent years [5–8]. Despite of the multi-purpose applications, the mechanism of the dielectric non-linearity is lacking of comprehensive understanding, therefore we need pay more attention to the bias field related dielectric experimental study. In the present study, we measured the *C–V* (capacitance–voltage) curve of barium stannate titanate ceramics and found abnormal hysteresis in temperature range of 10–40 °C.

Lohse et al. [9] and Bolten et al. [10] integrated the capacitance with voltage to calculate the reversible part of polarization, and they detached conventional hysteresis loop into contributions of both reversible and irreversible parts. It bridges the physical meaning of *C–V* curve with reversible polarization. Following the same procedure, we had got a clockwise reversible hysteresis loop as shown in the present study. After successfully explained the rubber-like elasticity of shape alloy [11], Ren [12] interpreted a closed single polar strain hysteresis loop of single crystal barium titanate by appreciating strong interaction between defects and domain walls. Approving his point, we may have basic understanding of the slim-waist or pinched shape hysteresis loop measured by Sawyer–Tower circuit.

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 [13], it riveted many research interests due to its abnormal dielectric properties and strong dielectric non-linearity recently [14–17].

2. Experimental

BTS10 ($BaTi_{0.90}Sn_{0.10}O_3$) ceramic was prepared by solid-state reaction. Reagent grade barium carbonate, strontium carbonate and titania were used as starting materials. Stoichiometric proportioning raw materials were ground by zirconia balls for twice time with a 1000–1100 °C calcination introduced between the twice grinding. 12 mm diameter green pallets were fired at about 1400 °C for 2 h. The ceramic prepared is dense (relative density > 95%) and the average grain size is less than 10 μm. XRD results indicate that only pure

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perovskite structure exists for both calcinated and fired bodies. Sample pallets were cut into 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.

The direct current field was generated by a high voltage source (SRS 350, Stanford Research System Inc.). Two high precision LCR meter (HP4284A, Hewllet Packards Corp. and TH2816, Tonghui Electronic Instrument Corp.) were employed to measure the field-dependent dielectric constant of the above samples. A protection circuit was introduced between the source and the LCR meter to prevent devices from any high voltage damage. A set of Sawyer–Tower circuit was used to measure hysteresis loop. Sample was put into a temperature chamber (Delta9023, Delta Design) for purpose of temperature control.

3. Results

As shown in Fig. 1, there are dielectric constant maxima around 57 °C, indicating the ferroelectric to paraelectric phase transition. Also there are two groups of dielectric absorption maxima. One of them located at 50–56 °C, which shows slight frequency dispersion, is correlated with the above mentioned phase transition. The other one located around 20 °C may represent phase transition of rhombohedral to orthorhombic or orthorhombic to tetragonal or even the sum of the both. It is hard for us to tell the difference between those phases because all of these phases may

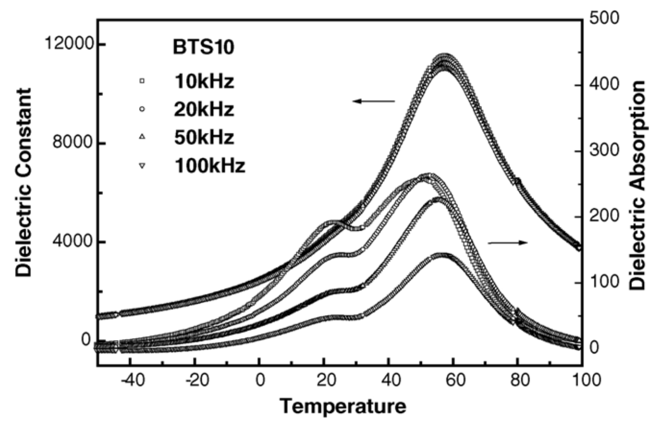

Fig. 1. Temperature dependence of dielectric constant and dielectric absorption of BTS10 ceramics.

exhibit cubic like diffraction patterns by laboratory X-ray diffraction.

Fig. 2 shows dielectric constant variation with biased electrical field of BTS10 at temperatures from 50 to −20 °C. At −20 °C and −10 °C, there are “normal” *C–V* curve, which is characterized of the hysteresis of dielectric constant maxima with sweeping bias voltage. At 0 °C, the *C–V* curve is hysteresis free. For the cases of temperature rising up to 10, 20, 30 and 40 °C, the curves are abnormal, which means that the dielectric constant maxima precedes to instead of lags behind the sweeping bias voltage. At 50 °C, the *C–V* curve is hysteresis free again. The detailed variations are plotted in Fig. 2, where the arrows indicating the bias voltage sweeping direction. Fig. 3 shows the integrated clockwise polarization

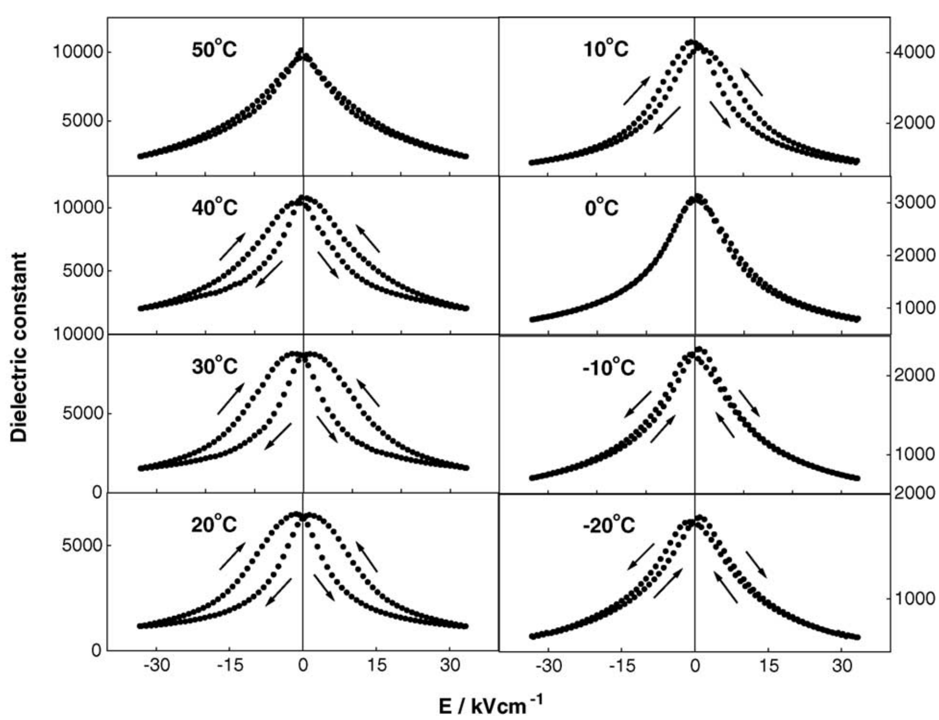

Fig. 2. Dielectric constant variation with biased electrical field of BTS10 at temperatures from 50 to −20 °C.

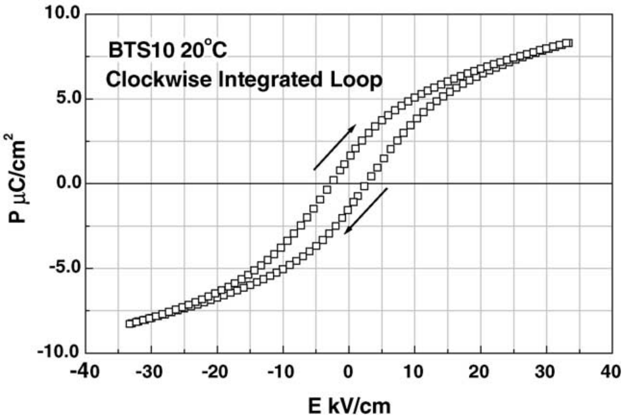

Fig. 3. Clockwise integrated polarization hysteresis loop of BTS10 at 20 °C.

hysteresis loop of BTS at 20 °C. The mathematical process followed the next equation:

$$\Delta P = \varepsilon_0 \varepsilon_r \Delta E \quad (1)$$

where, ΔP and ΔE are the step increases of polarization and electrical field, respectively. It should be noted again that, the integration of small signal dielectric constant produces reversible part of polarization only, which is different to the polarization measured by conventional Sawyer–Tower circuit. Thus the clockwise reversible hysteresis loop does not introduce any contradiction with positive energy consumption which is equal to the area inside convention hysteresis loop.

To investigate the origin of abnormal *C*–*V* curve, we had measured hysteresis loops of BTS10 at several temperatures by Sawyer–Tower circuit as shown in Fig. 4. Corresponding to the normal *C*–*V* curves at −30 and −20 °C, the hysteresis loops seem similar to that of ordinary soft ferroelectrics. While for that at 10 and 20 °C corresponding to the abnormal *C*–*V* curves, the loops are slim-waist or pinched, that means the remanent polarizations drastically decrease when *E* sweeps across zero.

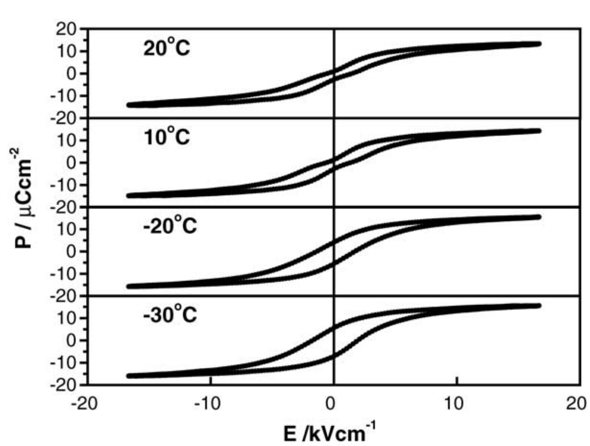

Fig. 4. Polarization hysteresis loop measured by Sawyer–Tower circuit of BTS10 at temperatures from −30 to 20 °C. The curves were smoothed and loss corrected.

4. Discussion

In order to interpret the origin of the abnormal *C*–*V* curve and clockwise reversible hysteresis loop, we need to talk about the mechanism of slim-waist or pinched hysteresis loop measured by Sawyer–Tower circuit first.

There were several reports on slim-waist or pinched hysteresis loop, such as that reported by Li et al. [18] and the references cited in Li's paper. Li attributed the pinched loop to the existence of defect dipoles. He believed that the dipoles will prevent domains from switching. This may be reasonable and roughly consistent with the earlier explanations he cited. Ren [12] proposed that the point defect will keep symmetry similar to that of crystal. Therefore, the existence of point defect drives switched domain walls back to their original position when external field is removed. This produces double hysteresis loop as observed.

The present authors agree that the strong interaction between point defects and domain walls may induce the slim-waist or pinched shape hysteresis loop, such as that we observed in barium stannate titanate. Actually, this is further supported by both the aging and fatigue experimental results. Lacking of aging time after annealing or repeating of 10^4 fatigue cycles decline the trend of abnormal.

Based on the above mechanism, abnormal *C*–*V* curve is easy to be understood. When field is decreased after domains were fully orientated, point defects may drive domain walls back to the original positions. This equilibrium state may rise small signal dielectric constant up to its maximum. Therefore, the strong interaction between point defects and domain walls is the reason for both abnormal *C*–*V* curve and clockwise reversible hysteresis loop. At very low temperatures, there is strong damping for domain wall to move, so the above mechanism is prohibited. Obviously, the mechanism is also disabled at temperature high enough to destroy domain structure. Therefore, this procedure is temperature related.

A competitive explanation is related with field injected homocharge near sample surface, the author tends to ignore this due to the absent observation of slow relaxation of piezoelectric resonance in BTS10 [14]. Another competitive explanation is field induced phase transition. Although, we cannot approve or disapprove this point with direct evidence of X-ray diffraction, this explanation can be ignored yet, because the wide temperature range of abnormal *C*–*V* curve and abnormal hysteresis loop rule out the possibility of phase transition.

5. Conclusion

Abnormal *C*–*V* curve and clockwise reversible hysteresis loop were observed in barium stannate titanate ceramics in the temperature range 10–40 °C. The polarization hysteresis loop measured by Sawyer–Tower circuit showed slim-waist or pinched shape at that temperatures. This phenomenon may reveal abnormal switching mechanism and is believed to be related with the strong interaction between point defects and domain walls.

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