Maximum self-generated electric field induced by pyroelectricity of PZT 95/5

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Abstract
Electric field induced by pyroelectric effect is often observed in the ferroelectric devices when they subject to temperature change. But the maximum value of ferroelectric field is still unknown. If this value exceeds the coercive field or even reaches breakdown field, the ferroelectric devices may be damaged. In this study, pyroelectrical experiment of PbZr0.95Ti0.05O3 (PZT 95/5) ferroelectric ceramics was conducted to understand maximum self-generated pyroelectric field. An equivalent circuit and path of pyroelectricity was built to analyze the pyroelectric field of PZT 95/5. Results indicated that maximum pyroelectric field is about 1.1 kV/mm. This value is controlled by the internal resistivity of PZT 95/5. A mean internal resistivity of PZT 95/5 is about $1 \times 10^9 \, \Omega\cdot m$ during the low-temperature to high-temperature rhombohedral phase transformation.

1 INTRODUCTION

Phase transformation between low-temperature to high-temperature rhombohedral phase transformation ($FE_{LT}$→$FE_{HT}$) was first reported by Barnett through electrical measurements. The transformation in the PZT ferroelectric rhombohedral region is characterized by anomalies in the dielectric loss, pyroelectric current, and transformational strain. Neutron and X-ray diffraction studies have shown additional superstructure reflections in the low-temperature rhombohedral phase, revealing the doubling of the perovskite unit cell. The space groups of the high- and low-temperature rhombohedral phases are $R3m$ and $R3c$, respectively. The charge released by lead zirconate titanate PbZr0.95Ti0.05O3 (PZT 95/5) is approximately 3 μC/cm², and the temperature of $FE_{LT}$→$FE_{HT}$ transformation is about 40°C. Because the phase transformation temperature is close to room temperature (RT) and the relative high current will produce, this kind of nonlinear pyroelectric effect induced by phase transformation can be used as thermoelectric application nearby RT. $FE_{LT}$→$FE_{HT}$ transformation is reversibility and far away from Curie temperature, the depolarization effect can be ignored. In most research, pyroelectric...
effect was studied in short circuit or low electric field.\(^4\,\,6\,-\,\,7\) But in thermoelectric application, high electric field may be introduced when high impedance load is used.\(^8\) So the maximum electric field induced by FE\(_{HT}\)–FE\(_{LT}\) transformation needs research.

PZT 95/5 has also been utilized in shock-driven pulsed power supplies for a number of years.\(^9\,\,11\) When the shock-driven pulsed power supplies were fabricated, tested, and experimented, the temperature of PZT 95/5 will increase from room temperature to the temperature above FE\(_{HT}\)–FE\(_{LT}\) transformation point or decreased from high temperature to room temperature. The reverse FE\(_{HT}\)–FE\(_{LT}\) transformation due to temperature change was occupied by pyroelectric current output. When the outside circuit of PZT 95/5 was high impedance or even in open condition, high electric field will be resulted. Does this kind of high electric field exceed coercive field or even make PZT 95/5 electric breakdown? In this investigation, a special focus has been placed on peak electric field induced by pyroelectric effect of PZT 95/5 when the reversed FE\(_{LT}\)–FE\(_{HT}\) phase transformation occurred.

## 2 | EXPERIMENTAL PROCEDURE

PZT 95/5 ceramic samples were prepared by a conventional mixed-oxide method using high-purity oxide powder. The mixtures were calcined at 1,123 K for 2 h; then, the green bodies were sintered at 1563–1603 K for 1 h in a controlled PbO atmosphere. Rectangular bars of the ceramic were cut and polished to form samples 10 mm × 10 mm × 0.1 mm in size. Silver electrodes were deposited on both the 10-mm and 10-mm surfaces. A 20 kV/cm poled field was applied to the bars. Polarization-electric field (P–E) hysteresis loops were measured using a hysteresistester (TF Analyzer2000) in a silicone oil bath at different temperatures in the range 20 - 150°C using triangular voltage waveforms. Dielectric constant was tested at the frequency of 1 kHz by an impedance analysis (Agilent 4294A).

Sample heating was conducted in a fast temperature change system (China Fangrui, WDW-100). Sample was heated from RT to 80°C (FE\(_{HT}\)–FE\(_{LT}\) transformation happened) in air at a rate of 3°C/s and then kept at this temperature (the temperature was tested by thermocouple nearby sample). Pyroelectric voltage was directly measured using a KeithleyP6517a electrometer (Inner resistance: 200 GΩ, Capacitance: 10 pF, Maximum voltage: 200 V). The data were automatically acquired by the computer, and the sampling rate was 2 points per second.

When the pyroelectric voltage was past, the sample was cooled by directly immersed in silicon oil at room temperature. The same measurement was conducted.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Simple theory analysis

According to the early pyroelectric experimental results, the electric charge, released by FE\(_{HT}\)–FE\(_{LT}\) transformation, is about 3 μC/cm\(^2\) in short circuit condition.\(^4\) If all the charge cumulates on the samples, the electric field (E) is expressed by the following equation.

\[
Q = CU \Rightarrow \Delta PS = \epsilon_0 \epsilon_r \frac{S}{d} U \Rightarrow \Delta P = \epsilon_0 \epsilon_r \frac{U}{d} \Rightarrow E = \frac{\Delta P}{\epsilon_0 \epsilon_r} \quad (1)
\]

where \(Q\) is the electric charge, \(C\) is capacitance, \(U\) is voltage, \(\Delta P\) is the change of polarization during to FE\(_{HT}\)–FE\(_{LT}\) transformation (~3 μs/cm\(^2\)), \(S\) is the area of electrode face, \(\epsilon_0\) is the dielectric constant of vacuum, \(\epsilon_r\) is the relative dielectric constant (~260), and \(d\) is the thickness of sample.

According to Equation (1), the electric field can reach 13 kV/mm. This value is higher than coercive field and even reaches the breakdown strength. PZT 95/5 samples will be electric breakdown in such condition. But in fact, PZT 95/5 is heated from RT to high temperature above the FE\(_{HT}\)–FE\(_{LT}\) transformation point in open circuit condition, electric breakdown is not observed. Equation (1) is too simple to describe the pyroelectric behavior of PZT 95/5 in open circuit.

### 3.2 | Experimental results

Figure 1 and 2 give the pyroelectric voltage of PZT 95/5 subjected to heating and cooling, respectively.

![FIGURE 1 Pyroelectric field of PZT 95/5 in open circuit during heating process (RT → 80°C, 3°C/s)](image-url)
From Figures 1 and 2, pyroelectric voltage is about 110 V, and the thickness of sample is 0.1 mm, and the final electric field is about 1.1 kV/mm. This value is much lower than the estimated electric field from Equation (1) and is consistent to the fact that PZT 95/5 has not electric breakdown when it was heated from RT to high temperature without any load. Comparing with the coercive field, electric field resulted by pyroelectric effect is close to the coercive field at RT.

Comparing Figure 1 with Figure 2, pyroelectric voltage is positive when the sample is heated, and on the contrary, it is negative. Figures 1 and 2 are not strictly mirrored, part of the reason is that the different temperature change rate is applied. The peak value of pyroelectric voltage is almost same regardless of heating and cooling. When the voltage reaches peak value, pyroelectric voltage decreases with time increasing, which means that electric leakage exists in pyroelectric process. This kind of leakage is not considered in Equation (1).

### 3.3 Path of polarization change and equivalent circuit of pyroelectricity

In order to get the right value of polarization change, P – E hysteresis loops of PZT 95/5 at different temperatures are given in Figure 3.

When sample was heated from RT to 80 °C, the polarization shifted from point A to point B in short condition. But in open state, the repolarization effect should be considered, the polarization shifted from point A to point C and \( \Delta P_{A-C} < \Delta P_{A-B} \). In the same way, when samples were cooled from 80 °C to RT, the polarization shifted from point B to point D in open state, and \( |\Delta P_{B-D}| < |\Delta P_{B-A}| \). Equation (1) did not consider the repolarization effect of PZT 95/5 under high electric field. Here, \( \Delta P_{A-C} \) and \( \Delta P_{B-D} \) are 2.3 μC/cm² and −0.45 μC/cm², respectively. The unequal value of \( \Delta P_{A-C} \) and \( \Delta P_{B-D} \) also makes that Figure 1 and 2 are not strictly mirrored. The value of \( \Delta P \) in Equation (1) is replaced by \( \Delta P_{A-C} \) or \( \Delta P_{B-D} \). Pyroelectric voltage estimated by Equation (1) decreased to 10 kV/mm, and −2.0 kV/mm, respectively. These values are still higher than that of experimental results.

In order to explain the difference of theoretical and experimental value, leakance in whole pyroelectric system must be considered. There are two parts of leakance: one is the leakance of PZT 95/5 sample and another is the leakance of a KeithleyP6517a electrometer. Figure 4 gives the schematic of equivalent circuit of pyroelectric system.

In this equivalent circuit, PZT 95/5 sample was simplified to be a current source in parallel with a capacitor \( C_0 \) and an internal resistance \( R_0 \). External load is a capacitor \( C_1, 10 \) pF in parallel with a resistance \( R_1, 200 \) GΩ from a Keithley P6517a electrometer. Because \( C_1 « C_0 \) and \( R_1, R_0 \), \( C_1 \) and \( R_1 \) can be ignored, almost open circuit condition reaches. According to Kirchhoff’s current and voltage laws, the relationships below were obtained.

\[
Q = C_0 U + \int_0^t \frac{U}{R_0} dt
\]  

(2)
where \( t \) is time. Comparing Equation (2) with Equation (1), the charge leakage of internal resistance \( (R_0) \) is main reason why the theoretical voltage estimated by Equation (1) is higher than the experimental value.

When a mean value \( R_{0M} \) is used to replace \( R_0 \), this value can express as

\[
R_{0M} = \frac{\int_0^t U dt}{Q - C_0 U} = \frac{\int_0^t U dt}{\Delta PS - C_0 U}
\]  

(3)

Here, \( t = 0 \) defined as beginning of pyroelectric effect. Denominator of Equation (3) can be calculated according to Figure 1 or Figure 2. \( R_{0M} \) estimated by Equation (3) is about 1 GΩ (resistivity of \( 10^9 \)Ω·m). This resistivity is lower than the bulk resistivity of PZT95/5 under ambient conditions. Decreasing of resistivity is related to FELT–FEHT phase transformation. Resistivity of \( 10^9 \) Ω·m is still a dielectric not a semiconductor, and this kind of resistance limits maximum electric field induced by pyroelectric of PZT 95/5 during ferroelectric phase transition.

4 | CONCLUSION

Experimental results indicate that maximum electric field induced by pyroelectric of PZT 95/5 during ferroelectric phase transition is about 1.1 kV/mm. This value is greatly less than theoretical value without considering repolarization effect and leakage of PZT 95/5. When repolarization effect is considered, the estimated pyroelectric field decreases, but is still higher than experimental value. Leakage of PZT 95/5 plays an important role on limiting the pyroelectric field in open circuit, and the mean value of resistive of PZT 95/5 is about 1 GΩ·m during ferroelectric phase transition.

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