

## Effect of Polarization on Mechanical Properties of Lead Zirconate Titanate Ceramics

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**Abstract:** This study concerns two following commercial lead zirconate titanate (PZT) materials, “soft” PZT-5H and “hard” PZT-8 piezoelectric ceramics. Young’s modulus and internal friction versus temperature at different vibration frequencies were investigated by means of Dynamic Mechanical Analysis (DMA) before and after polarization. The phase transition temperatures ( $T_c$ ) of PZT-5H and PZT-8 ceramics were 438 K and 550 K. PZT-8 ceramic had higher Young’s modulus than PZT-5H ceramic at ferroelectric phase, which resulted from the increase of internal local stress in PZT-8 ceramic. After polarization, the Young’s modulus of both PZT ceramics increased, the influence of the piezoelectric effect was investigated. A relaxation peak emerges in internal friction curve of each PZT sample. Considering the hard ceramic, this peak is a pure relaxation mechanism controlled by oxygen vacancies diffusion. Considering the soft ceramic, the relaxation peak can be related to viscous motion of domain walls and the interaction between domain walls and point defects. The activation energy of the relaxation peak increased after polarization, which resulted from the increased local internal stress and directional arranged space charges caused by polarization.

**Key words:** Young’s modulus; internal friction; DMA; PZT; polarization

Piezoelectric materials are widely used for applications in microelectronics or power transducers. One of the most commonly piezoelectric materials, lead zirconate titanate (PZT) ceramics, are widely used in industry: they are used as transducers between electrical and mechanical energy, such as phonograph pickups, air transducers, underwater sound and ultrasonic generators, delay-line transducers, wave filters, *etc.*<sup>[1-5]</sup>. In order to improve dielectric, piezoelectric and mechanical properties, the PZT ceramics with perovskite structure ( $\text{ABO}_3$ ) are usually substituted in A-or/and B-sites<sup>[6-7]</sup>. The major reasons for these improvement are the creation of cation vacancies in donor doped PZT (“soft” PZT) and oxygen vacancies in acceptor doped PZT (“hard” PZT). So “soft” PZT ceramics like PZT-5H always possess high permittivity and electromechanical coupling factor, which suitably serve as receiver type transducers. And “hard” PZT ceramics like PZT-8 are used as emission type transducer due to their high tensile strength and mechanical quality factor, as well as low loss.

In the case of applications in piezoelectric damping devices and piezo-actuators, the mechanical properties of piezoelectric materials always determine their using environment and life<sup>[8-9]</sup>. So studies on elastic modulus, inter-

nal friction and fatigue behavior, *etc.* by mechanical tests are meaningful for piezoelectric materials. In addition to studying the important parameters for mechanical properties, the mechanical tests are also very sensitive to reflecting relaxation process of point defects, phase transitions, domain walls and its mobility, which significantly affect the ferroelectric properties<sup>[10]</sup>. So the mechanical properties have been used as applicable means to investigate substantial information on structural features and to explore the fundamental principles in ferroelectric materials and their applications<sup>[11-12]</sup>. As an efficient technique of mechanical measurement, dynamic mechanical analysis (DMA) has a lot of advantages such as wide applicability and simple operation. In addition, DMA can supply information about major transitions as well as secondary and tertiary transitions not readily identifiable by other methods<sup>[12]</sup>. However, DMA is rarely used to study phase transitions in metals and ceramics in the present work although it is widely used to determine glass transitions in polymers and co-polymers<sup>[13-14]</sup>. Therefore, we explored the Young’s modulus and internal friction of two typical PZT ceramics, one “soft” (PZT-5H) and one “hard” (PZT-8) by a dynamic mechanical analysis system. The relaxation processes of these PZT ceramics are ana-

lyzed and the mechanisms controlling the relaxation processes were discussed. The effect of polarization on the Young's modulus and internal friction was also investigated.

## 1 Materials and Methods

PZT-5H and PZT-8 ceramics were provided by the Baoding Hongsheng Acoustics Electron Apparatus Co., Ltd. And the samples were prepared as chips of 25 mm×10 mm×1 mm. The mechanical properties of PZT ceramics were measured by a dynamic mechanical analysis system (DMA8000, PerkinElmer). The two obvious features of DMA are that first, the frequencies applied are extremely low (0.1–100 Hz); second, the sample is stressed by an oscillating external stress. The analysis system of DMA8000 contains various deformation modes, such as tensile, compression, shear, bending (including three point bending, single cantilever and double cantilever beam). In this study, we chose three point bending deformation modes. The bending test was performed with a constant span length of 10 mm, and a fixed driven amplitude of 0.001 mm. Then the Young's modulus and internal friction at a temperature spectrum during the experiment at a fixed frequency was obtained. The piezoelectric constant  $d_{31}$  of PZT samples were measured using a quasi-static  $d_{33}/d_{31}$  meter (ZJ-6A, Institute of Acoustics, Beijing, China). The dielectric constants were measured using a high-precision LCR meter (Agilent E4980A).

## 2 Results and discussion

### 2.1 Young's modulus of PZT ceramics

The Young's modulus of PZT-5H and PZT-8 ceramics versus temperature at different vibration frequencies of 0.1, 0.5, 1, 5 and 10 Hz were measured by DMA before and after polarization, as shown in Fig. 1 and Fig. 2. An obvious valley appeared with frequency independence was induced by the phase transition of ferroelectric-paraelectric, and the phase transition temperatures ( $T_c$ ) were 438 K (Fig. 1) and 550 K (Fig. 2). There was a kink at ferroelectric phase in each Young's modulus curve. The kinks appeared at 374 K (Fig. 1), 470 K (Fig. 2) with the vibration frequency of 0.1 Hz, and they shifted to higher temperature with the increasing frequency. After polarization, the turning temperature and turning angle of this kink were raised in each sample. This kink may be produced by a relaxation process, the studies of the mechanism would be detailed in an upcoming sections. Young's modulus of PZT-8 was higher than PZT-5H below phase transition temperature before and after polarization, which was

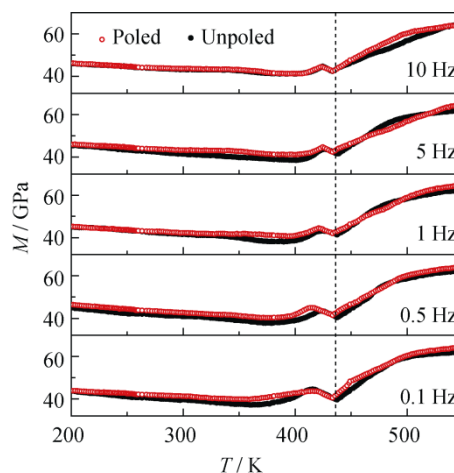


Fig. 1 Temperature dependent Young's modulus of unpoled and poled PZT-5H at different frequencies

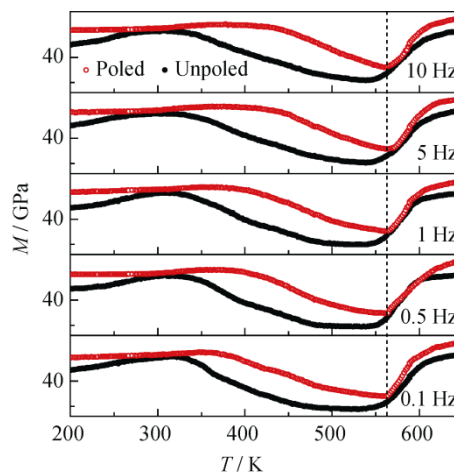


Fig. 2 Temperature dependent Young's modulus of unpoled and poled PZT-8 at different frequencies

probably due to the increase of internal local stress in PZT-8 ceramic<sup>[15]</sup>. There were additional oxygen vacancies produced by low valence doping ions ( $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ , etc.) in PZT-8 ceramic, which played a pinning effect in domain movement, and made the local stress difficult to release. The PZT-5H ceramic doped by high valence irons ( $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ , etc.), in contrast, had more cation vacancies to balance the valence state. These cation vacancies played an opposite effect. Which enabled the local stress induced by domain rotation more easily release. In other words, the effects of the local stress induced by domain rotation were cushioned by these cation vacancies in PZT-5H.

It showed that the Young's modulus of PZT-5H and PZT-8 ceramics increased at ferroelectric phase after polarization. We believed that this maybe related to piezoelectric effects. When the contraction stress  $X_1$  applied perpendicular to polarization axis, elastic strain  $x_1^{(1)}$  was produced. At the same time,  $X_1$  generated an electric field

$E_3'$  due to piezoelectric effects.

$$x_1^{(1)} = s_{11}^E X_1 \quad (1)$$

$$E_3' = -d_{31} X_1 / \varepsilon_{33}^X \quad (2)$$

Here the elastic compliance  $s_{11}^E$ , the dielectric constant  $\varepsilon_{33}^X$  and the piezoelectric constant  $d_{31}$  are temperature-dependent. An additional elastic strain  $x_1^{(2)}$  was produced by  $E_3'$  through secondary converse piezoelectric effect. So the elastic strain  $x_1$  is the sum of  $x_1^{(1)}$  and  $x_1^{(2)}$ .

$$x_1^{(2)} = -d_{31}^2 X_1 / \varepsilon_{33}^X \quad (3)$$

$$x_1 = (s_{11}^E - d_{31}^2 / \varepsilon_{33}^X) X_1 \quad (4)$$

The piezoelectric constants ( $d_{31}$ ) of poled PZT-5H and PZT-8 piezoelectric ceramics were measured at room temperature, as  $-262 \times 10^{-12}$  C/N and  $-90 \times 10^{-12}$  C/N. It was found that  $d_{31}$  of both unpoled PZT samples were close to zero, so we calculated that  $s_{11}^E$  of PZT-5H and PZT-8 samples were approximately equal to the reciprocal of Young's modulus measured before polarization, which were  $25.3 \times 10^{-12}$  m<sup>2</sup>/N and  $20.3 \times 10^{-12}$  m<sup>2</sup>/N, respectively. And the dielectric constant of poled PZT samples were studied at room temperature with frequency of 1 KHz, and the values were  $4600 \times 8.85 \times 10^{-12}$  F/m and  $1068 \times 8.85 \times 10^{-12}$  F/m for PZT-5H and PZT-8 samples, respectively. According to the formula (4), PZT-5H and PZT-8 samples

had respectively 7% and 4% increases in Young's modulus after polarization. It is shown that values computed by formula have approached the practical data, reflected the important influence of piezoelectric effect on Young's modulus in PZT piezoelectric ceramics.

## 2.2 Internal frictions of PZT ceramics

As shown in Fig. 3 and Fig. 4, the internal frictions of PZT-5H and PZT-8 ceramics at different frequencies during the continuous increase of the temperature were measured before and after polarization. There were two peaks ( $P_t$ ,  $P_r$ ) in each internal friction curve of two PZT samples. The  $P_t$  with  $\lambda$ -like shape in each curve, existing at around  $T_c$ , was produced by ferroelectric-paraelectric phase transition. The  $P_r$  showed an obvious shift towards high temperature with increasing frequency, and as a result, it was controlled by relaxation process.

The calculation of its activation parameters with the Arrhenius plots (Fig. 5) help to determine the nature of relaxation processes. From Arrhenius Law, activation energy ( $H$ ) and relaxation limit time ( $\tau_0$ ) are linked as<sup>[16-18]</sup>.

$$\tau = \tau_0 e^{H/kT} \quad (5)$$

where  $T$  is the absolute temperature,  $k$  the Boltzmann constant,  $\tau$  is relaxation time. For the case of a Debye-type

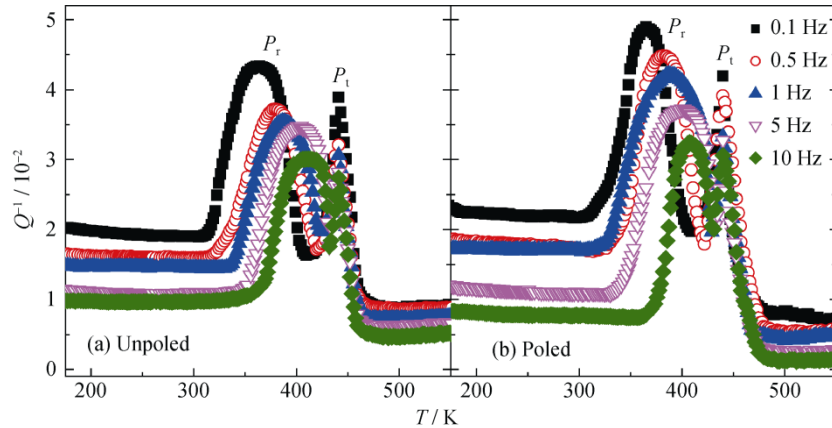


Fig. 3 Temperature dependent internal friction of unpoled (a) and poled (b) PZT-5H at different frequencies

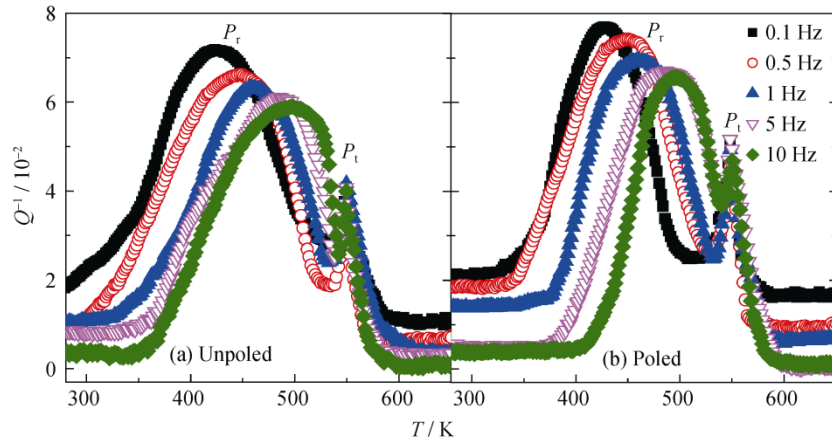


Fig. 4 Temperature dependent internal friction of unpoled (a) and poled (b) PZT-8 at different frequencies

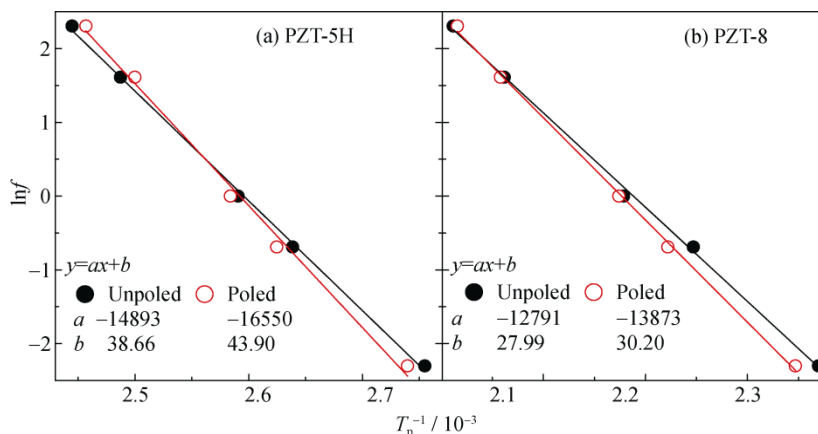


Fig. 5 Arrhenius plots and fitting lines for Pr in PZT-5H (a) and PZT-8 (b)

relaxation peak,  $\ln(2\pi f\tau) = 0$  at  $T_p$ , this gives:

$$\ln f = -H/kT_p - \ln 2\pi\tau_0 \quad (6)$$

Where  $T_p$  and  $f$  corresponds to the peak temperature and the measurement frequency, are shown in Table 1. It is clearly to see that the  $1/T_p$  has a liner connection with  $\ln f$  from formula (6). Subsequently, the Arrhenius plots were made according to the data of Table 1, as shown in Fig. 5. From the slope and intercept of the straight lines we can calculate  $\tau_0$  and  $H$  of each  $P_r$ , as shown in Table 2. The results obtained are close to ones reported with undoped<sup>[17]</sup> and doped PZT materials<sup>[19]</sup>.

The  $H$  of  $P_r$  in PZT-8 ceramic is close to the one for oxygen vacancies diffusion (0.9 eV)<sup>[20-21]</sup>. It is suggested that the relaxation process has a pure relaxation mechanism controlled by the migration of oxygen vacancies. Our opinion is supported in other aspects by the fact that the  $P_r$  height decreases with increasing temperature. According to the point defect relaxation theory<sup>[20]</sup>, the temperature dependence of the  $P_r$  strength  $\Delta$  (the square of  $P_r$  height) will be analogous to the Curie-Weiss law due to the interactions between point defects:

$$\Delta^{-1} \propto (T - T_0) \quad (7)$$

Where  $T_0$  is the critical temperature for a “self-induced” ordering. For clarity, the relationship between the  $\Delta$  of PZT-8 ceramic (prior to and after polarization) and the temperature are shown in Fig. 6(b), where linear relations are observed in the range of experimental errors and  $T_0$  (254 K and 246 K) are deduced. The linear relation clearly indicated that this relaxation process is induced by point defect diffusion. Considering the point defect structure of perovskite oxides, there is no evidence of interstitial defects, and only vacancies need to be considered<sup>[22]</sup>. Therefore, the point defects responsible for relaxation peak of PZT-8 ceramic are in most probabilities by the oxygen vacancies. Table 2 shows the  $H$  of  $P_r$  increases after polarization, that is, the migration of oxygen vacancies in PZT-8 ceramic becomes more difficult. In the process of polarization, the rotation of the 90° domains can cause a local stress inside the crystal. In the subsequent polarization reversal of the domains, it is too fast for this local stress to be released and as a result the migration of oxygen vacancies was constricted after polarization. In addition, there are space charges in almost all ferroelectrics, and the carriers in the ferroelectrics induced by electrode can change to space charges under the action of polarization. After polarization, these directional arranged space charges will make a pinning effect on the motion of oxygen vacancies.

It is supposed that the relaxation process of PZT-5H ceramic is also related to oxygen vacancies diffusion, due to the  $H$  of  $P_r$  only a little higher than oxygen vacancies diffusion. But the  $\tau_0$  was very small. The relationship between the  $\Delta$  of PZT-5H ceramic (before and after polarization) and the temperature are shown in Fig. 6(a). The weak linear dependence relations suggested that the relaxation process is not solely induced by point defect diffusion. In PZT-5H ceramic, the cation vacancies increased and oxygen vacancies decreased due to the doping with high valence ions as  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ . So this relaxation peak

Table 1 Relaxation internal friction peak temperatures of PZT ceramics at different frequencies

$T_p/\text{K}$ $f/\text{Hz}$	PZT-5H (Unpoled)	PZT-5H (Poled)	PZT-8 (Unpoled)	PZT-8 (Poled)
0.1	363	365	422	426
0.5	379	381	445	450
1	386	387	459	460
5	402	400	485	486
10	409	407	497	496

Table 2 Relaxation parameters for the relaxation internal friction peaks of PZT ceramics

	PZT-5H (Unpoled)	PZT-5H (Poled)	PZT-8 (Unpoled)	PZT-8 (Poled)
$H/\text{eV}$	1.28	1.43	1.10	1.19
$\tau_0/\text{s}$	$2.6 \times 10^{-18}$	$3.7 \times 10^{-20}$	$1.1 \times 10^{-13}$	$1.2 \times 10^{-14}$

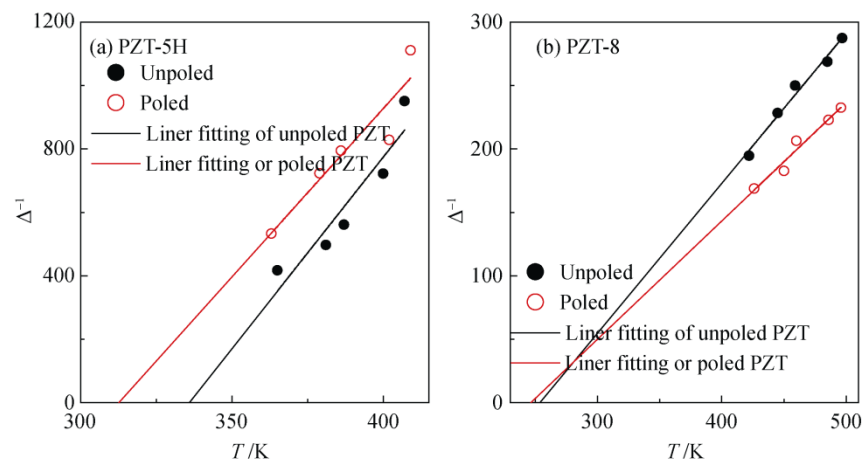


Fig. 6 Relationship of the Pr strength ( $\Delta$ ) and temperature in PZT-5H (a) and PZT-8 (b)

can be related to a complex mixture of various mechanisms, for example, combination of the viscous motion of domain walls and the interaction between domain walls and vacancies<sup>[23-25]</sup>. The  $H$  of  $P_r$  also increases after polarization, as shown in Table 2. The same as PZT-8 ceramic, the increase of  $H$  was due to the local stress and directional arranged space charges produced by polarization process. They made the motion of domain walls and vacancies more difficult, and hindered the interaction between domain walls and vacancies.

### 3 Conclusions

The phase transition temperatures ( $T_c$ ) of PZT-5H and PZT-8 ceramics were 438 K and 550 K, respectively, by DMA measurement. Young's modulus of PZT-8 was higher than PZT-5H at ferroelectric phase, which was probably due to the increase of internal local stress in PZT-8 ceramic. After polarization, the Young's modulus of both PZT ceramics increased, and it reflected the important influence of piezoelectric effect on elastic modulus in PZT ceramics. A relaxation peak  $P_r$  emerged in each internal friction curve, and its relaxation parameters were calculated by Arrhenius law. The results suggested that the  $P_r$  of PZT-8 ceramic is produced by the migration of oxygen vacancies. The  $P_r$  of PZT-5H ceramic can be related to viscous motion of domain walls and the interaction between domain walls and vacancies. The activation energy increased after polarization, which resulted from the increased local internal stress and directional arranged space charges caused by polarization.

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## 极化对锆钛酸铅陶瓷力学性能的影响

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**摘 要:** 本工作所采用的样品为锆钛酸铅陶瓷 PZT-5H 与 PZT-8, 用动态力学分析仪(DMA)测试了极化前后 PZT-5H 与 PZT-8 在不同力学荷载频率下的杨氏模量和内耗与温度的关系。结果表明: PZT-5H 和 PZT-8 的铁电-顺电相变温度( $T_c$ )分别为 438 K 和 550 K。极化前后 PZT-8 的杨氏模量都高于 PZT-5H, 这是由于硬性取代导致 PZT-8 的内应力大于 PZT-5H。极化后, PZT-5H 与 PZT-8 的杨氏模量增大, 本文研究了极化前后压电效应对模量变化的影响。测试得出两种样品都存在一个弛豫内耗峰。分析表明, PZT-8 的弛豫内耗峰由氧空位的扩散引起, 而 PZT-5H 弛豫内耗峰的形成机制则比较复杂, 与畴壁运动及畴壁在运动过程中与点缺陷的相互作用有关。计算得出极化后两种样品的弛豫激活能增加, 原因是极化导致局部内应力升高, 空间电荷沿极化电场排列, 两种因素都会对畴壁及空位的运动产生钉扎效应, 从而使弛豫过程更加困难。

**关 键 词:** 杨氏模量; 内耗; DMA; PZT; 极化

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