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Comparative study on the phase transitions in PZT-based ceramics by mechanical and dielectric analyses

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Abstract

This paper investigated the low-frequency mechanical properties of ferroelectric ceramics (PZT-5H and PZT-8) and anti-ferroelectric ceramics $((Pb_{0.97-x}Ba_xLa_{0.02})(Zr_{0.50}Ti_{0.10}Sn_{0.40})O_3$, $x = 0.08$, 0.09, 0.10, 0.11) by a dynamic mechanical analyzer (DMA). The dynamic mechanical analysis was performed from −100 to 400 °C in temperature and 0.1–4 Hz in frequency. The dielectric properties were also measured as a comparison. The results showed an obvious turning point (T_m) where tan δ reached its maximum and the modulus began to increase for all the samples. tan δ revealed an relaxation region in the ferroelectric ceramics and no corresponding region in the anti-ferroelectric ceramics, which may be originated from the domain walls' motion in the ceramic. The tan δ started to decrease to nearly zero around the tetragonal to cubic phase transition temperature (T_c) for all of the tested samples.

Keywords: C. Low-frequency mechanical properties; C. DMA; C. Ferroelectric; C. Anti-ferroelectric

1. Introduction

Ferroelectric ceramics are widely used in electrical industries, ranging from high-dielectric-constant capacitors to developments in piezoelectric transducers, positive temperature coefficient devices, and electrooptic light valves [1]. Anti-ferroelectric ceramics are extensively used in the applications of actuators, explosive electrical transducers, energy storage capacitors, pyroelectric detector, and so on [2].

Different measuring techniques are employed to characterize electric ceramics. The dielectric-frequency measurement is a widely used electrical method, which measures the dielectric constant, tangent of loss angle. However, the electrical measurement in frequency spectrum is limited to higher frequency (≥100 Hz). Low-frequency mechanical properties are typically measured using the technique of dynamical mechanical analysis (DMA) [3–8]. Harrison et al. [4] investigated the elastic and anelastic properties of perovskite single crystal $LaAlO_3$ using the DMA technique. Kityk et al. [6] clarified the inconsistencies in existing elastic constant data of $SrTiO_3$ in the vicinity of the 105 K phase transition and the elastic anomalies in the quantum paraelectric region of about 25–45 K. Jakeways et al. [8] studied $LaGaO_3$ perovskite by DMA to relate internal friction to the mechanisms controlling first order phase transitions in both crystal and polycrystalline samples. All of these suggest us that dynamical mechanical analysis is a useful way to investigate the phase transition.

This paper deals with the dielectric and elastic modulus as a function of temperature for ferroelectric PZT ceramics and anti-ferroelectric Ba-doped PSZT ceramics. The PZT materials can be classified into two families "hard ceramics" and "soft ceramics". PZT-5H is a typical "soft" ceramic and is used in sensitive receivers and applications requiring fine movement control. PZT-8 is a "hard" ceramic which is used in high power application. The comparison of the low-frequency mechanical properties of hard and soft PZT materials helps us to understand the different properties in PZT ceramics. The potential application of DMA in the electric ceramics was explored.

2. Experimental procedures

PZT-5H and PZT-8 were provided by the Baoding Hongsheng Acoustics Electron Apparatus Co., Ltd. $(Pb_{0.97-x}Ba_xLa_{0.02})(Zr_{0.50}Ti_{0.10}Sn_{0.40})O_3$ antiferroelectric ceramics with $x = 0.08$, 0.09, 0.10 and 0.11 (denoted as Ba8, Ba9,

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Ba10 and Ba11, respectively) were prepared by conventional solid-state reaction sintering method. The detailed method can be found elsewhere [12].

Dielectric properties were characterized using a high-precision LCR meter (Agilent E4980A) connected with a temperature controlled chamber.

Low-frequency mechanical properties have been measured by a dynamical mechanical analyzer (DMA8000, Perkin-Elmer) operating in three-point bend geometry. The sample is positioned, balanced on two supporting knife edges, with a third knife edge resting halfway between the two supporting edges. The sample is subjected to a given static force which is modulated by a dynamic force of chosen amplitude and frequency. The amplitude of deflection u, and phase difference δ, are measured via electromagnetic inductive coupling with resolution of amplitude to 10 nm and phase lag to 0.01°. The parameters of u and δ determine the real and imaginary parts of the elastic compliance, which can be used to calculate Young's modulus. The experiments are based on the dynamic mechanical analysis technique. The two obvious features of DMA are: first, the frequencies that are applied are extremely low (0.1–10 Hz); second, the sample is stressed by an oscillating external stress. The modulus and mechanical loss measured by DMA can provide information of the motion of point defects, domain walls, and other imperfection [3–11].

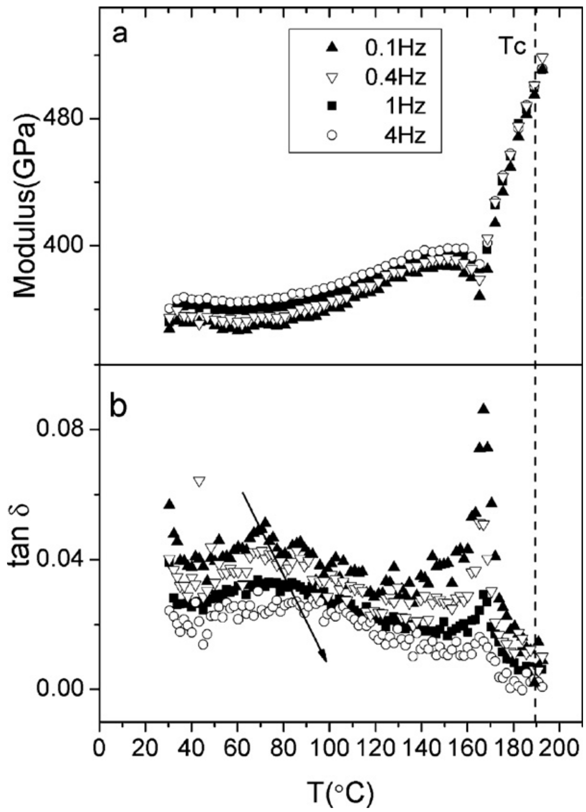

Fig. 1. The variation of the modulus and tan δ of PZT-5H with the temperature at four different frequencies (0.1, 0.3, 1 and 4 Hz). The dash line is Curie temperature (T_c).

3. Results and discussion

The temperature dependence of modulus and tan δ for a PZT-5H ceramic sample has been measured at 0.1, 0.3, 1, and 4 Hz, as shown in Fig. 1. The tetragonal to cubic phase transition temperature (T_c = 190 °C) determined by the dielectric measurement is marked in Fig. 1. Two different peaks appear below T_c in Fig. 1b. The first peak (P1) is a relaxation peak extended from 60 °C to 90 °C, which shows a relaxation nature because the peak shifts to higher temperature as the frequency increases. This is a signature of a thermally activated underlying mechanism [7]. The P1 peak may originate from point defects [5,13]. The second peak (P2) is at 165 °C, which is independent of the frequency. And there is a minimum peak at 165 °C in the modulus correspondingly. The P2 peak may be related to the phase transition. There are two reasons for the temperature difference between T_c and the temperature of P2, both of which are related to the phase transition. First, it may be affected by the temperature measurement error for the different sample chambers used in DMA and dielectric-temperature measurement. Second, the P2 peak possibly related to domain motion, defects, or other transition, which now cannot be definitely defined. The tan δ is almost zero above T_c, indicating ideal elastic behavior [5]. The modulus of PZT-5H is frequency dependent below 165 °C and frequency independent above 165 °C, which may be due to a combination of the structure changes associated with the tetragonal to cubic phase transition [4].

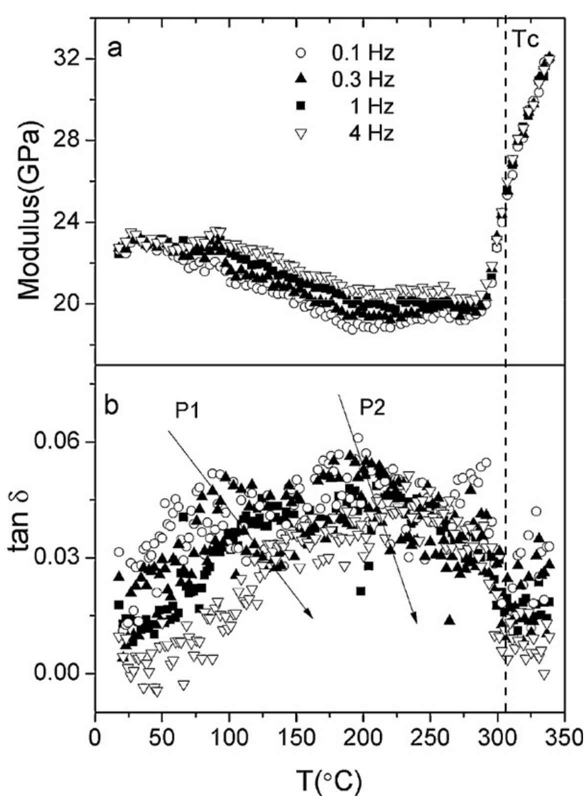

Fig. 2. The variation of the modulus and tan δ of PZT-8 with the temperature at four different frequencies (0.1, 0.3, 1 and 4 Hz). The dash line is Curie temperature (T_c).

The temperature dependence of modulus and tan δ for a PZT-8 ceramic sample has been measured at 0.1, 0.3, 1, and 4 Hz, as shown in Fig. 2. The tetragonal to cubic phase transition temperature ($T_c = 309$ °C) determined by the dielectric measurement is also marked in Fig. 2. Three peaks appear below T_c in Fig. 2b. These peaks cannot accurately determine as they are overlapping. The first peak is around 80 °C at 0.1 Hz and the second peak is about 180 °C at 0.1 Hz. They both shift to high temperature as the frequency increases. The third peak is accompanied with the increase of the modulus. The tan δ is nearly zero above T_c, which is identical with the tan δ of PZT-5H. There is no obvious loss peak in the tan δ at the temperature of 289 °C where the modulus begins to increase.

The difference low frequency properties of PZT-5H and PZT-8 originate from the doping effect in PZT ceramics. This may provide a good method to investigate the doping effect on electric ceramics [13].

The relative dielectric constant and the low frequency mechanical properties as a function of temperature for the samples of Ba8, Ba9, Ba10 and Ba11 are shown in Fig. 3. It is obvious that the modulus of every sample decreased with temperature to the minimum point, and then increased to its stable value. The T_c according to the dielectric measurement and minimum point (T_m) in the modulus measurement are shown in Table 1. The temperature difference between T_c and T_m is about 25–35 °C, which is unlikely related to the temperature measurement error. All the experiment data show that the temperature of the modulus begins to increase is ahead of the T_c, which is associated with the phase transition [13]. As

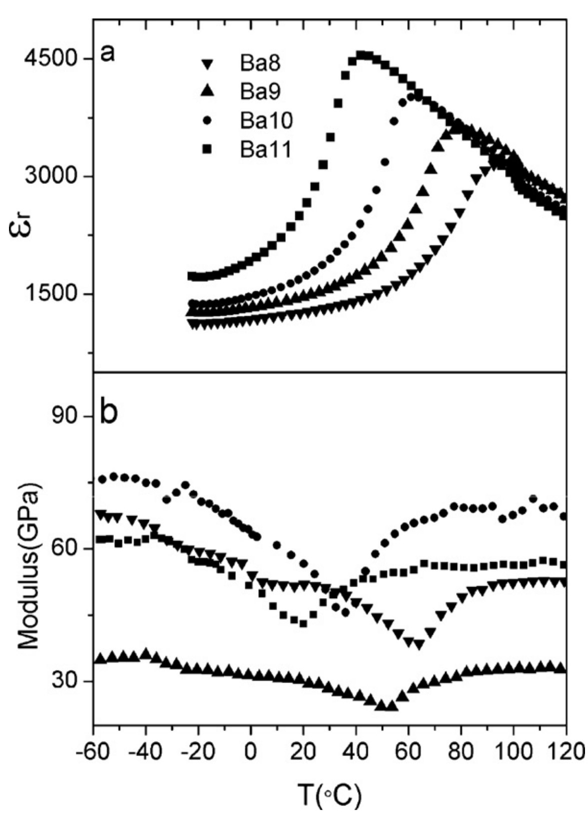

Fig. 3. (a) The relative dielectric constant of Ba8, Ba9, Ba10 and Ba11 as a function of temperature at 1 kHz; (b) the modulus of Ba8, Ba9, Ba10 and Ba11 as a function of temperature at 1 Hz.

Table 1
The T_c and T_m of Ba8, Ba9, Ba10 and Ba11.

	Ba8	Ba9	Ba10	Ba11
T_c (°C)	97	80	63	46
T_m (°C)	63	52	36	20

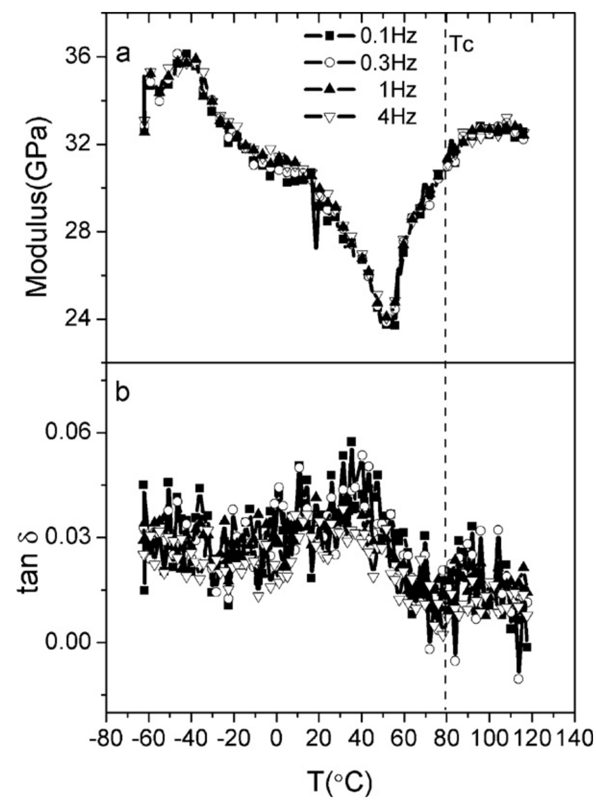

Fig. 4. The variation of the modulus and tan δ of Ba9 with the temperature at four different frequencies (0.1, 0.3, 1 and 4 Hz). The dash line is curies temperature (T_c).

the four samples display similar characters both in the dielectric measurement and in the mechanical measurement, here the sample of Ba9 is taken as an example. The temperature dependence of modulus and tan δ for the Ba9 ceramic sample has been measured at 0.1, 0.3, 1, and 4 Hz, as shown in Fig. 4. There is no relaxation phenomenon in the mechanical loss. The loss peak is not obvious at the temperature of 52 °C where the modulus of Ba9 reaches its minimum point. It cannot be accurately determined because several peaks are overlapped. The tan δ is nearly zero above T_c, indicating ideal elastic behavior [5], similar to the discussion on PZT-5H and PZT-8 above.

4. Conclusions

The mechanical properties of ferroelectric ceramics (PZT-5H and PZT-8) and anti-ferroelectric (B8, B9, B10 and B11) by DMA shows an obvious turning point (T_m) where the loss reach maximum and the modulus begin to increase. As the modulus in the ferroelectric ceramics showed obvious relaxation phenomena and no corresponding phenomena were observed in the anti-ferroelectric ceramics, the origin of the relaxation may be originated from the domain walls in the ceramic, as the domain walls arrange different in the ferroelectric and anti-ferroelectric. Another result is that the tan δ begins to decrease to nearly zero around T_c for the ferroelectric and anti-ferroelectric ceramics, which indicates ideal elastic behavior.

Acknowledgements

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