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Dielectric and relaxor ferroelectric properties of Ba-doped $Pb(Zr,Ti)O_3$ ceramics

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Abstract $(Pb,Ba)(Zr,Ti)O_3$ is a relaxor ferroelectric material. Dielectric and ferroelectric properties of $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ ceramics have been investigated for compositions varying in the range of $0.20 \leq x \leq 0.30$. Reagent grade PbO, ZrO_2, TiO_2 and $BaCO_3$ raw powders were used, ceramics were fabricated by convenient solid state reaction. The experimental results show that the substitution of Ba for Pb can enhance the ferroelectric relaxor characteristics. With the Ba content increasing, the electric hysteresis was narrowed and the polarization was reduced. Meanwhile the temperature T_m that corresponding to the maximal dielectric constant was decreased. It has also been found that the hydrostatic pressure may cause the phase transition more diffuse and move T_m to higher temperature.

Keywords $(Pb,Ba)(Zr,Ti)O_3$ · Compounds · Compositional variations · Relaxor ferroelectric

1 Introduction

Ferroelectric materials with diffuse phase transition (DPT) supply the basic requirements to obtain ceramics with high dielectric permittivity and low temperature coefficients. These properties are vital for multilayer ceramic capacitor applications [1]. Many studies on DPT and dielectric properties in perovskite type ceramics of $(Pb,La)(Zr,Ti)O_3$ (PLZT) and $(Pb,Ba)(Zr,Ti)O_3$ (PBZT) have been reported, due to their physical and technical aspects [2–5]. In addition, the PBZT ceramics also display promise for piezoelectric and actuator use.

The first systematic investigation of the PBZT system was reported by Ikeda in 1959 [6]. In his work, Ikeda studied the crystal structure and dielectric properties of a series of compositions, and determined the phase diagram of the whole system on the basis of dielectric and X-ray diffraction data. Large electrostrictive effects in PBZT ceramics were discovered in 1980 by Leung et al. [7]. Their results indicated that the electrostrictive coefficients and the equivalent piezoelectric constants of the composition 27:70:30 (Ba/Zr/Ti) were found to be much larger than those of $BaTiO_3$ and PLZT 7:60:40, respectively. Systematic investigation on the field-induced strain properties of the PBZT family has been performed by Li and Haertling [8]. They studied the field-induced strain, dielectric and ferroelectric properties of a number of compositional series with a wide region of special interest.

The main objective of this paper was to investigate the DPT, ferroelectric and dielectric properties of the $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ (PBZT) ceramic with $0.20 \leq x \leq 0.30$. Little attention has been given to hydrostatic pressure dependence of the dielectric response for this material. To better understand physical properties of PBZT ceramics, investigations have been performed on the dielectric response as functions of temperature under different hydrostatic pressure. The preparation of samples is described, and measurement results are presented.

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Table 1 Properties of $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ ceramics.

Ba content (x)	P_{40} (μC/cm^2)	E_c (V/mm)	d_{33}	1 kHz		10 kHz		100 kHz	
				T_m (°C)	ε_m	T_m (°C)	ε_m	T_m (°C)	ε_m
0.20	35.76	779.94	154	144	13886.48	148	13358.00	153	12658.18
0.25	29.91	331.58	102	100	10673.73	106	10210.00	113	9644.18
0.30	23.38	175.47	18	49	7593.06	58	7234.28	68	6802.48

2 Experimental procedure

The ceramics were prepared by a conventional mixed oxide synthesis and processing. Amounts of chemically pure oxides such as PbO, ZrO_2, TiO_2 and $BaCO_3$ were weighted according to $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$. It should be noted that a small amount of bismuth oxide was added to all of the compositions to improve sinterability and control sample microstructure [8]. To prevent Pb loss during high temperature, an excess 1 wt% PbO was added. The mixtures were ball-milled with ZrO_2 balls for 5 h in alcohol following by an oven drying, and the powders were calcined at 700 °C for 2 h in an aluminum crucible. The calcined, milled and sieved material was pressed into the cylindrical pellets. Compacts were then sintered at 1250 °C for 3 h in a double aluminum crucible to avoid the loss of PbO caused by its sublimation.

The samples were coated with silver electrodes for the measurements of electrical properties. Dielectric properties at various frequencies (1–100 kHz) were measured by a frequency impedance analyzer HP4284A conjuncted with a computer-controlled temperature chamber to measure capacitance as a function of temperature from 20 to 210 °C. The temperature increased at a speed of 3 °C/min. Electric hysteresis loops (P-E loops) were measured by using a modified Sawyer–Tower system. To study the temperature dependence of dielectric properties under different hydrostatic pressure, the specimens were amounted into the pressure vessel, heated by a small resistance-heating furnace. Dielectric properties were simultaneously recorded by a HP4274LCR meter at 1, 10 and 100 kHz frequencies.

3 Results and discussion

The important data of the PBZT samples with different compositions obtained in this study are illustrated in Table 1. The ferroelectric and dielectric properties are sensitive to variation of Ba content. The values of the piezoelectric coefficient d_{33} at room temperature decreased from 154 to 18 with the Ba content increasing in the $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ compositions.

The relationships between polarization and electric field for the $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ ceramic samples are demonstrated in Fig. 1. A slim-loop characteristic was found for these samples. It can be seen that these slim loops exhibit a marked saturation at some higher electric fields. This behavior indicates that the samples are in a quasi-polar state, which is often referred to an intermediate phase between polar and nonpolar [8]. For the samples in this study, hysteresis became narrow with increasing barium content. At the same time, P_{40} (the polarization at an electric field of 40 kV/cm) and E_c (the coercive field) decreased monotonously, as shown in Table 1.

Dielectric spectra in wide frequency range (from 1 to 100 kHz) as a function of temperatures of the PBZT ceramic samples are shown in Fig. 2. All the compositions shown in the figure were characterized by a diffuse phase transition that is manifested as a corresponding broad maximum in the change of dielectric constant with temperature. The magnitude of the dielectric constant maximum is reduced and the Curie point is shifted to a higher temperature with increasing frequency. Continuous substitution of Ba for Pb ions makes the dielectric constant peaks at the Curie point more and more diffuse. It is commonly believed that the relaxor phenomenon originates from compositional fluctuations in microregions of the order of about 10 nm [8].

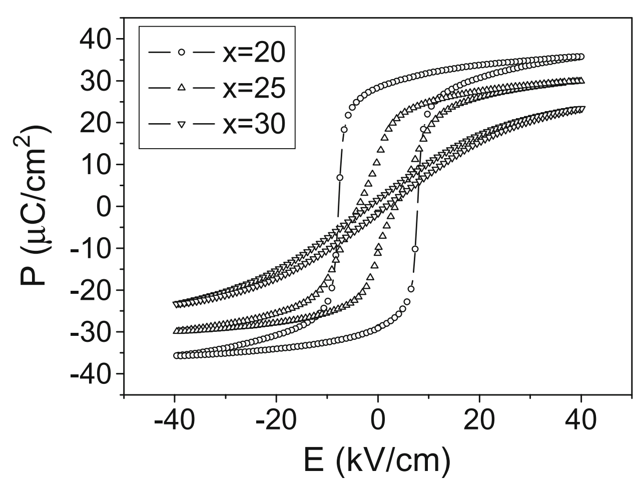

Fig. 1 Relationship between polarization and electric field for the PBZT ceramics with constant Zr/Ti ratio

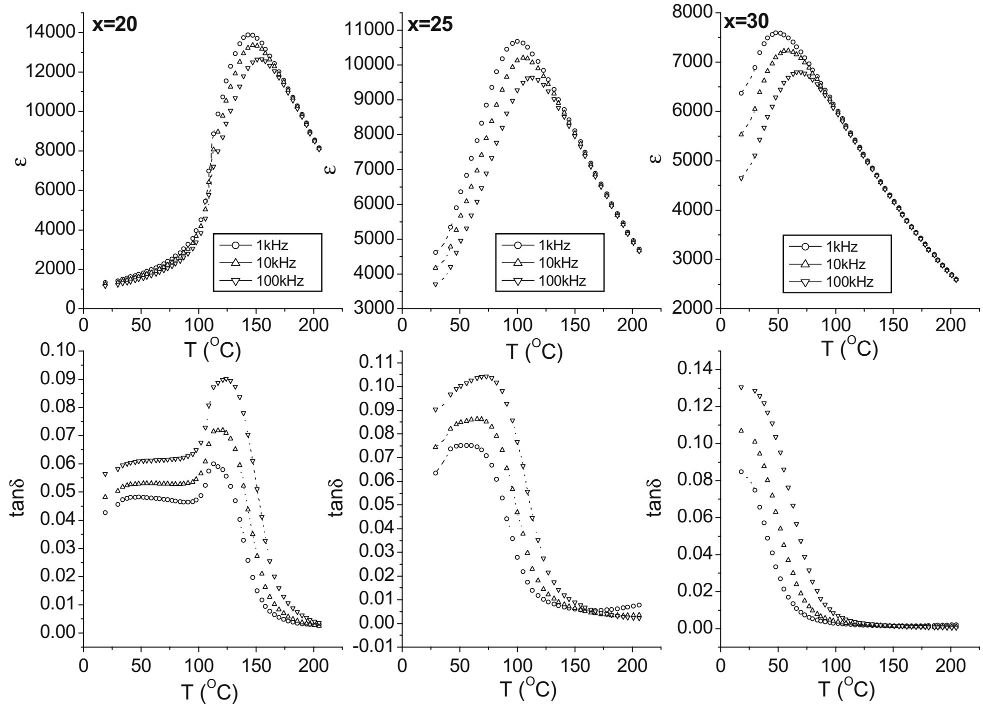

Fig. 2 Variation of dielectric constant (ε) and loss factor (*tanδ*) as a function of temperature of PBZT at three different frequencies

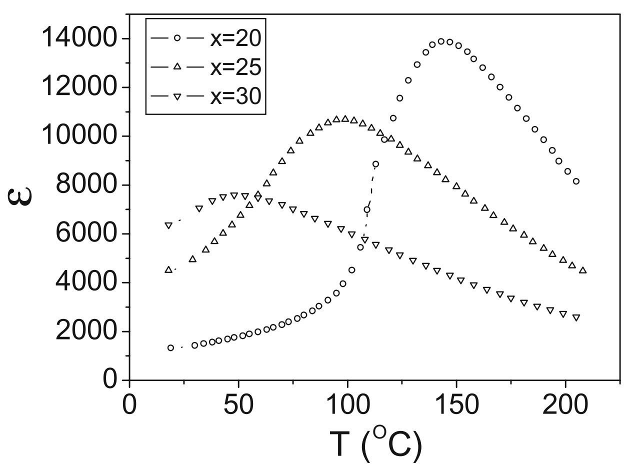

Fig. 3 Temperature dependence of dielectric constant and for the PBZT compositions, measured at 1 kHz

The temperature dependence of dielectric constant for the PBZT compositions at 1 kHz was studied and the related results are shown in Fig. 3. The temperatures at the maximum dielectric constants were considered to be the temperatures of transition from the ferroelectric phase to the paraelectric phase. The magnitudes of maximum dielectric constants ε_m and the transition temperatures T_m for the compositions with constant Zr/Ti are, as expected, reduced with increasing Ba content. The loss factors increased as Ba content increasing.

Figure 4 shows the dielectric response as a function of temperature for the $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ samples under different hydrostatic pressure. The dielectric responses change gradually as pressure increases. Dielectric peaks are broadened and frequency dispersion is evident step by step. The peak temperatures T_m at three different frequencies increase with pressure increasing as shown in

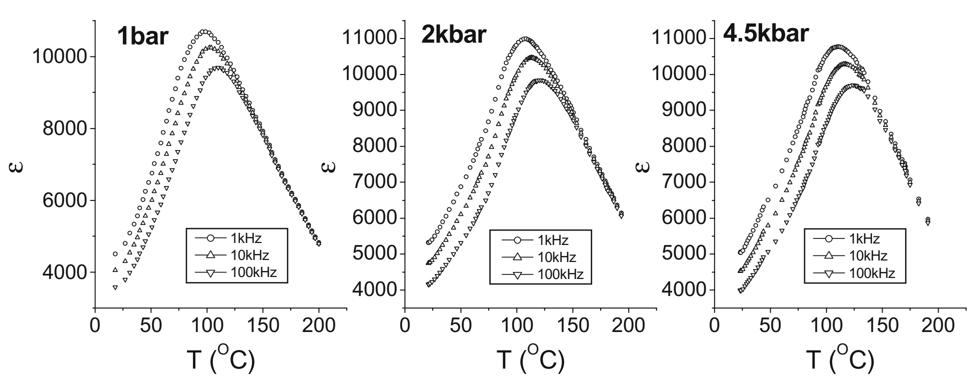

Fig. 4 Temperature dependence of dielectric constant for the $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ composition at 0, 2 and 4.5 kbar

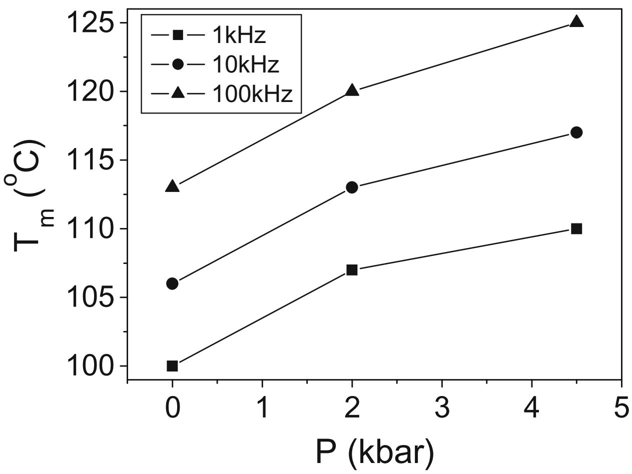

Fig. 5 Transition temperature T_m as a function of the hydrostatic pressure for the $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ composition, measured at 1, 10 and 100 kHz

Fig. 5. A more detailed study is now in progress in order to understand pressure effects on PBZT ceramics.

4 Conclusions

Ceramics with nominal compositions $(Pb_{1-x}Ba_x)(Zr_{0.70}Ti_{0.30})O_3$ were prepared by a solid-state reaction technique. Ba varying in PBZT ceramics exhibits many interesting features, such as shift in transition temperature, diffuse phase transition and modification of dielectric properties. Characteristic of ferroelectric relaxors slim hysteresis loops and frequency dependence of ε (T) curves were identified for the ceramics of these compositions. Detailed studies of dielectric constant show a ferroelectric diffuse phase transition of these compounds. The addition of Ba shifted the temperatures of maximal dielectric constant toward lower temperatures. The dielectric constant, coercive field and polarization decrease as the Ba content increases. The temperature dependences of dielectric response for these PBZT compositions under different hydrostatic pressure have also been investigated. Hydrostatic pressure makes T_m shift to higher temperature and induces phase transition more diffuse with increasing pressure. The dielectric and ferroelectric properties obviously imply that PBZT can be a good candidate for some devices.

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