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LOW TEMPERATURE DIELECTRIC BEHAVIOR IN $PB(Zr_{1-x}Ti_{x})O_3$ FERROELECTRIC CERAMICS

M.Sc. E. Pérez-Delfin[I], Lic. A. Vega-García[II], Dr. Y. Leyet[II], Dr. F. Guerrero[II], Dr. J. A. Eiras[I]

delfin@cnt.uo.edu.cu

[I]Physics Department, Universidade Federal de São Carlos, São Carlos-SP, Brazil; [II]Physics Department, Oriente University, Santiago de Cuba, Cuba

● Resumen

El comportamiento dieléctrico en cerámicas oxidadas y reducidas de PZT (60/40) y PZT (40/60) fue analizado en los rangos de temperatura y frecuencia de 15 K a 400 K y 1 kHz a 10 MHz, respectivamente. Los resultados revelan una anomalía dieléctrica a temperaturas cercanas a los 250 K en las muestras de PZT oxidadas y reducidas. La dependencia de la polarización con la temperatura en las medidas piroeléctricas muestra un cambio de monotonía en el mismo rango de temperaturas. El comportamiento del momento dipolar pudiera ser la causa del efecto encontrado.

Palabras clave: estructura perovskita, comportamiento dieléctrico, oxidación, reducción, PZT.

● Abstract

Temperature dielectric behavior in oxidized and non-oxidized PZT (60/40) and PZT (40/60) ceramics were analyzed in a frequency and temperature range of 1 kHz-10 MHz and from 15 to 400 K, respectively. The results revealed an anomalous dielectric behavior at temperatures closed to 250 K in oxidized and non-oxidized PZT samples. Temperature polarization behavior in pyro-electric measurement shows monotony changed in the same temperature range. Dipolar behavior could be the cause of detected anomaly.

Keywords: perovskite structure, temperature dielectric behavior, oxidation, reduction, PZT.

● Introduction

Lead zirconate titanate (PZT) has been widely studied due to unquestionable technological applications /1/, especially those at morphotropic phase boundary (MPB) /1-3/. It is well known that the properties of this material strongly depend on the ferroelectric phase. In the so called MPB the ferroelectrics properties become exceptional[1] due to the coexistence of both tetragonal and rhombohedral phases /4/ or to the appearance of monoclinic phase /5/.

Temperature dielectric behavior in PZT based ferroelectrics materials has been studied by several authors /1, 5-8/. At temperatures lower than ambient the dielectric responses include the crystalline elemental cell contribution (intrinsic properties) and ferroelectrics domain response (extrinsic properties) /9, 10/. Has been reported at T < 300 K a very small temperature dependence dielectric behavior, but more detailed studies highlights a dielectric anomalous behavior at this temperature range. This anomaly appears in ceramics with tungsten bronze /11-14/ and perovskite structures /15/.

According to the Devonshire theory, the anomaly found in the dielectric response in $(Ba_{0.7}Sr_{0.3})TiO_3$ samples at 150 K, is attributed to second order structural phases transitions /16/. Povoa et al. associated this anomaly to a polarization fluctuation "freezing in", originated from the relaxor nature of

SBN solution and related presumably with the transformation of the incommensurate super-structure /17/. De los Santos et al. proposed that the anomaly observed in PN ceramics is associated to the existence of incommensurate super-lattices (ISL) similar to the low symmetry orthorhombic one-dimensional ISL observed for the BNN system /14/. Recent studies in $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) suggest that dielectric response shows an evident dependence with domain walls dynamics in the ferroelectric phase /7, 8/. Domain wall mobility is influenced by lattice defects explained by the interaction between the domains walls and the oxygen vacancies. It is assumed that the anomaly is observed in samples where the oxygen vacancies and its effect are important, independently of the sample crystallographic phase /8/. The oxygen vacancies are sufficiently mobile to form defects complex to pining the domain walls provoking a domain wall mobility reduction /15/. Nevertheless the physical phenomenon that causes the dielectric anomalous response is explained using different arguments, however still not clearly understood. The aim of the present work is to investigate in detailed the dielectric and polarization behavior at the temperature range between 15 K and 400 K for PZT ferroelectrics ceramics.

Experimental procedure

Ferroelectric samples were evaluated with two different stoichiometric compositions: $Pb(Zr_{1-x}Ti_x)O_3$, x= 0,40 (PZT64) and x= 0,60 (PZT46). Starting with different precursors powders all the samples were uniaxially pressed at 100 MPa and then isostatically pressed at 120 MPa. The systems were fired between 1 100 °C and 1 200 °C for 2 h and sintered in a Pb-rich atmosphere to prevent stoichiometric losses. Samples were cut into disks of 10-12 mm in diameter and 0,8-1,9 mm in thickness. Ceramic bodies were polished to ensure parallel surfaces, after which platinum electrodes were sputter-deposited onto their surfaces. Experimental setup was placed in a closed loop cold finger cryogenic systems for a measurements from 15 up to 400 K. Dielectric response was measured using HP-4194A impedance analyzer at frequencies from 100 Hz to 10 MHz. For the oxidation the samples were placed in an isolated system with oxygen atmosphere and increasing the temperature to 800 °C (30 °C/min).

Room temperature X-ray diffraction (XRD) patterns for all PZT samples were collected using a Rigaku diffractometer and the conditions: CuKa radiation, continuous scan type with 2θ from 20 to 60° at scanning rate of 2°/min. Results revealed single-phase compounds with perovskite structure.

• Results and discussion

Figure 1 shows temperature behavior of real (e´) and imaginary (e´´) component of complex dielectric permittivity for PZT46 and PZT64 ferroelectrics ceramics at 100 kHz. Both samples shown a normal ferroelectric-paraelectric phase transition temperature closed to 600 K and a conductivity influence is evident in imaginary component function.

Temperature behavior of e´ and e´´ for oxidized and non-oxidized PZT64 samples are displayed in figure 2 for two selected frequency. It could be appreciated the anomalous behavior in both e´ and e´´at temperature closed to 250 K.

The dielectric behavior in non-oxidized sample (usually used sample) agreement with other results reported previously /7, 8/. However unexpected dielectric response was appreciated for oxidized sample. According with previously reports the dielectric anomaly could be due to the pining actions provoked by the oxygen vacancies /7, 9/. It´s therefore hoped that oxygen vacancies absence in the structure should be eliminated or minimized the dielectric behavior anomaly. This result opens another investigate way to explain the physical phenomena causing the dielectric anomaly. Moreover the anomalous dielectric behavior coincidence in oxidized and non-oxidized PZT64 samples show the possible independence of oxygen vacancies presents in the structure.

On the other hand, figure 3 shows a dielectric behavior comparison between oxidized PZT64 and PZT46 samples. The dielectric anomaly behavior was observed approximately at the same temperature range. This could be means the anomaly is independent of PZT compositions too. The differences observed in dielectric values and function shape could be caused by the each sample structural properties.

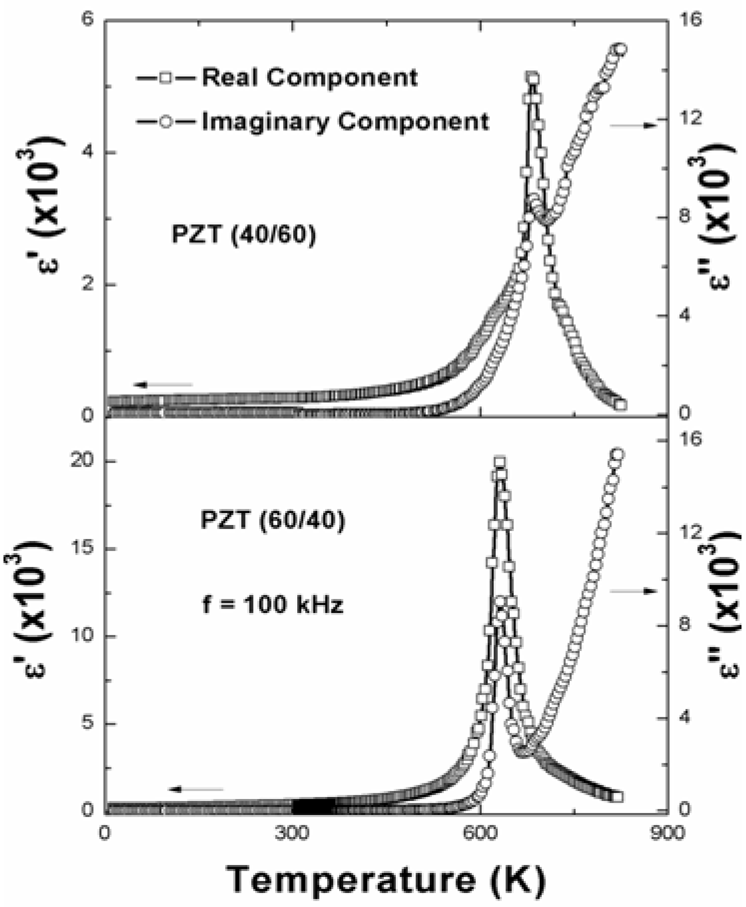

Fig. 1 Temperature dielectric behavior for PZT46 and PZT64 samples at 100 kHz.

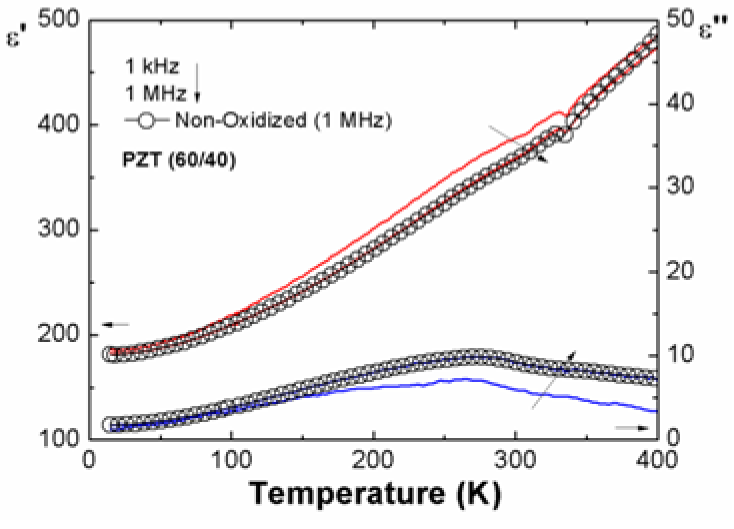

Fig. 2 Temperature dielectric dependence for oxidized and non-oxidized PZT (60/40) samples.

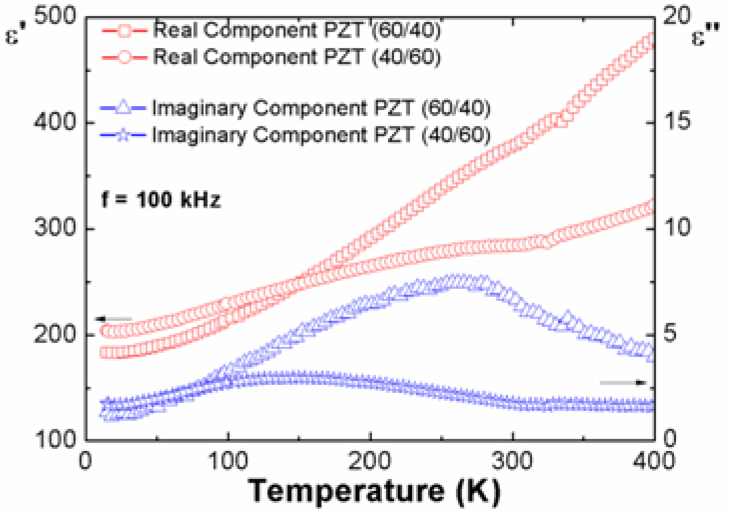

Fig. 3 Temperature dielectric dependence of oxidized PZT (60/40) and PZT (40/60) samples at 100 kHz.

PZT phase diagram reported a structural transition in rhombohedral phase at temperatures below to 300 K /1, 18, 19/. However in tetragonal phase has not been reported any phase transition in this temperature range. Therefore the anomaly could not be caused by a structural phase transition.

A pyro-electric analysis in PZT64 and PZT46 samples reveals an evident monotony change in temperature polarization dependence (figure 4). The decreasing polarization behavior and imaginary dielectric anomaly occurring in the temperature range between 100 and 350 K. Polarization behaviors could be the confirmation of the dipolar rearrangement at these temperatures which influence on the dielectric behavior provoking the anomaly apparition. Nevertheless other studies should be developed to confirm the possible structural phase transition responsible to the dipolar modification at this temperature ranges.

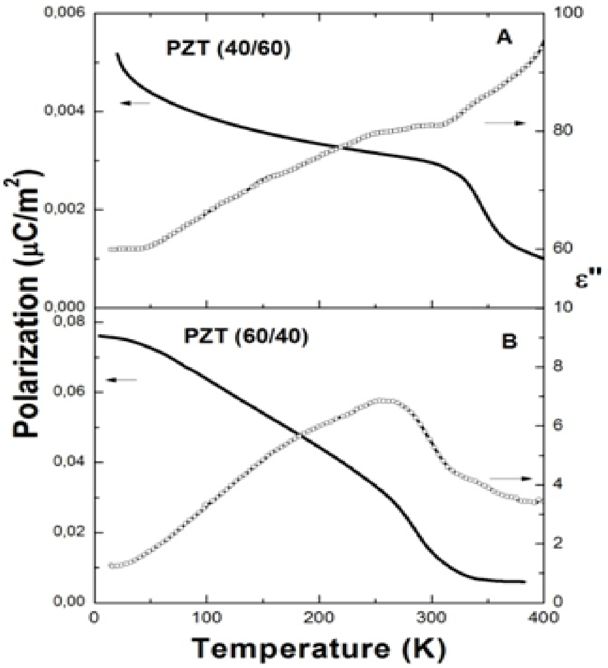

Fig. 4 Temperature polarization and imaginary permittivity dependence for PZT46 (A) and PZT64 (B) samples.

Conclusions

In summary, the dielectric response of oxidized and non-oxidized PZT ceramics was investigated by complex dielectric permittivity and pyro-electric analysis over a wide temperature and frequency range. An anomalous dielectric behavior was observed at temperatures closed to 250 K, coinciding with polarization monotony changed. Unexpected dielectric behavior was observed in oxidized PZT samples which suggest the anomaly independence of oxygen vacancies presence. Dipolar rearrangement could be the responsible to this anomalous dielectric behavior.

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