Elastic Modulus and Mechanical Loss Associated with Phase Transitions and Domain Walls Motions in PZT Based Ceramics

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Abstract : Elastic modulus (shear modulus G or Young's modulus E) and internal friction Q^{-1} were measured as a function of temperature on undoped $Pb(Zr_{50}Ti_{50})O_3$, $Pb(Zr_{52}Ti_{48})O_3$, $Pb(Zr_{54}Ti_{46})O_3$ ceramics from -180°C to 500°C. Experiments were performed at low and medium frequencies (0.1 Hz - 4 kHz). The E(T) curves show two anomalies which are due to following phase transitions: tetragonal to cubic (T_C) and rhombohedral to tetragonal (T_{R-T}). The T_C temperatures are in good agreement with phase diagram from litterature. The T_{R-T} temperatures allow to complete the phase diagram of the morphotropic phase boundary of PZT in the low temperature range. Moreover,Q^{-1}(T) curves recorded at low frequencies show two relaxation peaks; their activation energy and relaxation time are determined using the Arrhenius plots. These two relaxation peaks could be attributed to the interaction of domain walls with point defects.

1. Introduction

Lead titanate zirconate $Pb(Zr_xTi_{1-x})O_3$ ceramics are one of the most common piezoelectric materials 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. [1] Generally, all those applications need high piezoelectric constants as well as low electrical and mechanical losses. Variations of internal friction and elastic modulus as a function of temperature and excitation frequency can provide direct information on energy dissipation in the material. For example, Postnikov *et al.* [2] have shown that the internal friction in the PZT is not only associated with domain walls but also with point defects. The Zr/Ti ratio in $Pb(Zr,Ti)O_3$, the nature and concentration of substituting elements, the shaping procedure of green bulk, the sintering temperature and atmosphere are the controlling factors which provide the suitable properties for applications. With their many applications and controlling factors, the PZT materials have been the subject of continuous research for the past few decades. In the present study, the elastic modulus and the internal friction were measured at different temperatures, in order to determine phase transition temperatures and to study the motion of domain walls.

2. Samples and Experimental Procedures

Undoped PZT ceramics were prepared by solid diffusion of PbO, ZrO_2, and TiO_2 powders with the following Zr/Ti ratio: $Pb(Zr_{0.50}Ti_{0.50})O_3$, $Pb(Zr_{0.52}Ti_{0.48})O_3$ and $Pb(Zr_{0.54}Ti_{0.46})O_3$. shortly called PZT50/50, PZT52/48 and PZT54/46.

Young's modulus E and internal friction Q^{-1} have been measured as a function of temperature. Samples were driven in flexural vibration at resonance frequency of about 3 kHz. Specimen dimensions, experimental measurement device and calculation formula were described in [3]. The measurements at low frequencies of shear modulus G and internal friction Q^{-1} were measured by an inverted pendulum. The temperature range is located between -180°C and 500°C.

3. Results and Discussions

The **Figure 1** presents E(T) and Q^{-1}(T) curves obtained with PZT52/48 ceramic. The E(T) curve shows two anomalies called A_1 and A_2 located at 375°C and -69°C. The A_1 anomaly of elastic modulus is correlated to a sharp internal friction peak called P_1. Both A_1 anomaly and P_1 peak are due to the phase transition from cubic to tetragonal phases. The A_2 anomaly is due to the second phase transition between tetragonal and rhombohedral phases. This A_2 anomaly is not correlated to an internal friction peak. Similar E(T) and Q^{-1}(T) curves were obtained for other composition PZT50/50 and PZT54/46 ceramics.

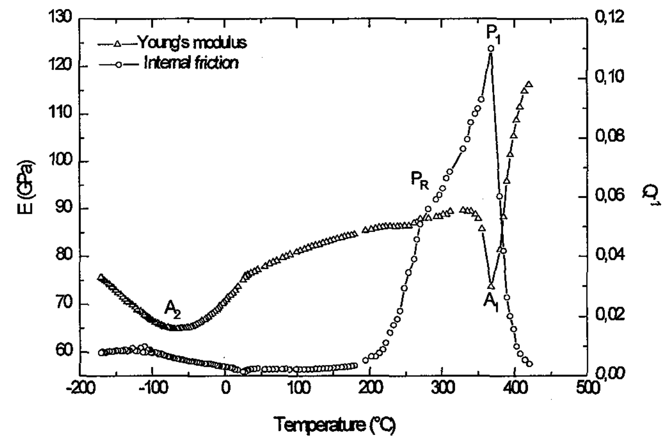

Figure 1: E(T) and Q^{-1}(T) at kHz frequency.

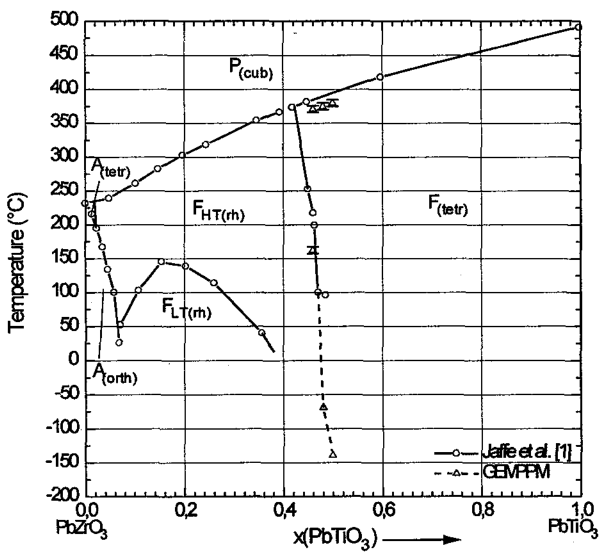

Figure 2 : Phase diagram of PZT.

The **Figure 2** shows the phase diagram from Jaffe et al. [1] on which our results on phase transition temperatures T_C and $T_{R\text{-}T}$ have been added. About T_C our results are in good agreement with Jaffe's diagram. Moreover, about the $T_{R\text{-}T}$ temperatures, our results allow to complete the morphotropic region of the phase diagram located below 0°C.

About the $Q^{-1}(T)$ curve shown in **Figure 1**, it is possible to divide the temperature range according to the level of internal friction. From the low temperature -180°C to 0°C, Q^{-1} decreases monotonically to a low level. Between 0°C and 180°C, Q^{-1} remains constant. Above 180°C, Q^{-1} increases strongly up to a maximum of the P_1 peak (at the Curie temperature). In the paraelectric region, the drastic decreasing of Q^{-1} remember us that the mechanisms of energy dissipation in ferroelectric state are obviously linked to the motion of domain walls. The same shape of the E(T) and $Q^{-1}(T)$ curves are obtained for all three compositions of PZT ceramics.

In order to determine which anelastic event is located at P_R in the increasing part of the $Q^{-1}(T)$ curves at kilohertz, the measurements of G and Q^{-1} versus temperature were performed at low frequencies of 0.1 to 1 Hz on two pendulums (which allow to cover the total temperature range). The results obtained with the PZT 52/48 ceramic are shown on **Figures 3** (low temperature) and **4** (high temperature). The G(T) curves show the A_1 and A_2 anomalies of shear modulus due to two phase transitions: T_c and $T_{R\text{-}T}$.

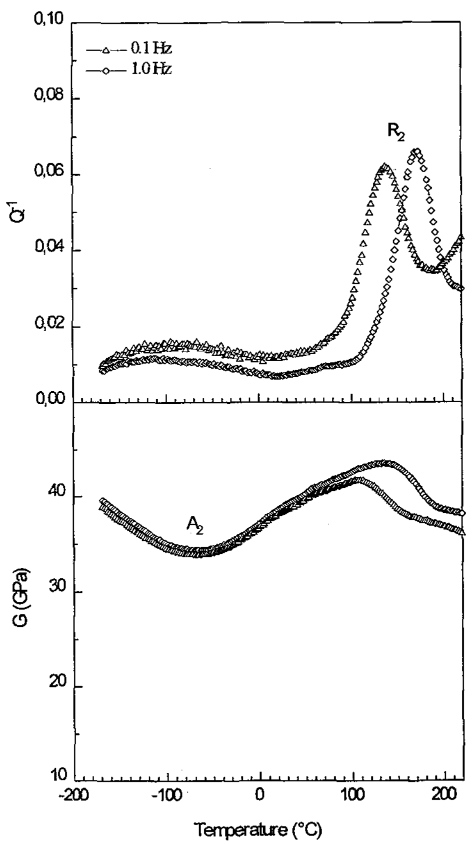

Figure 3 : $Q^{-1}(T)$ and G(T) at low temperature.

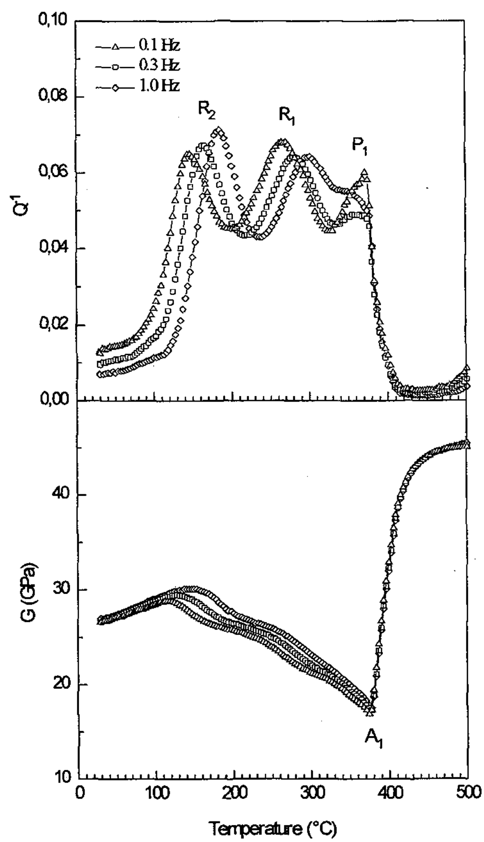

Figure 4 : $Q^{-1}(T)$ and G(T) at high temperature.

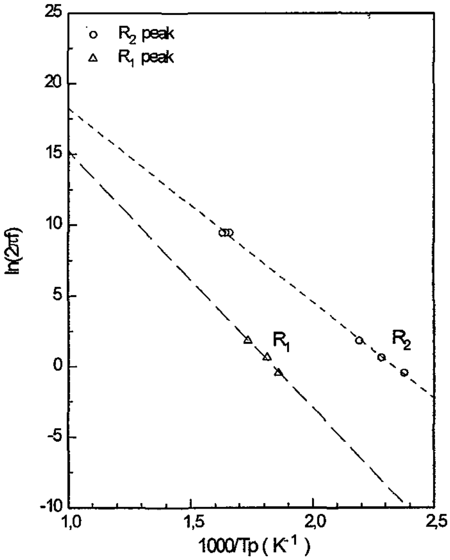

Figure 5: Arrhenius plot for PZT52/48.

On the $Q^{-1}(T)$ curves, two internal friction peaks R_1 and R_2 are observed. These two peaks have a relaxation behavior because they are frequency dependent.
The Arrhenius plot corresponding to this two peaks are given in the **Figure 5**. It is of interest to note that the R_2 peak is connected to the shoulder observed on $Q^{-1}(T)$ at kilohertz frequency.

Table 1: Activation parameters of R_1 and R_2 peak in the three PZT ceramics.

Peak	PZT50/50	PZT52/48	PZT54/46
R_1	H= 1.63 eV $\tau_0 = 8\times10^{-16}$ s	H= 1.56 eV $\tau_0 = 3\times10^{-15}$ s	H= 1.63 eV $\tau_0 = 1\times10^{-15}$ s
R_2	H= 0.99 eV $\tau_0 = 1\times10^{-12}$ s	H= 1.17 eV $\tau_0 = 1\times10^{-14}$s	H= 0.93 eV $\tau_0 = 2\times10^{-12}$ s

The **Table 1** gives the activation energy and the relaxation time for the R_1 and R_2 peaks. Fot the R_2 peak, the magnitude of the relaxation time is coherent with a point defect relaxation and the R_2 relaxation peak could be due to the interaction between domain walls and oxygen vacancies because the activation energy for diffusion of oxygen vacancy is about 0.9 eV. In order to verify this hypothesis, we intend to modify the concentration of oxygen vacancy by annealing in vaccum.
Concerning the R_1 peak, its activation energy is high (about 1.6 eV) and we intend to study the influence of annealing and strain amplitude. One can notice that the R_1 peak is not observed in the kilohertz range because its temperature is higher than the Curie temperature.

Conclusion

The E(T) curves lead to the determination of new points in the phase diagram of PZT in the morphotropic region. $Q^{-1}(T)$ curves obtained at low frequencies show two relaxation peaks R_1 and R_2. The R_2 peak located at lower temperature, could be attributed to the interaction of domain walls and oxygen vacancies. The R_1 peak is probably due to the interaction of domain walls and another point defect.

Reference

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