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Mechanical Loss and Elastic Modulus Associated with Phase Transitions in PLZT Ceramics

B.L. Cheng*, M. Gabbay, M. Gimenez** and G. Fantozzi

GEMPPM, UMR 5510 du CNRS, INSA Lyon, Bât. 502, 69621 Villeurbanne, France

** Department of Physics, South China University of Technology, Guangzhou 510641, China*

*** Depto. Física de Los Materiales, UNED, Ciudad Universitaria, 28040 Madrid, Spain*

Abstract : The phase transition in lanthanum modified lead zirconate-titanate ceramic of 6/60/40 is studied by mechanical loss Q^{-1} and elastic modulus measurements. The shear elastic modulus measured from 50°C to 250°C shows that the Curie temperature is located at 180°C for the transition from cubic to rhombohedral phase. The Q^{-1} curves at low frequencies show clearly a peak corresponding to such phase transition. This phase transition is confirmed by measurements of Young's modulus and Q^{-1} using resonance curve technique from -100°C to 300°C at kilohertz. Moreover, between 50°C and 90°C, the resonance curve recorded at kHz frequency shows two resonance peaks. Such existence of double peaks means that a phase transition takes place between two rhombohedral phases FE2 and FE1 in the ferroelectric state. These phase transitions are also studied by DSC measurement.

1. INTRODUCTION

Lanthanum modified lead zirconate-titanate (PLZT) ceramic is used for application in electro-optic and has a potential use in non-volatile random access memory (RAM) devices since the discovery of transparent electro-optic ceramic by Haertling and Land [1]. Recently, Ramesh et al. reported that metal-oxide electrodes yield better fatigue properties in PZT and PLZT than those with conventional Pt electrodes [2]. However, the apparent dielectric constant of PLZT was influenced by the electrode materials, and the domain switching was also influenced by the electrode materials at low temperature [3]. Concerning the application as holographic recording material, the holographic sensitivity is also controlled by both phase transition temperature and defect concentrations [4].

For obtaining a clear picture on the domain switching, and interaction of the ceramic with electrodes in PLZT, it could be helpful to get clear information on the phase transition and motion of domain walls in PLZT. It is known that PLZT ceramic is a ferroelectric-ferroelastic material [5]. Upon cooling down from cubic paraelectric phase to tetragonal or rhombohedral phase, the ferroelectric-ferroelastic PLZT ceramic is associated with shear strains that can be reoriented by applied stress. In this paper the mechanical loss and elastic modulus are studied on PLZT ceramic in order to find out dynamics of the phase transition in this donor doped ceramic.

2. SPECIMENS AND EXPERIMENTAL PROCEDURES

The PLZT studied is $(\text{Pb}_{94}\text{La}_6)(\text{Zr}_{60}\text{Ti}_{40})\text{O}_3$, noted as PLZT 6/60/40. The sample was pre-sintered for 1h at 1150 °C in oxygen, and sintered at 1240 °C under pressure of 3 MPa for 13h. Density of the ceramic was 7.70 g/cm³ by dimension measurement. The average grain size is about 2.5 µm by scanning electron microscope. The compacts were sliced into bars of 1.5x5x40 mm³ for mechanical loss and elastic modulus measurements.

Differential scanning calorimetry (DSC) measurement was carried out by using Perkin-Elmer DSC7 system with heating rate of $10^{\circ}\text{C}/\text{min}$. The result was obtained after subtraction of the background. X-ray diffraction (XRD) measurements at room temperature were performed on a Rigaku diffractometer with graphite monochromator [0002] by using Cu K α radiation. X-ray scans were carried out with a 2θ step of 0.02° and $1.00^{\circ}/\text{min}$. The voltage of x-ray tube was 40 kV, and the current was 25 mA. Mechanical loss and elastic modulus measurements were carried out by two methods. The shear elastic modulus G and Q^{-1} are measured from 50°C to 250°C by an inverted pendulum. Young's modulus E and Q^{-1} are measured at kilohertz range by using resonance curve method from -100°C to 300°C .

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the phase diagram of PLZT ceramics ($\text{Pb}_{100-x}\text{La}_x\text{Zr}_{65}\text{Ti}_{35}\text{O}_3$) [6]. In the diagram, PE is para-electric phase with cubic crystalline structure, FE's are ferroelectric phases, AFE is anti-ferroelectric phase. FE1 and FE2 have rhombohedral structures, and FE3 is considered as quasi-cubic phase.

For the concentration of $x = 6$ at% La, there are three phase transitions during cooling:

- 1) from para to ferroelectric phases: PE to FE3, 190°C ; 2) from FE3 to FE2 in the ferroelectric state, 170°C ; 3) from FE2 to FE1 in the ferroelectric state, 60°C .

The phase structure of PLZT 6/60/40 cannot easily be determined, because the composition is close to the morphotropic phase boundary with the rhombohedral and tetragonal phase. By comparing the variations of dielectric constant before and after polarization, Paletto et al. pointed that the PLZT 6/60/40 has the rhombohedral phase [7]. However, from the XRD pattern of PLZT 6/60/40 in **Fig. 2**, the crystal structure of PLZT 6/60/40 could be indexed as a tetragonal phase. The parameters of unit cells are determined as $a = 0.4080$ nm; $c = 0.4097$ nm. Considering the shape of the diffraction peaks of [002] and [200] and the values of $c/a = 1.004$, the crystal structure of the material might be considered as quasi-rhombohedral as indicated in the **Fig. 1**.

Figure 2: Room Temperature XDR from 42° to 47° of 2θ

Figure 1: Phase diagram for PLZT (X/65/35) [6]

Figure 3: DSC measurement of PLZT 6/60/40

Fig. 3 gives the result of DSC measurement on PLZT ceramic. There are three peaks located at 180°C (T_c), 160°C (T_{c-s}), and 96°C (T_{r-r}), respectively. It is possible to attribute the peak T_c as the para-

ferroelectric transition of PE-FE3, the peak T_{c-s} as the transition of FE3-FE2, and T_{r-r} as the transition of FE2-FE1 as it is shown in the phase diagram of the Fig. 1.

Fig. 4 shows the results of Q^{-1} and shear modulus of PLZT 6/60/40 ceramic during heating (0.5°C/min). There is one large loss peak located at 188°C and another small peak located at 95°C. The heights of both peaks are reciprocally proportional to the vibration frequency. This is the feature of mechanical loss due to phase transition [8]. The peak located at 188°C corresponds to the ferro-paraelectric phase transition. This peak is connected to the anomaly of elastic modulus located at 180°C. However, there is no minimum on the elastic modulus at 95°C. So other study is needed to clarify the origin of the 95°C peak.

Figure 4: $G(T)$ and $Q^{-1}(T)$ at low frequencies

Figure 5: Exponent of phase transition at T_c

Concerning mechanical loss with phase transitions, it is accepted that the Q^{-1} associated with first order phase transition can be divided into three parts [9]:

- 1) Q^{-1}_t , transient component occurring under non-isothermal conditions and at sufficiently low frequencies. It is determined by the thermally induced phase transformation rate.
- 2) Q^{-1}_s , stationary component occurring under either isothermal conditions or at frequencies at least in the kilohertz. It is related to the change in transformed fraction induced by the vibrating stress.
- 3) Q^{-1}_i , attributed to the intrinsic damping generated in the two coexisting phases and can be written as $Q^{-1}_i = \kappa Q^{-1}(\text{new phase}) + (1-\kappa)Q^{-1}(\text{parent})$, where κ = the fraction of the new phase.

Figure 6: $E(T)$ and $Q^{-1}(T)$ at kilohertz

Figure 7: Double peaks on the resonance curves

Concerning the Q^{-1} peak at low frequencies, it can be expressed as $Q^{-1}_t = A(T)((dT/dt)/2\pi f)^\alpha$ with $0 < \alpha < 1$, where dT/dt = the heating rate, f = the frequency of the vibration [9]. **Fig. 5** shows the dependence of Q^{-1}_t on $1/f$ of the material. The results show that the loss peak height changes with vibration frequency during the phase transition. Concerning such dependence of Q^{-1}_t , Wang et al. [10] consider that the nucleation rate of the new phase is in first approximation proportional to the stress, and the proportionality

coefficient, K , is controlled by the lattice softening near a first-order phase transition. They make an ad hoc hypothesis that K can be written as $K = \beta / |T_c - T|^n$ with $0 < n < 1$, and $n = 1 - \alpha$. So that the exponent α is determined by the nucleation rate of the phase transition. The α is determined to be 0.4.

Fig. 6 gives the results of Q^{-1} and Young's modulus E at kilohertz from -100°C to 300°C on PLZT 6/60/40. The Q^{-1} peak located at 185°C is linked with the Young's modulus anomaly which begins at 170°C . Besides, we notice that between 50°C and 90°C , the Q^{-1} values are scattered. Such scattering is explained by the modification of resonance curves as it is shown in Fig. 7. Along this temperature range (50 - 90°C), we observe a second small resonance peak which height is temperature dependent. For temperatures higher than 100°C , this second resonance peak disappears and the Q^{-1} values are no more scattered. So, it is reasonable to suppose that in the 50°C - 90°C temperature range, the two FE1 and FE2 rhombohedral phases coexist. Complementary experiments are needed in order to confirm such hypothesis and to verify if the ratio of resonance peak heights is connected with the fraction of transformed phase.

4. Conclusions

In PLZT 6/60/40 ceramic, the shear elastic modulus shows that the T_c is located at 180°C for the transition from cubic to rhombohedral phase. The Q^{-1} curves at low frequencies (0.1 Hz to 1 Hz) show clearly a peak of such phase transition. The height of this peak is frequency dependent. About the transition between the two rhombohedral FE1 and FE2 phases no elastic modulus anomaly and no Q^{-1} peak is observed. However, from 50°C and 90°C the resonance curves show two peaks and each of them could be attributed to one phase FE1 or FE2. Below 50°C the phase structure is only FE1 and above 90°C the transformation of the FE1 is finished. Such suggestion about this progressive phase transition needs complementary experiments.

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