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LOW-FREQUENCY INTERNAL FRICTION STUDY ON MODIFIED LEAD METANIOBATE CERAMICS

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Six Q^{-1} peaks in freshly-worked $PbNb_2O_6$ ceramics are observed by low-frequency internal friction measurement so far as we know for the first time. P_1, P_2, and P_4 appear at the first heating process with remarkable shear modulus anomalies. But they are not observed during the cooling process or in the well-annealed samples. Those peaks are considered to be related with the working processes. P_3 is a widened Debye relaxation peak in nature. The activation energy and pre-exponential factor are about 1.01 eV and 2.5×10^{-12} s, respectively. This peak is attributed to the interaction of domain walls and oxygen vacancies. P_6 is corresponded with the paraelectric and ferroelectric phase transition. P_5, appearing near T_c, is thought to be caused by the viscous movement of the domain walls.

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I. INTRODUCTION

Internal friction (IF) measurement is one of the most microstructure-sensitive methods. It can give valuable information on the local reorientation of defect dipole and the interaction between point defects and other imperfections for many materials.[1] For ferroelectric materials, it can provide a lot of direct information on interaction between the domain walls and point defects.[2−5] Up till now, most of the jobs are mainly concentrated on ferroelectric single crystals such as KDP, TGS, LNPP and $BaTiO_3$,[2−3] few work has been done for polycrystalline ceramics, and the present authors have not found any other reports concerning the internal friction studies on the lead metaniobate ($PbNb_2O_6$) ceramics. Lead metaniobate is an excellent candidate material for high-temperature transducers and detectors for its significant advantages:[6] high Curie temperature, a large anisotropy in electromechanical coupling factors between thickness mode K_t and planar mode K_p ($K_t \gg K_p$) and a very low mechanical quality factor Q_m. Owing to some reasons of technological characters, this ferroelectric ceramics has high concentration of point defects,[7] which may inhibit the movement of domain walls and affect the piezoelectric properties of this material. Therefore the interaction of point defects with the domain walls, which leads to the internal friction, is of great interest. Here, we firstly report the low frequency internal friction (Q^{-1}) measurement results of $PbNb_2O_6$ ceramics, and highlight some details of domain walls movement and mechanical dissipation in this material.

II. EXPERIMENTAL PROCEDURE

The fundamental formula of the samples is $Pb_{0.95}Sr_{0.05}(Nb_{1.98}Ti_{0.02})O_{5.99}$. Reagent-grade Pb_3O_4, Nb_2O_5, $SrCO_3$ and TiO_2 powders were used as starting materials. The powders were weighted and mixed in a ball mill using distilled water as a medium, then dried at 120℃ for 24 h, the mixed powders were calcined at 1000℃ for 1 h (first time) and 1260℃ for 1 h (second time). The purity of orthorhombic $PbNb_2O_6$ powders was checked by X-ray diffraction (XRD) analysis. As shown in Fig.1, no second phase was found. The powders were pressed uniaxially at 30 MPa to make prismatic bars (8 mm×8 mm×70 mm) and then pressed isostatically at 200 MPa, the green compacts were sintered at 1280℃ for 2 h in a sealed Al_2O_3 crucible. The sintered compacts were sliced into rectangular plates with the dimensions of 50 mm×3.5 mm×1 mm. The low frequency Q^{-1} measurements were performed on an inverted torsion pendulum in the mode of free decay. Internal friction Q^{-1} and the square of the oscillation frequency f^2, which is proportional to the shear modulus G, were recorded as functions of temperature T at a heating or cooling rate of 2–5 K/min. The starting surface strain is about 10^{-5}. The experiments for multi-frequencies were performed on a multifunctional internal friction meter in the mode of forced-vibration.

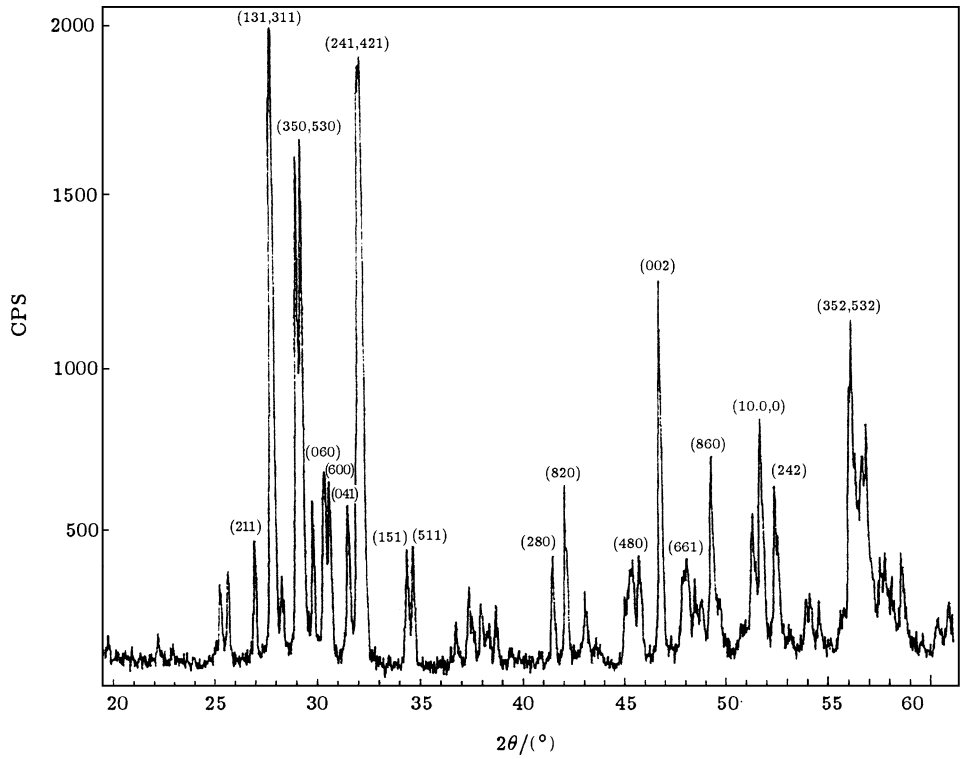


Fig.1. XRD pattern for the modified $PbNb_2O_6$ ceramics.

Ⅲ. RESULTS AND DISCUSSION

Figure 2 shows the Q^{-1} and f^2 versus T curves of a freshly-worked $PbNb_2O_6$ sample, measured at about 1.2 Hz. Six Q^{-1} peaks located around 70℃ (P_1), 90℃ (P_2), 200℃ (P_3), 260℃ (P_4), 440℃ (P_5) and 510℃ (P_6) are observed. P_6 is attributed to the paraferroelectric phase transition, which agrees reasonably with the published results of T_c measurement.[8] P_5, which appears at about 70℃ below T_c, is similar to that of TGS and KDP crystals. It has been confirmed to be caused by the viscous motion of domain walls.[3] P_1, P_2, and P_4 are fully developed on the first heating excursion with good reproducibility for different samples, but they are not observed in the second heating processes or in well-annealed samples. The remarkable anomalies of shear modulus on the $f^2(T)$ curves shown in Fig.2 (a) reveal as if they were caused by phase transition, but both phase equilibrium plot and DTA investigations fail to verify them. So P_1, P_2 and P_4 may be correlated with the working processes, the details of these peaks will be further discussed in a future paper. For P_3, we notice that it has the following features: 1) It shifts to higher temperature with increasing frequency, characterizing that it is a thermally activated relaxation peak in nature. 2) It is insensitive to heating or cooling rate. 3) Its height increases on cooling processes in air and simultaneously it slightly

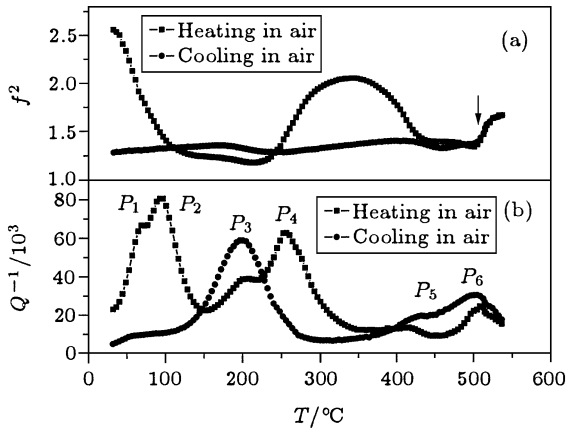


Fig.2. Temperature dependence of Q^{-1} and f^2 for freshly-worked $PbNb_2O_6$ ceramics.

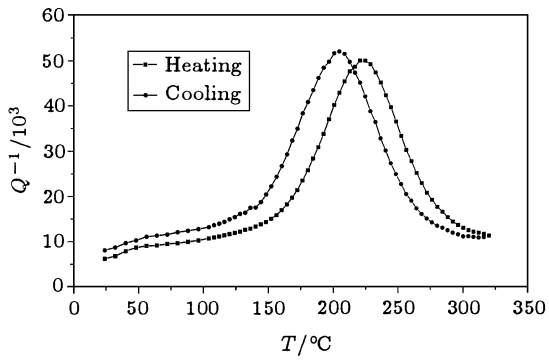


Fig.3. Temperature dependence of Q^{-1} for $PbNb_2O_6$ ceramics on the second heating and cooling excursion in air.

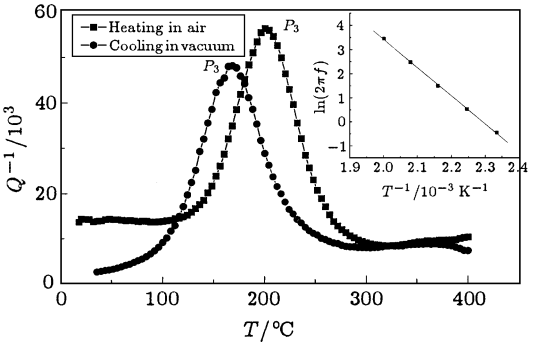


Fig.4. Effect of vacuum annealing in-situ (at 400 ℃ for 1 h) on the Q^{-1} of P_3. The Arrhenius plot for P_3 is shown in the inset.

shifts to lower temperature (Figs.2 (b) and 3); a vacuum annealing in-situ at 400℃ for 1 h was found to decrease the height of the peak, and the peak position shifts 50℃ toward lower temperature (Fig.4). 4) The peak is commonly about one and a half as broad as the standard Debye peak.

According to anelastic theory,[1] at the peak temperature $2\pi f\tau = 1$, for a thermal activation process, the relaxation time τ satisfies Arrhenius law $\tau = \tau_0 \exp(Q/kT)$, where Q is the activation energy, T is absolute temperature, τ_0 is pre-exponential factor and k is the Boltzmann constant. Thus from the Arrhenius plot of $\ln 2\pi f$ versus $1/T$, shown in the inset in Fig.4, Q and τ_0 for P_3 are determined to be 1.01 eV and 2.5×10^{-12} s, respectively. Considering that an activation energy of about 1 eV is near the typical value for the migration enthalpy of oxygen vacancy in ferroelectric oxide,[9,10] and the modified $PbNb_2O_6$ has high concentration of oxygen vacancy because of partial reduction of Nb^{5+} to Nb^{4+} and the replacement of Ti^{4+} for Nb^{5+},[7] we think that P_3 is connected with the oxygen vacancy relaxation. However, P_3 is unlikely caused by the simple relaxation of lattice oxygen vacancies. Because P_3 is found to be decreased with increasing the concentration of oxygen vacancy by thermal treatment in different atmospheres (Figs.3 and 4), and the pre-exponential factor τ_0 is also larger than the typical value of 10^{-14} for the simple point defects relaxation. Similar damping peaks were also observed in PZT by Posnikov et al.,[11,12] and two possible mechanisms were proposed to explain the nature of the peaks[12]: 1) the oscillation damping of 90° domain walls by mobile point defects; 2) the interaction between mobile charged point defects and immobile 90° and 180° domain walls. According to the first mechanism of Posnikov's models, the Q^{-1} peak height should be proportional to the concentration of point defects, which is contrary to our experimental results. Furthermore, with the increase of concentration of oxygen vacancy, the activation energy for oscillation damping of domain boundaries will increase for its stronger pinning to domain boundaries. So P_3 should shift to higher temperature according to Arrhenius law, which is also contrary to the results that P_3 shifts to lower temperature after treatment in vacuum at 400℃. In a word, both simple oxygen vacancy relaxation and oscillation damming of domain walls mechanisms cannot provide a satisfactory explanation for P_3.

We propose that P_3 be attributed to the interaction between oxygen vacancies-related defects and domain walls. At low concentration of oxygen vacancy, the pinning of oxygen vacancy to the domain walls is comparatively weak, thus the oscillation damping of domain walls will dominate the relaxation processes. At lower temperature oxygen atoms diffuse into the sample more quickly than they diffuse out of the sample according to the dynamic study of in-diffusion oxygen,[13,14] consequently the concentration of oxygen vacancy is decreased after heating process, and the internal friction caused by the domain walls oscillation will increase due to its easier mobility. At the sametime, the activation energy for the domain walls damping is also decreased for the weaker domain walls pinning, so the peak will slightly move to lower temperature during the cooling process in air according to Arrhenius equation $\tau = \tau_0 \exp(Q/kT)$. When the concentration of oxygen vacancy is very high, excess oxygen vacancy will segregate at the domain walls and the domain walls become less mobile. So simple oxygen vacancy relaxation may become the dominant relaxation factor under such conditions. This relaxation process requires comparatively smaller activation energy and leads to lower relaxation strength. Therefore annealing in vacuum (10 Pa), which greatly increases the concentration of oxygen vacancy, will decrease the height of P_3 and shift the location of it to lower temperature.

Deviations between our experimental results and Posnikov's theory probably imply that the theory is oversimplified. It is noted that only electrostatic interaction of point defects with domain walls was taken into account in the derivation of the internal friction equations. Actually, the interaction between the point defects and domain walls is far more complicated. According to Huang et al.,[15] there are five forces acting on domain walls that must be considered: 1) the configuration force by the external stress, 2) the interac-

tion force among the walls, 3) the viscous force as the domain walls move in the crystals, 4) the recovering force due to the pinning defects, and 5) the Peierls force.

IV. CONCLUSIONS

Six Q^{-1} peaks in freshly-worked $PbNb_2O_6$ ceramics had been observed by low-frequency internal friction measurement for the first time. Among these peaks, P_3 is a relaxation peak in nature with an activation energy of 1.01 eV and a pre-exponential factor of 2.5×10^{-12} s, and it is attributed to the interaction of domain walls and oxygen vacancy. P_1, P_2 and P_4 appear on the first heating process with remarkable anomalies of shear modulus. But they are not observed in cooling process or in well-annealed samples at high temperature. They are connected with the working processes. The physical mechanisms responsible for such peaks will be discussed in detail in a future paper.

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