

Mechanical properties related to the relaxor-ferroelectric phase transition of titanium-doped lead magnesium niobate

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(Received 3 May 2002; accepted for publication 7 June 2002)

The dielectric properties, internal friction, and Young's modulus of $(1-x\%) \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\% \text{PbTiO}_3$ (for $x=13, 23$, and 33) ceramics have been measured. A phase-transition-like internal friction peak associated with Young's modulus softening has been observed at temperature T_{R-F} , which can be attributed to the relaxor-to-ferroelectrics ($R-F$) phase transition. Therefore, the $R-F$ phase transition can be explained in terms of the paraelectric-to-ferroelectric phase transition of paraelectric matrix in the materials. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1498498]

Relaxor ferroelectrics has a very complicated phase diagram.¹⁻³ The transition from the paraelectric phase to the ergodic relaxor phase corresponds to the appearance of polar nanodomains below the temperature T_d .⁴ Cooled under a high enough bias electric field, relaxor ferroelectrics would undergo a transition to the long-range ferroelectric phase below a certain temperature T_{R-F} . Otherwise, it would evolve to a nonergodic state without long-range ferroelectric order.^{2,3,5} The ergodic-to-nonergodic transition shows the Vogel-Fulcher freezing process of nanodomains, which can be simulated with the spin glass model.^{1,2,6-9} The relaxor-to-ferroelectric ($R-F$) phase transition, as reported in some papers, was assumed to be due to the increase of the correlation length among nanodomains with the decrease of temperature,^{6,10} and could be explained by the spin glass model as well. However, some neutron inelastic diffraction measurements on relaxors show a zone center transverse optic mode which softens in a manner consistent with that of a ferroelectric soft mode at a high temperature.^{11,12} So there would be not only the change of correlation length of polar domains but also a structural change around the $R-F$ phase transition. Therefore, the $R-F$ phase transition of relaxors is not very clear and further investigation is needed.

It is well known that the complex perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) is a typical relaxor ferroelectrics which has been studied for more than 40 years since it was discovered by Smolenskii.¹³ Doping PMN with PbTiO_3 (PT), a complete crystalline solution of $(1-x\%) \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\% \text{PbTiO}_3$ ($0 \leq x \leq 100$) (abbreviated as PMNT_x) is formed. With the addition of PT, PMNT_x will change continuously from relaxor ferroelectrics to normal ferroelectrics (for $x > 35$).⁵ As reported in some papers, in the range of $13 \leq x < 35$, a $R-F$ phase transition can happen spontaneously even without bias voltage.^{14,15} So, in this paper, we focused on the mechanical and dielectrical properties of PMNT_x ceramics with $x=13, 23$, and 33 for it is more

convenient to study the $R-F$ phase transition. Because internal friction and Young's modulus measurements are very sensitivity to phase transition and relaxation process, we think our results will be very helpful for the understanding the $R-F$ transition.

The PMNT_x ceramic samples were prepared with raw materials of high purity, and were sintered at 1200°C for 2 h using the Columbite precursor method as described by Swart and Shrut.¹⁶ The samples were of pure perovskite structure and no pyrochlore phase was detected by x-ray diffraction. Silver electrodes were evaporated onto the surfaces of the samples. The dielectric properties were measured using a HP4194A impedance analyzer in the frequency from 100 Hz to 100 kHz range in a vacuum chamber in the temperature range from 170 to 520 K measured by a thermal couple attached to the bottom electrode. The mechanical properties of the samples were measured by the free-free bar apparatus¹⁷ in a vacuum chamber in the temperature range from 90 to 570 K measured by a thermal couple. The measurement frequency is around 1 KHz.

As shown in Fig. 1, the dielectric permittivities of PMNT_x ($x=13, 23$, and 33) ceramics are strongly frequency dependent and show peaks with the peak temperatures T_M of

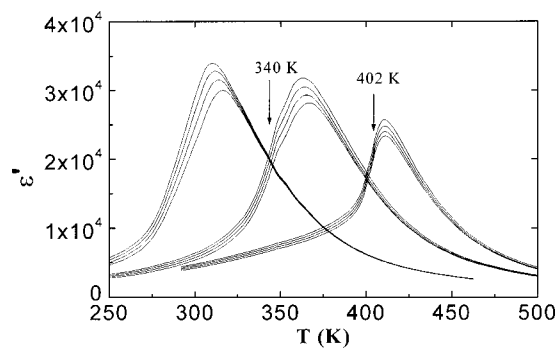


FIG. 1. Real part of dielectric permittivities of PMNT_x ($x=13, 23$, and 33) from the left- to right-hand side) measured at the heating rate of 1 K/min using HP4194A. The measurement frequencies are 0.1, 1, 10, and 100 kHz, respectively, from top to bottom.

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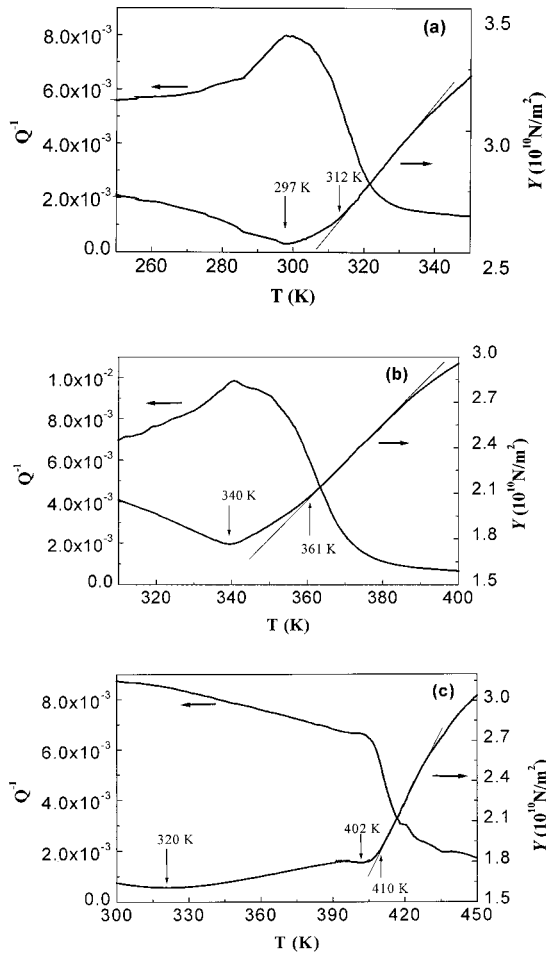


FIG. 2. Internal friction and Young's modulus of PMNT x measured in the heating run. (a) of PMNT13, (b) of PMNT23, and (c) of PMNT33.

312, 363, and 410 K for three different samples, respectively. For PMNT23, there is a weak drop of dielectric permittivities at the temperature of 340 K, and for PMNT33, a steeper drop happens at 402 K. We attribute the drop of dielectric permittivities to the spontaneous $R-F$ phase transition, which has been reported and pointed out in some papers. The drop of dielectric permittivities at the transition temperature T_{R-F} is not as sharp as that of single crystals that we reported before.¹⁸ We assume it is due to the reason that the component of the ceramics is not homogeneous and the transition temperatures of different parts have a distribution around the temperature T_{R-F} . No dielectric anomaly related to $R-F$ phase transition can be observed in PMNT13 ceramics. As reported by Colla *et al.*,⁵ the $R-F$ phase transition of PMNT13 hardly can be detected by dielectric measurement without bias voltage applied.

The internal friction Q^{-1} and Young's modulus Y of PMNT ceramics are shown in Fig. 2. An internal friction peak associated with Young's modulus minimum appears at 297, 340, and 402 K for $x=13$, 23, and 33, respectively. Because the internal friction peak and the Young's Modulus minimum appear at almost the same temperature, we consider that the internal friction peak is due to a phase transition which happened at that temperature and the peak is induced by the motion of new phase boundaries or the fluctuation of a new phase under periodically applied stress. For $x=23$ and 33, the internal friction peak temperatures are

of the same value as that of $R-F$ phase transition. Therefore, it can be explained in terms of the $R-F$ phase transition. Thus, the $R-F$ phase transition for PMNT13 should be at 297 K. Because the internal friction method is very sensitivity to the phase transition, so the $R-F$ phase transition can be detected more obviously by this method than by dielectric measurement. A kink of Young's modulus can be observed at 312, 361, and 410 K for $x=13$, 23, and 33, respectively, which is the same value as that of the peak temperature T_M of dielectric permittivity of 1 kHz. Therefore, it may be due to the dynamic relaxation of nanodomains, which will be explained carefully next. Another very broad internal friction peak associated with a modulus minimum at 320 K is found for PMNT33. It corresponds to the phase transition from tetragonal to rhombohedral structure, which has been reported before.³

The dynamic relaxation of nanodomains may affect the dielectric permittivity and Young's modulus. The relationship between the dielectric permittivity and frequency and that between Young's modulus and frequency due to the relaxation of the nanodomains are:

$$\epsilon'(\omega, T) = \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) \int_0^{\infty} g(\tau, T) / (1 + \omega^2 \tau^2) d\tau, \quad (1)$$

$$M(\omega, T) = M_0(T) - \Delta M(T) \int_0^{\infty} g(\tau, T) / (1 + \omega^2 \tau^2) d\tau, \quad (2)$$

where ω is the measurement frequency, ϵ_s is the static dielectric constant, ϵ_{∞} is the high-frequency dielectric constant, and $g(\tau, T)$ is the distribution of relaxation units with relaxation time τ . $M_0(T)$ is the modulus if there is no nanodomains relaxed with applied stress. $\Delta M(T)$ is the relaxation modulus, which depends on the number and size of nanodomains. Polar nanodomains appear below T_d , which is higher than ~ 600 K, and with the decrease of the temperature the number and the size of them increase. So $\Delta M(T)$ increases with the decrease of temperature below T_d . Even if $M_0(T)$ did not change with frequency, $M(\omega, T)$ would decrease with the decrease of temperature for the increase of $\Delta M(T)$. But in this case, modulus would show a minimum near the peak temperature of dielectric permittivity of same measurement frequency for the function $g(\tau, T)$ in Eqs. (1) and (2) is the same. However, the modulus minimum appears at the $R-F$ phase transition temperature T_{R-F} . So $M_0(T)$ also changes with temperature and has a minimum value at T_{R-F} . Since a kink of modulus appears at the peak temperature of dielectric permittivity T_M , the relaxation of nanodomains did influence the modulus as shown in Eq. (2). So the decrease of modulus with the decrease of temperature above T_{R-F} is due to two factors: one is the $R-F$ phase transition, another one is the relaxation of nanodomains.

The modulus softening near the $R-F$ phase transition is exactly like the paraelectric-ferroelectric ($P-F$) phase transition of some normal ferroelectrics, which can be explained by Landau's theory considering the coupling between strain and order parameter in the free energy.¹⁹ In the relaxor phase, the polar nanodomains are already in the ferroelectric phase. So only the paraelectric matrix around polar nanodomains may change to the ferroelectric phase and induce

the softening of $M_0(T)$. Therefore, we consider the $R-F$ phase transition corresponds to the $P-F$ phase transition of paraelectric matrix. Because the dielectric measurements are very sensitive to the relaxation of nanodomains, the change induced by $P-F$ phase transition of paraelectric matrix is too small to be separated from the effect of nanodomains. Therefore, in some reported papers, the $R-F$ phase transition was also described by the spin-glass model related to nanodomains.⁹ From our mechanical measurements, the two effects can be separated and the $R-F$ phase transition can be confirmed not to be due to the interaction of nanodomains.

In conclusion, we have found internal friction peak and softening of Young's Modulus related to the $R-F$ phase transition in PMNTs, which indicate the $R-F$ phase transition is due to a $P-F$ phase transition of the paraelectric matrix. The modulus softening of PMNTs can be attributed to both the phase transition of paraelectric matrix and the relaxation of the nanodomains.

The authors acknowledge the financial support by the Center for Smart Materials of The Hong Kong Polytechnic University and the National Natural Science Foundation of China.

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