Internal friction and Young's modulus of titanium-doped lead magnesium niobate

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The dielectric properties, internal friction and Young's modulus of (1-x%) $Pb(Mg_{1/3}Nb_{2/3})O_3$ $-x\%PbTiO_3$ (for x=13,23,33) 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. The softening of Young's modulus corresponding to the appearance of polar nano-domains is also found at the temperature far above T_m.

INTRUDUCTION

Relaxor ferroelectrics has a very complicate phase diagram [1-3]. The transition from paraelectric phase to the ergodic relaxor phase corresponds to the appearance of polar nano-domains below the temperature T_d [4]. Cooled under bias electric field high enough, relaxor ferroelectrics would undergo a transition to long-range ferroelectric phase below a certain temperature T_{R-F}. Otherwise, it would evolve to nonergodic state without long-range ferroelectric order [2,3,5]. The ergodic to nonergodic transition shows the Vogel-Fulcher freezing process of nano-domains, 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 nano-domains 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 (TO) mode which softens in a manner consistent with that of a ferroeleIctric soft mode at high temperature [11,12]. So there would be not only the change of correlation length of polar domains but also a structural change happened 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 $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is a typical relaxor ferroelectrics which has been studied for more than forty years since it was discovered by Smolenskii[13]. It is widely accepted that the disorder induced polar nano-domains play a significant role in the relax properties of the PMN. The polar nano-domains are firstly found by Burns and Dacal[4]. They found out that the manodomains appears at the temperature of T_d□620K. And then, the polar nano-domains in relaxor ferroelectric is confirmed by many other experiments [10,11, 14, 15]. But till now, the details of the microstructure of the polar nano-domains is still unclear.

Doping PMN with $PbTiO_3$ (PT), a complete crystalline solution of (1-x%)$Pb(Mg_{1/3}Nb_{2/3})O_3$ $-x\%PbTiO_3$ (0 x 100) (abbreviated as PMNTx) is formed. With the addition of PT, PMNTx will change continuously from relaxor ferroelectrics to normal ferroelectrics (for x>35) [5]. As reported in some papers, in the range of 13 x<35, a R-F phase transition can happen spontaneously even without bias voltage [15,16]. So in this paper we focused on the mechanical properties of PMNTx ceramics with x= 13, 23, 33 for it's 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 to R-F transition.

EXPERIMENTAL

The PMNTx ceramic samples were prepared with raw materials of high purity, and were sintered at 1200°C for 2 hours using the columbite precursor method as described by Swart and Shrout [18]. The samples were of pure perovskite structure and no pyrochlore phase was detected by X-ray diffraction. Sliver electrodes were evaporated onto the surfaces of the samples. The dielectric properties were measured using HP4194A impedance analyzer in the frequency from 100Hz to 100kHz range in a vacuum chamber in the temperature range from 170K to 520K measured by a thermal couple attached to the bottom electrode. The mechanical properties of the samples were measured by the free-free

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bar apparatus in a vacuum chamber in the temperature range from 90K to 800K[19]. The measurement frequency is around 1KHz.

RESULTS AND DISCUSSION

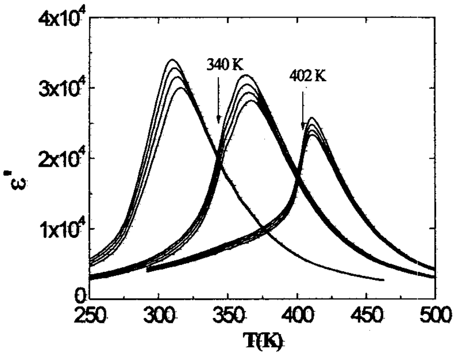


FIG.1 Real part of dielectric permittivities of PMNTx (x=13,23,33 from left to right) measured at the heating rate of 1K/min using Hp4194A. The measurement frequency is 0.1, 1, 10, 100kHz respectively from top to bottom.

As shown in fig.1, the dielectric permittivities of PMNTx (x=13, 23, 33) ceramics are strongly frequency-dependent and show peaks with the peak temperatures T_M of 312K, 363K and 410K for three different samples, respectively. For PMNT23, there is a weak drop of dielectric permittivities at the temperature of 340K, and for PMNT33, a steeper drop happens at 402K. 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 so sharp as that of single crystals that we reported before [20]. 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 E. V. Colla [6], the R-F phase transition of PMNT13 hardly can be detected by dielectric measurement without bias voltage applied.

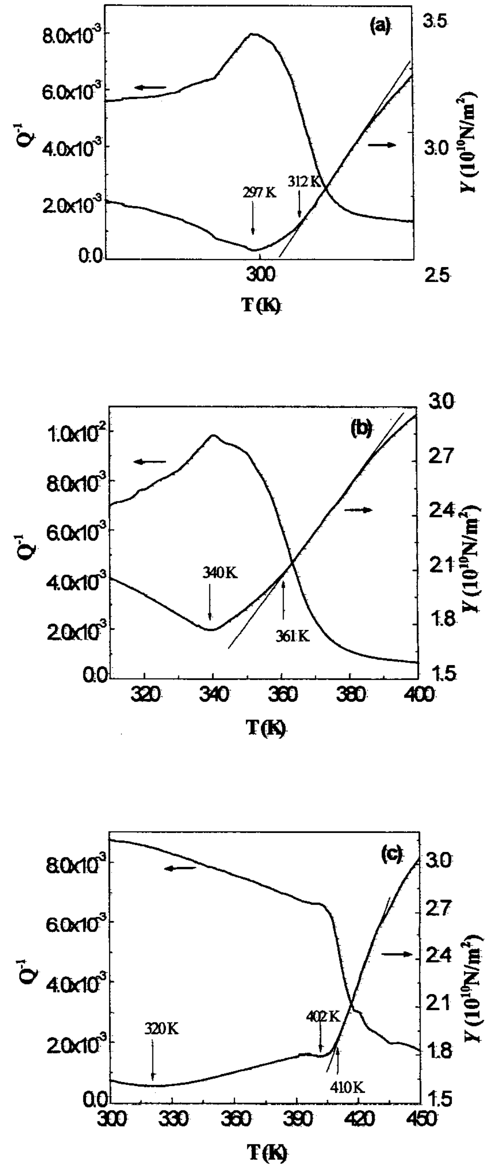


FIG.2 Internal friction and Young's modulus of PMNTx measured in the heating run. (a) of PMNT13; (b) of PMNT23; (c) of PMNT33.

As shown in Fig.2, an internal friction peak associated with Young's modulus minimum appears at 297K, 340K and 402K 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 the internal friction peak is due to a phase transition happened at that temperature and the peak is induced by the motion of new phase boundaries or the fluctuation of 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 297K. 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 312K, 361K and 410K for x=

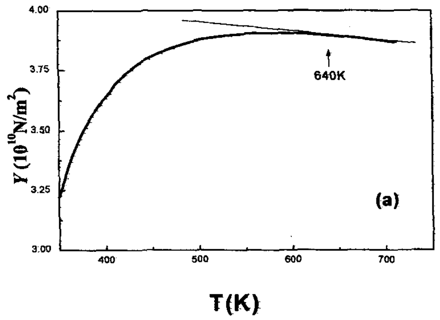
13, 23 and 33, respectively, which is the same value as that of the peak temperature T_M of dielectric permittivity of 1KHz. Therefore it may be due to the dynamic relaxation of nano-domains, which will be explained carefully below. Another very broad internal friction peak associated with a modulus minimum at 320K 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 nano-domains will affect the dielectric permittivity and the 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 nano-domains are shown below:

$$\varepsilon'(\omega,T)=\varepsilon_\infty+(\varepsilon_s-\varepsilon_\infty)\int_0^\infty g(\tau,T)/(1+\omega^2\tau^2)d\tau \quad (1)$$

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

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 nano-domains relaxed with applied stress. $\Delta M(T)$ is the relaxation modulus, which depends on the number and size of nano-domains. It is well known that polar nano-domains appear below T_d, 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 $\Delta M(T)$. Thus, the modulus will begin to soften at T_d where the nano-domains appear. The different T_d for PMNT (x=13,23,33) is illustrated in the Fig.3. Suppose that the T_d increase linearly with the addition of the PT, we can get the T_d temperature for pure PMN and PT is 623K and 764K respectively



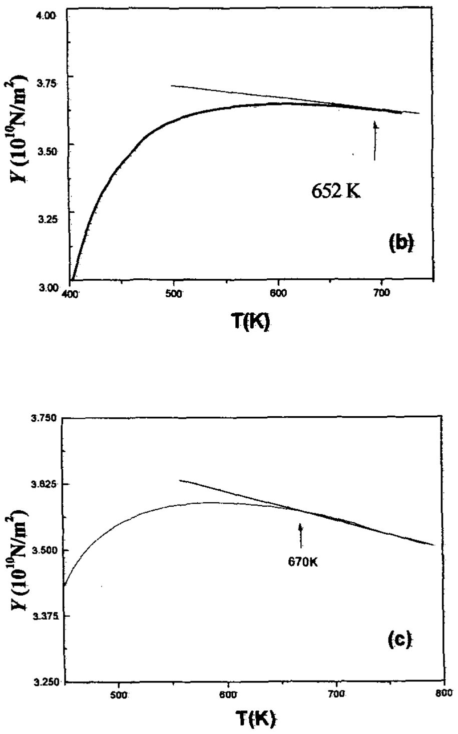


FIG.3 Young's modulus of PMNTx measured at high temperature. (a) PMNT13; (b) PMNT23; (c)PMNT33. The arrows indicate temperatures (T_d) where the nano-domains appear.

According equations (1) and (2), we expect that modulus would show a minimum near the peak temperature of dielectric permittivity of same measurement frequency for the function $g(\tau,T)$ in two equations (1) and (2) is a same one. However, the modulus minimum appears at the R-F phase transition temperature $T_{R\text{-}F}$. So $M_0(T)$ also changes with temperature and has a minimum value at $T_{R\text{-}F}$. Since a kink of modulus appears at the peak temperature of dielectric permittivity T_M, the relaxation of nano-domains did influence the modulus as shown in equation (2). So the decrease of modulus with the decrease of temperature above $T_{R\text{-}F}$ is due to two factors: one is the R-F phase transition, another one is the relaxation of nano-domains.

The modulus softening near 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[21]. In relaxor phase, the polar nano-domains are already in ferroelectric phase. So only the paraelectric matrix around polar nano-domains may change to 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 nano-domains, the change induced by P-F phase transition of paraelectric matrix is too small to be separated from the effect of nano-domains. Therefore, in some reported papers, the R-F phase transition was also described by the spin-glass model related to nano-domains[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 nano-domains.

CONCLUSIONS

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 nano-domains. We also have found the softening of modulus induced by the appearance of the polar nano-domains below T_d.

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