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Mechanical and dielectric loss related to ferroelectric and relaxor phase transitions and domain walls*,**

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Abstract

Two internal friction (Q^{-1}) and dielectric (D) peaks (P_1, P_2) for potassium dihydrogen phosphate, triglycine sulfate and two Q^{-1} peaks for $La_{1-x}Nd_xP_5O_{14}$ were investigated. P_1 is attributed to fluctuations near a second-order phase transition and P_2 is related to domain walls (DWs). Taking into account the temperature dependence of the density and the viscosity of DWs as well as the order parameter, and the interaction between DWs, Q^{-1} and D due to the viscous motion of DWs were calculated and compared with the experimental data for the kilohertz range.

Q^{-1} and D peaks were also measured in the relaxor ferroelectric $0.8Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.2PbTiO_3$ for various frequencies. A qualitative analysis based on DWs and other factors for the peak is suggested.

1. Introduction

The attribution of an internal friction (Q^{-1}) peak measured during step heating ($\dot{T}=0$) a first-order phase transitions (PTs), to coherent interfaces has been widely accepted [1]. Since phase interfaces of coexisting phases, interfaces of variants and twin boundaries in the new phases are all included, separation of the contributions to Q^{-1} due to interfaces of individual type is impossible, and a quantitative investigation of the correlation between Q^{-1} and domain walls (DWs) is not easy. $La_{1-x}Nd_xP_5O_{14}$ (LNPP) undergoes an *mmmF2/m* second-order ferroelastic transition at 141 °C [2]. Thus, in LNPP single-crystal phase interfaces are absent and the presence of twin DWs only in the ferroic phase as well as the simplicity of the domain structure (all walls are parallel planes crossing the whole sample) make the above-mentioned investigation possible [3]. The results will be given in the first part of the paper.

Dielectric investigations of ferroelectric crystals show that a dielectric loss (D) peak always appears slightly below T_c. This peak is considered to be related to DWs [4]. Due to the piezoelectricity of ferroelectrics, a corresponding Q^{-1} peak can also be expected [5].

The mobility of DWs plays an important role in the ferroelectric memory or shape memory effects respectively, and it can be studied by mechanical and dielectric measurements as well as corresponding theoretical analyses. Snead and Welch [6] have proposed a theory of Q^{-1} due to martensitic transitions in A15 alloys on the basis of the movement of DWs and found that Q^{-1} is proportional to the tetragonal deformation $(1-c/a)^2$. This result is in accordance with the experimental data at the high temperature side of the peak in pure A15 alloy, but it disagrees with other experimental results. Possibly because they have not considered the variation of the density of DWs with temperature, so-called domain coarsening, which often occurs in many ferroic phases and the temperature-dependent mobility of DWs. Taking these additional factors into account, we have calculated Q^{-1} and D by using the dynamic equation of DWs [7]. The results are compared with the experimental data of potassium dihydrogen phosphate (KDP) and triglycine sulfate (TGS).

Similarly, in many relaxor ferroelectrics, such as $Sr_{0.4}(Na_{0.5}Bi_{0.5})TiO_3$ (SNBT), $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST), $PbIn_{0.5}Nb_{0.5}O_3$ (PIN), $(1-x)Pb(Mg_{1/3}Ta_{2/3})O_3$–$PbTiO_3$ (PMT–PT), $0.8Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.2PbTiO_3$ (PMN–PT), *etc.*, there is always a D peak at about 10 degrees below T_{max} (the temperature of the maximum of dielectric constant), and the peak position (T_p) shifts to high temperature with increasing frequency [8]. Analysis of this dispersive D peak with the Arrhenius relation is known to yield erroneous results [9]. Viehland *et al.* [9] proposed that this is due to the glassy behaviour of the superparaelectric phase, and used the Vogel–Fulcher relationship, *i.e.* the relaxation time $\tau=\tau_0 \exp[E_a/(T-T_f)]$ to describe the relation between the peak temperature and frequency. According to the

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*Dedicated to Professor T.S. Kê on the occasion of his 80th birthday.

**Invited paper.

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relationship, D will equal zero when $T = T_f$. However, this phenomenon has not been observed. To overcome this difficulty, they introduced a distribution of τ which is dependent on both frequency and temperature [9]. Because domain coarsening [10] and temperature-dependent mobility of DWs also occur in relaxor ferroelectrics, these properties should be taken into account in the theory. In this paper, both Q^{-1} and D of PMN–PT were measured at various frequencies. A qualitative analysis is given below.

2. Experimental details

A two-mode-clamped reed vibration technique with an electrostatic drive and detection device, and the Marx three-component-resonator method were used to measure Q^{-1} in the kilohertz and 10 kHz range respectively. The latter were carried out in a special self-made furnace in which domains of a sample can be observed *in situ* with a polarization microscope during Q^{-1} measurements [3]. D and the dielectric constant (ϵ) were measured on a GR1615-A capacitance bridge with sample size about $10 \times 10 \times 1$ mm^3. The elastic constant C_{ij} was measured by a pulse-echo-overlap method on Matec 6600.

3. Experimental results and theoretical analysis

3.1. Q^{-1} peaks related to second-order PTs and DWs in $La_{1-x}Nd_xP_5O_{14}$

The LNPP samples were cut along the c-axis from a single crystal of composition $x = 0.9$. Two Q^{-1} peaks were obtained at 125 °C (P_2) and 141 °C (P_1), respectively with $f = 5$ kHz [1]. The X-ray analysis and measurement of the elastic constant C_{55} (Fig. 1(a)) show that the peak temperature of P_1 corresponds to T_c (141 °C), whereas there is no structural change at the peak temperature of P_2. *In situ* observations of DWs while the Q^{-1} measurement is being made show that, in the ferroic phase, the density of domain walls N is proportional approximately to $(T_c - T)^{-1}$. Figure 1(b) reveals the variation of N with T. The DWs disappear abruptly at T_c [2]. Figure 1(b) also shows Q^{-1} measured simultaneously for $f = 50$ kHz. Peak P_2 corresponds to the temperature range where N begins to increase rapidly ($N = (50 \pm 10)$ mm). Peak P_2 as well as the N–T curve shows remarkable thermal hysteresis depending on heating or cooling of the samples.

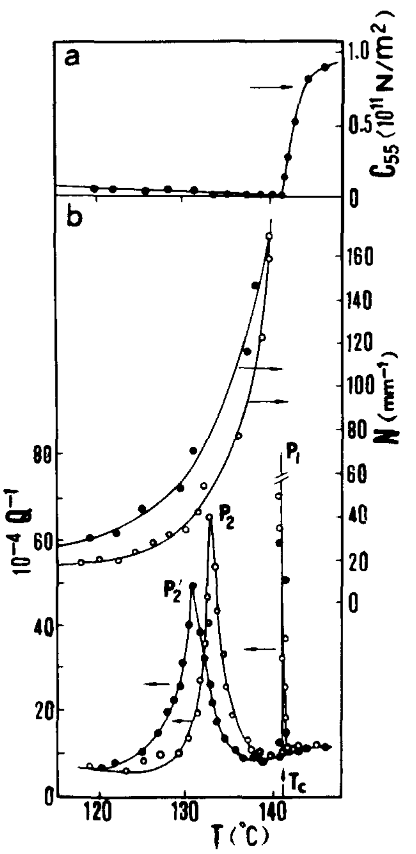

Fig. 1. (a) Elastic modulus and (b) DW density and Q^{-1} measured with the Marx three-component-resonator method *vs.* T (N and Q^{-1} were measured at the same time); ● cooling, ○ heating.

The reason why Q^{-1} appears as peak P_2 instead of varying monotonously with the number of DWs may be interpreted in terms of the interaction between DWs. It has been observed in LNPP that domains move away laterally as a result of the abrupt formation of a new domain like a martensite plate at a relatively larger domain density. The reduction of DW mobility due to interaction between DWs has also been observed in some ferroelastic substances [11]. The thermal hysteresis and abrupt formation of a new domain indicate that coarsening (or fining) of domains has the character of first-order phase transitions, which is also confirmed by the heat capacity results [12], and recent transmission electron microscopy study on lanthanum doped lead–zirconate–titanate (PLZT) leads to the same conclusion [10].

Peak P_1 that appears at 141 °C, has no thermal hysteresis within the resolution of 0.1 K. This means that it is related to the second-order phase transition [2, 13]. However, according to the conventional theories of energy dissipation of second-order phase transition, such as the theory of Landau–Khalatnikov's relaxation of the order parameter and the theory of fluctuation dissipation *etc.* [14], it is generally recognized that Q^{-1} is too small to be detected in the kilohertz range. So, peak P_1 at low frequency has been attributed to the stress-induced preferred orientation of dynamic new phase domains [1].

3.2. Q^{-1} and D related to the viscous motion of DWs in KDP and TGS

3.2.1. Experimental results [5, 7]

The results of Q^{-1} measured at kilohertz in KDP show that there are three peaks (P_{M1}, P_{M2} and P_{M3}) in the temperature range from 90 K to 130 K, as shown in Fig. 2. The P_{M1} peak always appears at T_c whether measured on cooling or heating and is attributed to the second-order PT just as P_1 in Fig. 1(b) [2, 3]. The P_{M2} peak appears about 5 °C below T_c, which exhibits thermal hysteresis for heating and cooling processes, similar to that of LNPP [3] and TGS [5] which have been confirmed to be caused by the movement of domain walls. The P_{M3} peak emerges at 96 K, which has been ascribed to the freezing effect [4].

Two D peaks (P_{D1}, P_{D2}) also appear near T_c in the KDP crystal [7]. P_{D1} appears at exactly T_c. P_{D2} emerges at about 5 °C below T_c, indicating hysteresis for heating and cooling processes as P_{M2} does. The result of D for TGS is similar to that for KDP. In order to verify that the P_{D2} peak for polydomain crystals is due to DWs, D of monodomain ferroelectric crystal α-alanine doped triglycine sulfate (LATGS) [7] was studied and showed that there is hardly any D peak near below T_c and the value of D is about 10^2 times smaller than that of the polydomain crystal TGS. Consequently, the P_2 peak definitely originates from domains.

In order to get more information about the mechanism of the P_{M2} and P_{D2} peaks, the dependence of both Q^{-1} and D loss on frequency was also surveyed. It was discovered that the high temperature sides of the P_{M2} and P_{D2} peaks were almost independent of frequency, but the low temperature sides were obviously frequency-dependent and the positions of the P_{M2} and P_{D2} peaks move to a higher temperature as the frequency increases (Figs. 3–6), but the relaxation time does not obey the Arrhenius relation [7]. These are quite different from the behaviour of thermally activated relaxation peaks.

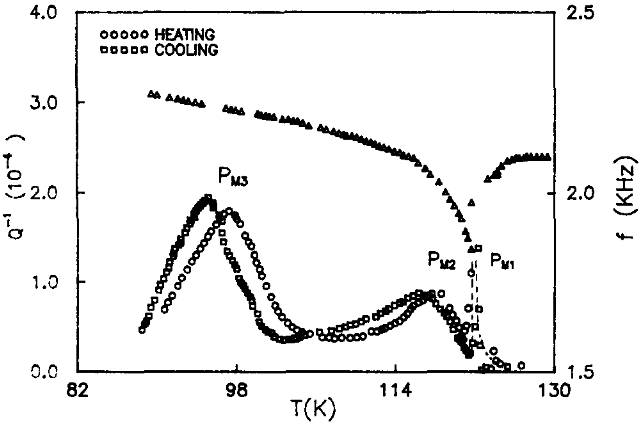

Fig. 2. Q^{-1} on heating and cooling processes and the resonant frequency (f) on heating for KDP *vs.* T.

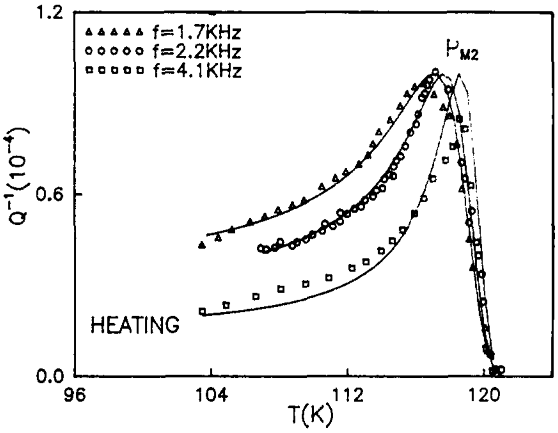

Fig. 3. Q^{-1} *vs.* T with various f of KDP. Theoretical curves (——) with $A_0 = 5.4 \times 10^{-3}$ s, $h_3 = 2 \times 10^{-4}$.

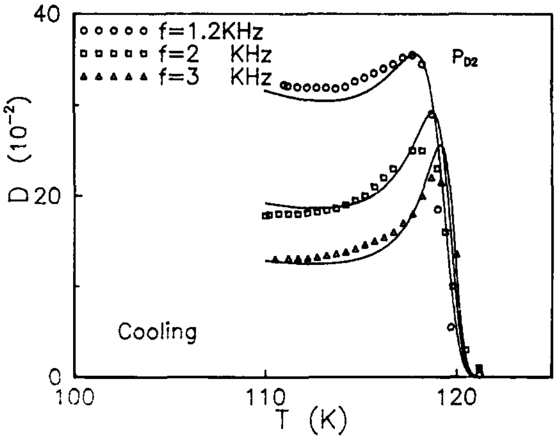

Fig. 4. D *vs.* T with various f of KDP. Theoretical curves (——) with $A_0 = 1.3 \times 10^{-2}$ s, $h_1 = 0.19$.

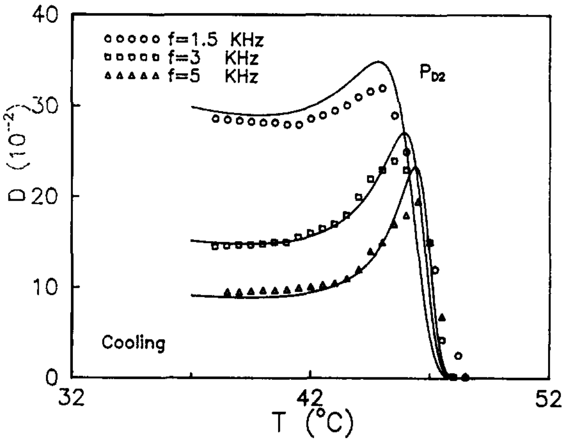

Fig. 5. D *vs.* T with various f of TGS. Theoretical curves (——) with $A_0 = 1.12 \times 10^{-2}$ s, $h_1 = 0.185$.

From all the results mentioned above, the P_{M2} and P_{D2} peaks may be considered to be a kind of peak related to complicated viscous movement of DWs.

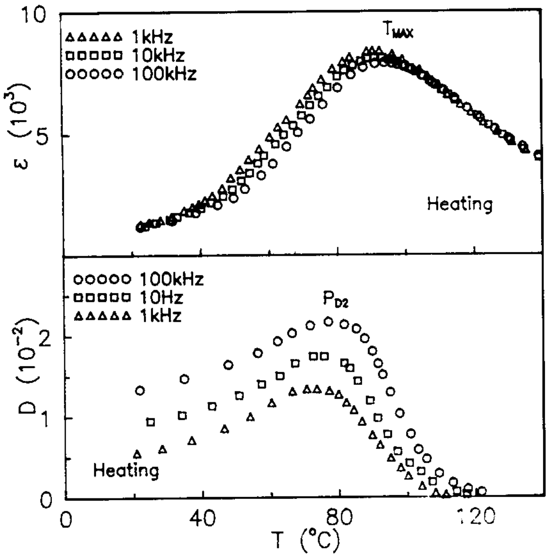

Fig. 6. D and ϵ *vs*. T with various f of PMN–PT.

3.2.2. Theoretical analysis [7]

There are five forces acting on domain walls [7]:

(i) the configuration force F^{C}_{ext} by the external stress;

(ii) the interaction force between the nearest-neighbour DWs F^{I};

(iii) the viscous force $-\Gamma\dot{x}$ [5, 15] as DWs move in the crystal, where Γ is the viscosity coefficient;

(iv) the recovering force $-k_0x$ due to the pinning defects, where k_0 is the force constant; and

(v) the Peierls force which, although existing, is relatively small and can be neglected here [15].

Let M be the effective mass per unit area of the wall, and x, the displacement of wall, the equation of motion of a domain wall is

$$M\ddot{x}+\Gamma\dot{x}+k_0x-F^{I}=F^{C}_{ext} \tag{1}$$

It is easily deduced that [7],

$$F^{I}=-2C_{stst}N\epsilon^{(s)2}_{st}x \tag{2}$$

$$F^{C}_{ext}=2\epsilon^{(s)}_{st}\sigma_{st} \tag{3}$$

where $\epsilon^{(s)}_{st}$ is the spontaneous shear strain ($s\neq t$); C_{stst} is the corresponding shear modulus; N is the number of parallel walls per unit length and σ_{st} is the effective shear stress, which can drive DWs to move. Then we have,

$$\sigma_{st}=C_{stst}\epsilon_{st}=\sum_{i,j}C_{stst}J_{stst}\sigma_{ij}=\sum_{i,j}a_{mi}a_{mj}C_{stst}J_{stij}\sigma_{mm} \tag{4}$$

where i and $j=1$, 2, 3; a_{mi}s are the direction cosines; and σ_{mm} is the applied longitudinal stress. Let $\sigma_{mm}=\sigma_0e^{i\omega t}$, and when $\omega^2\ll(k_0+2C_{stst}N\epsilon^{(s)2}_{st}/M)$, Q^{-1} can be obtained [7] from formulae (1)–(4)

$$Q^{-1}=\frac{C'}{J'}\frac{2N\epsilon^{(s)2}_{st}}{k}\frac{\omega\tau}{1+\omega^2\tau^2} \tag{5}$$

where

$$J'=\sum_{i,j,k,l}(2-\delta_{ij})(2-\delta_{kl})a_{mk}a_{ml}a_{mi}a_{mj}J_{klij} \tag{6}$$

$$C'=\sum_{i,j}(2-\delta_{ij})a_{ms}a_{mt}a_{mi}a_{mj}C_{stst}J_{stij} \tag{7}$$

where $\tau=\Gamma/k$, $k=k_0+2C_{stst}N\epsilon^{(s)2}_{st}$, and J_{klij}s are the components of a compliance.

Similarly, the dielectric loss D and dielectric constant ϵ_{mm} may be deduced [7] as

$$D=\frac{2Np_s^2/k}{[\chi_{mm}(\chi_{mm}+2NP_s^2/k]^{1/2}}\frac{\omega\tau}{1+\omega^2\tau^2} \tag{8}$$

where χ_{mm} is the susceptibility of monodomain crystals along the spontaneous polarization direction.

3.2.3. Results of calculation and comparison with experimental data

The existence of domains in crystals can lower the elastic energy but on the other hand it increases the interface energy. Consequently there is a definite number of domain walls in the crystals at each temperature T. When $T\to T_c$, the interface energy $\to 0$ [3] for the order parameter $\to 0$, so the density of DWs, $N\to\infty$. The relation between N and T is as mentioned in Section 3.1,

$$N=N_0/(T_c-T) \tag{9}$$

where N_0 is a constant [1].

When $T\to T_c$, the order parameter $\to 0$, so the difference between the domain wall and the domain interior becomes unclear, which leads to scattering by phonons to the domain walls $\to 0$ and then the viscous coefficient, $\Gamma\to 0$. Combs and Yip [15] obtained the expression for the viscous coefficient by computer simulation,

$$\Gamma=Ae^{-B/(T_c-T)} \tag{10}$$

where A and B are constants.

Taking into account the dependence of the density of DWs, N, and the viscous coefficient Γ on temperature, in addition to the well-known relations $P_s^2=P_0^2(T_c-T)$ [16], $\chi_{mm}=C/(T_c-T)$, $\epsilon^{(s)2}_{st}=\epsilon_0^2(T_c-T)$, $C_{stst}=C_0g(T_c-T)/[1+g(T_c-T)]$ [17], where k_0, N_0, P_0, C, ϵ_0, C_0 and g are constants independent of temperature, we get for $g\ll 1$ [17], and when Q^{-1} (and D)$\ll 1$ as well as $(T_c-T)/T_c\ll 1$,

$$\tau=\frac{\Gamma}{k_0}=A_0e^{-B/(T_c-T)} \tag{11}$$

$$Q^{-1}=h_3\frac{\omega\tau}{1+\omega^2\tau^2} \tag{12}$$

$$D=h_1(T_c-T)\frac{\omega\tau}{1+\omega^2\tau^2} \qquad (13)$$

where $A_0=A/k_0$, $h_1=2N_0P_0^2/(Ck_0)$, $h_3=2N_0\epsilon_0 2C'/J'k_0$.

The calculated results and experimental data of Q^{-1} and D are shown in Figs. 3–5 and the agreement is fairly satisfactory with $B=9.8$ K and 9.5 K for TGS and KDP, respectively. What is more important is that the viscous coefficient Γ and the recovering (or pinning) force k_0 of DWs can be determined from the Q^{-1} (or D) peak height and peak position respectively, which play a key role in the switching rate and the fatigue problem in memory devices.

3.3. Q^{-1} and D for PMN–PT relaxors

D and ϵ of PMN–PT *vs.* temperature and frequency ($f=1$, 10 and 100 kHz) are shown in Fig. 6. A loss peak (P_{D2}) occurs at about 10 degrees below T_{max}, and the peak temperature (T_p) shifts to a higher temperature when the frequency is increased.

Q^{-1} of PMN–PT *vs.* T and f ($f=1.0$, 1.9 and 3.0 kHz) are shown in Fig. 7. There is also a mechanical loss peak (P_{M2}) at some 10 degrees below T_{max}, similar to that of D. Because the variation of frequency in the measurements of Q^{-1} is smaller, T_p does not obviously change.

As shown in Figs. 6 and 7, Q^{-1} and D of PMN–PT are almost the same as that of non-dispersive KDP and TGS except for:

(a) the broadening on the high-temperature side of the loss peak;

(b) the shift of T_p with changing frequency is much smaller; and

(c) the peak height rises, rather than decreases as that of KDP and TGS, *etc.*, when f increases.

If we use eqn. (11) developed in Section 3.2 based on the viscous motion of DWs, we can resolve not only the relation between T_p and f, which cannot be described by an Arrhenius relation, but the difficulties can also be overcome, *i.e.* $D=0$ when $T=T_f$ obtained by using the Vogel–Fulcher model [9]. As for the broadening of the high-temperature side of the loss peak, this can be interpreted in terms of dispersion of T_c which is caused by heterogeneous constituents. The shift of T_p with increasing f, which is much smaller than that of KDP and TGS, *etc.*, may be attributed to the correlation between DWs with high density, and can be explained reasonably by using the coupling model [18]. As shown by eqn. (8), the height of the loss peak $\sim 1/k$ (k is force constant), and recent quasielastic–neutron scattering results [19] indicate that the correlation length and thus k decreases rapidly near T_p with increasing temperature. This may be the reason why the height of loss peaks rises rather than decreases, as in the case of KDP and TGS, *etc.*, when the frequency increases. Certainly, further quantitative studies are expected to give a comparison between experimental data and the calculation.

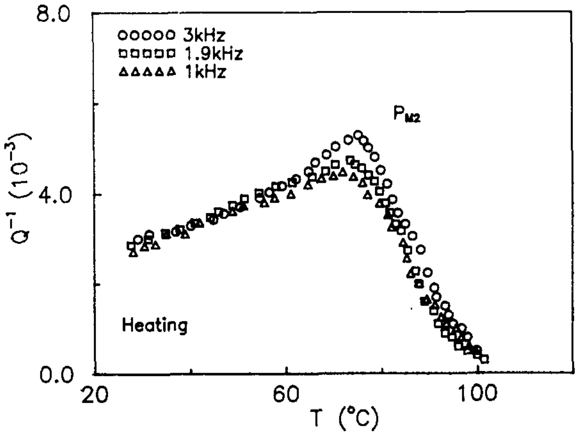

Fig. 7. Q^{-1} *vs.* T with various f of PMN–PT.2.

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