Relaxation Motion and Possible Memory of Domain Structures in Barium Titanate Ceramics Studied by Mechanical and Dielectric Losses

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Abstract. The relaxation motion and memory effect of domain structures have been investigated using mechanical and dielectric loss measurements in $BaTiO_3$ ceramics with grains sizes varied from 1 μm to 50 μm. The measurements of mechanical loss, elastic modulus, dielectric loss and permittivity show that each phase transition induces a loss peak and an anomaly in the dielectric constants and elastic modulus, furthermore, a number of relaxation loss peaks due to ferroelectric domains in the samples with large grain have been observed. All the relaxation peaks can be analysed by Arrhenius relationship for a wide range of frequency from 10^{-2} to 10^6 Hz. The activation energies of relaxation peaks have been determined as 0.92 eV, 0.68 eV, 0.47 eV, and 0.29 eV for the peaks located in the tetragonal, orthorhombic, and rhombohedral phase, with Arrhenius perfactor in the order of 10^{-13} s. Moreover, one relaxation process is insensitive to ferroelectric phase transitions, and it can exist in all the ferroelectric phases. This implies a possible memory effect of ferroelectric domain structures. Such a motion of domain wall is limited in fine-grained materials. Effect of vacuum annealing on the relaxation peak in the tetragonal phase is also studied to clarify the mechanisms of the peak. These relaxation peaks could be explained by the interaction between different domain walls and the diffusion of oxygen vacancy in the domains.

Keywords: $BaTiO_3$, domain wall, oxygen vacancies, mechanical and dielectric loss

1. Introduction

Ferroelectric barium titanate ($BaTiO_3$) ceramics are widely investigated in microelectronic devices such as multi-layer capacitors, non-linear positive-temperature-coefficient resistors, and piezoelectric transducers. In all these applications the motion of domain wall plays a decisive role. For instance, for a capacitor with X7R-specification, Nb and Co are commonly added to $BaTiO_3$ in order to stabilize permittivity and to reduce dielectric loss [1, 2]. The microstructure of such ceramics has a core-shell structure for smoothing the variation of the permittivity ε_r at the phase transitions of para-ferroelectric T_C, tetragonal-orthorhombic $T_{t\text{-}o}$, and orthorhombic-rhombohedral $T_{o\text{-}r}$, and for limiting the motion of domain walls. Therefore, it is necessary to get a clear picture on the motion of domain wall in undoped $BaTiO_3$ ceramics, and then to have knowledge on the influence of dopant on the motion of ferroelectric domain wall.

The study of mechanical loss and elastic modulus on undoped $BaTiO_3$ ceramics by flexural vibration at kilohertz frequencies and inverted pendulum at low frequencies (1 to 0.01 Hz) [3–6] has already shown that

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each phase transition induces a mechanical loss peak and a very sharp anomaly of elastic modulus. Moreover, a peak in the mechanical loss (R^m) is also observed within each ferroelectric phase. The peaks (R^m) have been considered to stem from the domain walls. Such a kind of domain wall motion peak has been reported in other perovskite ferroelectric ceramics, such as lead zirconate titanate (PZT) [7–9] by the mechanical loss measurements. However, there was no report of relaxation peaks in BaTiO$_3$ ceramics as a function of temperature by previous mechanical and dielectric measurements [10–17]. It is worth to mention that, among the early studies [10–21], Fang et al. [19] reported an excellent correlation about influence of morphology of grain size on dielectric constants in a series of samples with various densities and grain sizes, but they have only reported the results of the dielectric constants at 1 kHz for from −20°C to 150°C, and they have not found any relaxation peak in the materials. Moreover, a number of models concerning the mechanisms of the loss peak for the movements of domain walls have been proposed [7, 22–24]. However, there are still no coherent pictures on the domain walls motion in BaTiO$_3$ ceramics.

In this paper we present an overview of our results on motion of domain walls in BaTiO$_3$ ceramics with various microstructures using mechanical and dielectric measurements as a function of temperature in a wide frequency range from 0.01 Hz to 10^6 Hz. First, we will demonstrate correlation between microstructure and relaxation loss peaks, then study the influence of grain size on the activation parameters of the peak, and the effect of vacuum annealing at high temperature on the peak in order to highlight details of domain wall motion interacting with of oxygen vacancies in the material.

2.   Materials and Experimental Procedure

Barium titanate powder (ELMIC BT 100: 0.7–1.0 μm particle size, Ba/Ti = 0.996 ± 0.004, RHONE-POULENC) was mixed with suitable organic binders. After drying and de-agglomeration, the powders were pressed uni-axially at 50 MPa to make prismatic bars ($8 \times 8 \times 50$ mm), and then pressed isostatically at 380 MPa. The compacts were sintered in air for 2 h at 1250°C to 1325°C with a heating/cooling rate of 300°C/h. The compacts were then sliced into rectan-

gular plates ($1 \times 5 \times 40$ mm). Other kind of barium titanate powder (Ticon P) supplied by TAM Ceramics Inc. was used in tape casting form. The average grain sizes of the powders were about 1.7 μm. The powder was mixed with suitable organic dispersant (KD1), solvent (ethanol), plastizer (S160 and P400), homogeneisant (cyclohexanone), and binder (Acryloid B7). After tape formation, the samples were dried and heated at 10°C/h up to 600°C keeping for 2 h for debinding and cooled at 100°C/h to room temperature. Such tape was sintered in air for 2 h at 1250°C to 1325°C with a heating rate of 300°C/h and a cooling rate 500°C/h.

Scanning electron microscopy observations were made on samples polished mechanically and lapped from 6 to 1 μm roughness using diamond paste, followed by acid etching (5% HCl, 0.5 vol% HF, 94.5% H$_2$O). Figure 1(a), (c), (e) and (g) show the microstructure of the ceramics of BaTiO$_3$ prepared by isostatic pressing and sintered at 1250°C, 1275°C, 1300°C and 1325°C, respectively. The grains size is homogenous about 2 μm for the ceramic sintered at 1250°C. With the increasing of sintering temperature, a bi-modal distribution of grains sizes was formed, i.e., the large grains about 50 μm were surrounded by the fine grains about 2 μm and the volume percentage of large grains was also increased. Figure 1(b), (d), (f) and (h) give the microstructure of the BaTiO$_3$ ceramics prepared by tape casting and sintered at 1250°C, 1275°C, 1300°C and 1325°C, respectively. The grain size is almost homogenous and increased progressively from 8, 11, 15, to 26 μm with the sintering temperature. The domain walls structures in those materials are very similar to the observations by Arlt and Sasko [25].

The measurements of mechanical loss and elastic modulus were carried out at low frequencies (0.01 to 1 Hz) by an inverted pendulum, and at kilohertz by forced vibration of the samples driven electrostatically in their fundamental flexural mode. The details of experimental system were described in [4, 6]. Dielectric constant and loss were measured using an automatic impedance HP4192A (5 Hz < f < 13 MHz) for the same sample used for the mechanical measurements, with the dimensions of $1 \times 5 \times 5$ mm. Two opposite faces of the samples were electroded by gold vapour deposition. In order to describe the results clearly, the relaxation loss peaks are noted, such as R_r^m, for the peak located in the rhombohedral-phase and measured by mechanical vibrations, and R_o^e, for the peak located
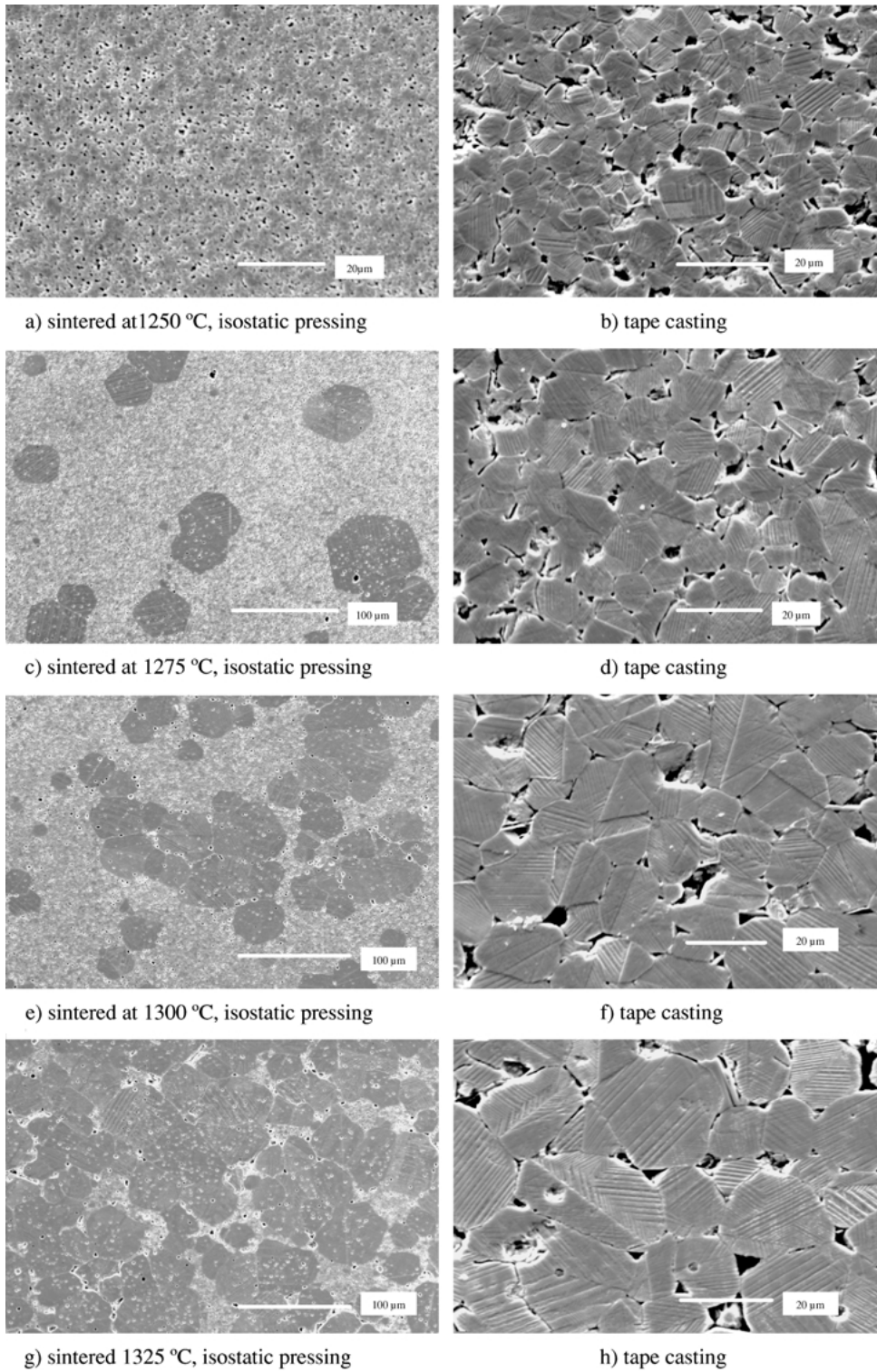
a) sintered at 1250 ºC, isostatic pressing

b) tape casting

c) sintered at 1275 ºC, isostatic pressing

d) tape casting

e) sintered at 1300 ºC, isostatic pressing

f) tape casting

g) sintered 1325 ºC, isostatic pressing

h) tape casting

Fig. 1. Microstructures of BaTiO$_3$ ceramics prepared by isostatic pressing (a, c, e, and g) and tape casting (b, d, f, and h).

in the orthorhombic-phase measured by impedance spectroscopy.

3. Results

3.1. Correlation of Microstructure and Mechanical Loss at Kilohertz Frequencies

The variations of Young's modulus E and mechanical loss Q^{-1} as a function of temperature for the ceramics prepared by isostatic pressing and sintered at 1275°C, 1300°C and 1325°C are shown in Fig. 2, respectively. The vibration frequency is about 3 kHz. The $E(T)$ curve shows three anomalies; A_1 (130°C), A_2 (4°C) and A_3 (−100°C) in decreasing temperature. Which corresponds to the following three phase transitions in the material: A_1: cubic to tetragonal phase. A_2: tetragonal to orthorhombic phase, A_3: orthorhombic to rhombohedral phase. The particular shape of modulus anomaly allows precisely determination of the transition temperatures. These anomalies are respectively associated with three narrow peaks P_1, P_2, and P_3 on the $Q^{-1}(T)$ curve.

Moreover, the $Q^{-1}(T)$ curve shows a large peak R_o^m, and a small peak R_r^m in the ceramic sintered at 1325°C. The letter R is chosen for such peak because it is supposed to be a relaxation process, the exponent m means the mechanical measurement in order to distinguish it from the dielectric measurement. Such relaxation peaks R_r^m and R_o^m do not exist in the ceramic sintered at 1275°C. All those results show clearly a possible correlation between the mechanical loss and the microstructure of the ceramics.

Figure 3 shows the variations of elastic modulus E and mechanical loss Q^{-1} as a function of temperature for the ceramics sintered at 1250°C, 1275°C, and 1325°C prepared by tape casting. The same anomalies on the elastic modulus A_1 (125°C), A_2 (15°C) and A_3 (−72°C), and the same peaks P_1, P_2, P_3 on the mechanical loss have been observed. In the ceramics prepared by tape casting, the anomaly A_2 is very sharp and the peak P_2 is much higher than that in the ceramics prepared by isostatic pressing. The appearance of relaxation peak R_o^m in the ceramics is also well identified. All those results show that the large grain is of prime condition for the appearance of relaxation peaks.

In order to investigate the influence of grain size on the relaxation peaks, only the samples prepared by isostatic pressing have been chosen to carry out low frequencies mechanical loss and high frequencies dielectric properties measurements. It is believed that the relaxation peaks related to domain wall motion could also be observed by the dielectric loss measurement in the large grain prepared by tape casting.

3.2. Relaxation Peak in Fine-Grain BaTiO₃ Ceramics

No mechanical loss peak in the ferroelectric phases for fine grain $BaTiO_3$ ceramic sintered at 1275°C has been observed at kilohertz frequency range (Fig. 2). It is also true for the ceramic sintered at lower temperature of 1240°C; see the results [4, 5]. Furthermore, no relaxation peak has been observed in the rhombohedral and orthorhombic phases, at low frequencies (0.01 to 1 Hz), as shown in Fig. 4. However, it seems that there is a small mechanical loss peak located at about 335 K for the frequency of 0.1 Hz in the tetragonal phase. Such a relaxation peak cannot be observed in the dielectric loss at higher frequencies of 10, 30 kHz for the fine grain $BaTiO_3$, Fig. 5. The $\varepsilon(T)$ curves show only three peaks at −65°C, 27°C, and 127°C, which correspond to the three phase transitions in the material. These peaks are respectively associated to the three peaks on dielectric loss curves.

In order to check the relaxation peak in the tetragonal phase, and to avoid the influence of the high loss peak at phase transition between the orthorhombic-tetragonal phase, which is inversely proportional to the vibration frequency, so larger vibration frequencies of 0.03, 0.1 and 1 Hz are chosen to measure mechanical loss as a function of temperature, the results are shown in Fig. 6. A relaxation peak in the tetragonal phase is well confirmed. The peak temperature is obtained as 52, 67, and 94°C for the frequencies of 0.03, 0.1, 1 Hz, respectively. According to Arrhenius equation [26]:

$$\tau = \tau_0 \exp(H/kT), \qquad (1)$$

where T is the absolute temperature and k is the Boltzmann's constant, H is the activation energy, τ_0 is the inverse of frequency factor. For a Debye peak, the condition for the peak is

$$\omega\tau = 1. \qquad (2)$$

This gives:

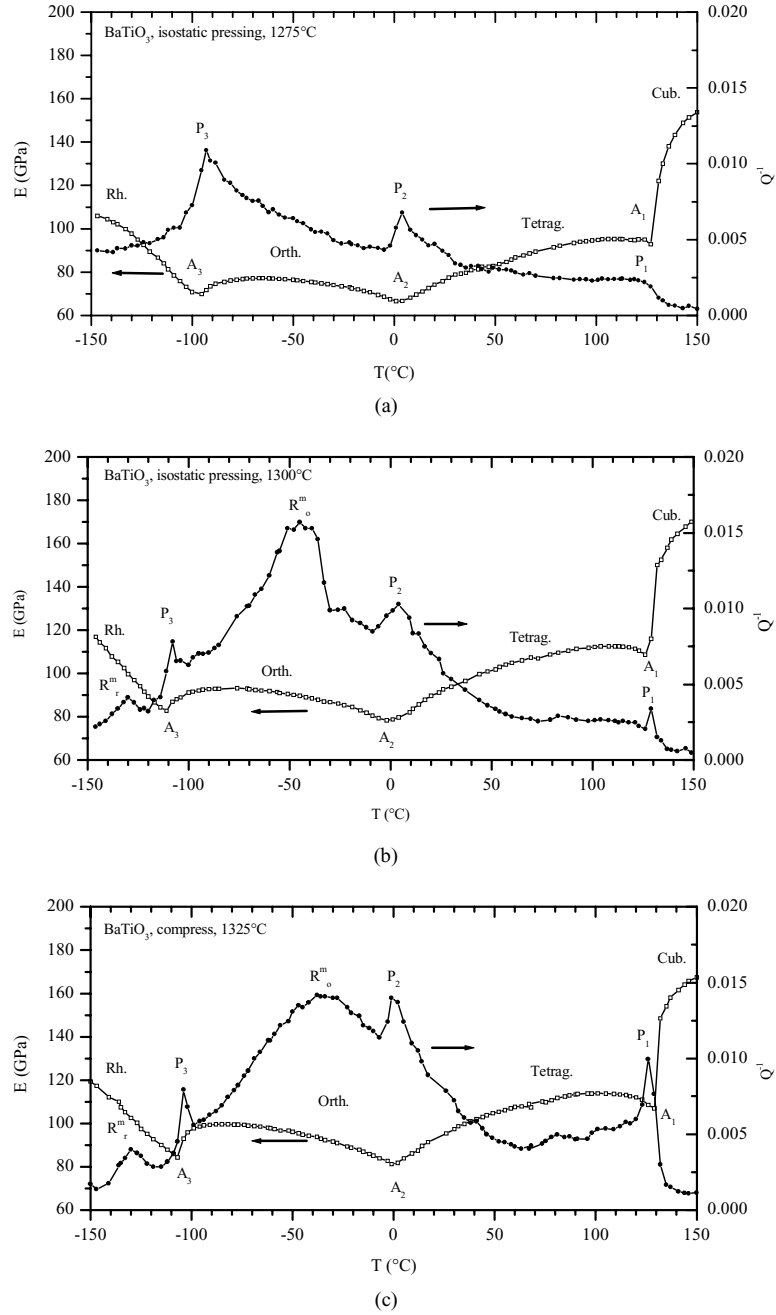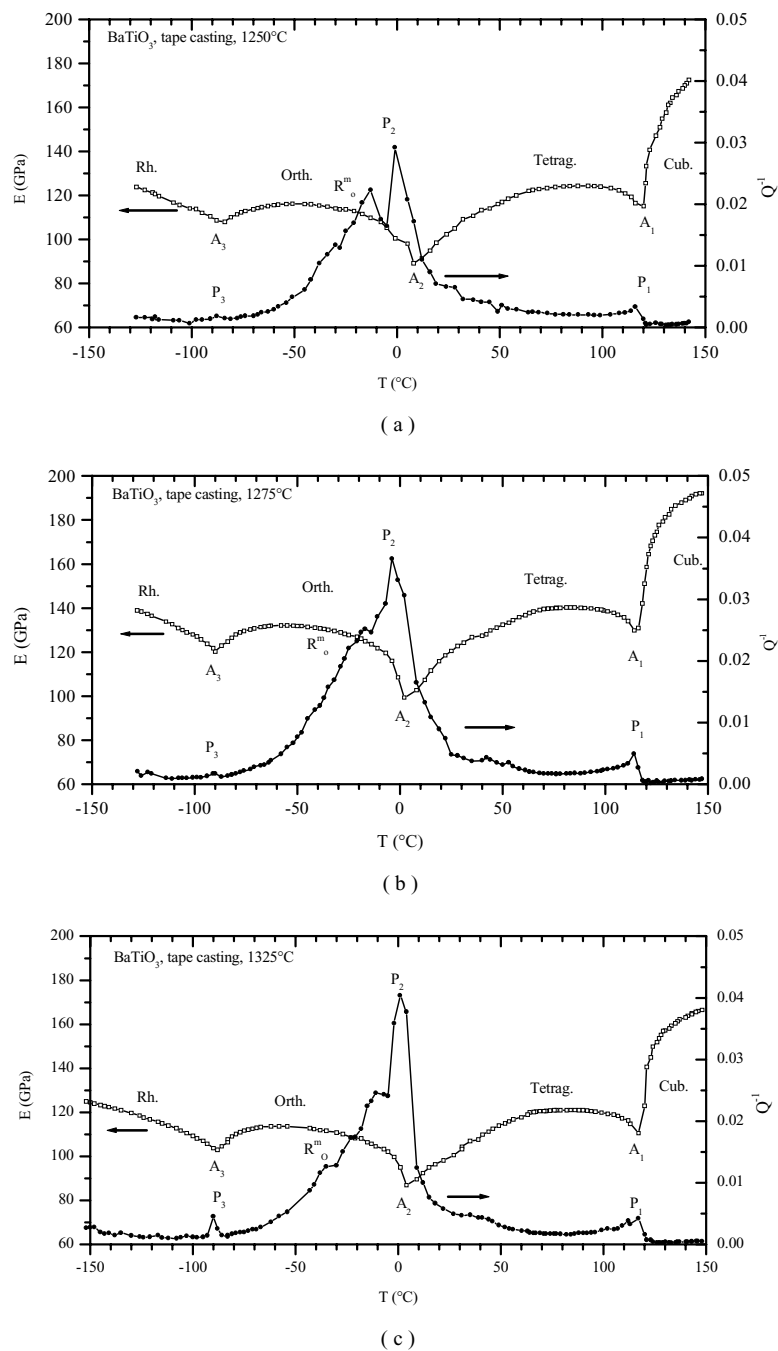$$\ln f = -\ln(2\pi\tau_0) - H/kT_P, \qquad (3)$$

Fig. 2. Young's modulus E and mechanical loss Q^{-1} as a function of temperature for the ceramics prepared by isostatic pressing in the kilohertz frequency range.

where T_P is the temperature of the peak, $\omega = 2\pi f$, f is the vibration frequency. The activation energy H and relaxation time τ_0 are determined to be 0.87 eV and 2.2×10^{-13} s. for the only peak in the fine-grained BaTiO$_3$ ceramic.

3.3. Multi-Relaxation Peaks in Large Grain BaTiO$_3$ Ceramics

The variations of the shear modulus $G(T)$ as a function of vibration frequency of 0.01, 0.1, and 1 Hz for

(a)

(b)

(c)

Fig. 3. Young's modulus E and mechanical loss Q^{-1} as a function of temperature for the ceramics prepared by tape casting in the kilohertz frequency range.

the undoped $BaTiO_3$ sintered at 1300°C for 2 h with large grain sizes (about 40 μm) are shown in Fig. 7. The $G(T)$ curves show three very sharp anomalies during heating: A_3 (−73°C), A_2 (20°C) and A_1 (127°C),

corresponding to the three phase transitions in the material. The Q^{-1} curves exhibit not only three peaks P_1, P_2, and P_3 corresponding to the anomalies of modulus, but also other peaks (R_r^m, R_o^m, and R_t^m) located in
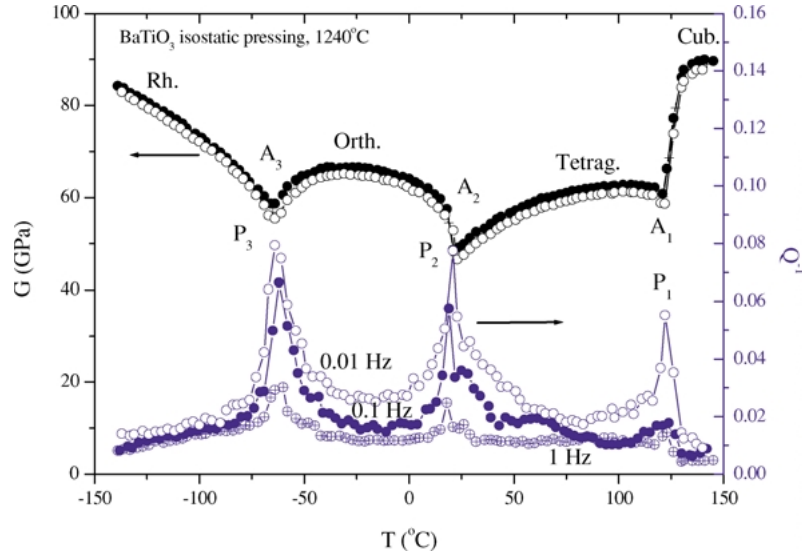
Fig. 4. Shear modulus G and mechanical loss Q^{-1} as a function of temperature at low frequency for fine-grained ceramic prepared by isostatic pressing.
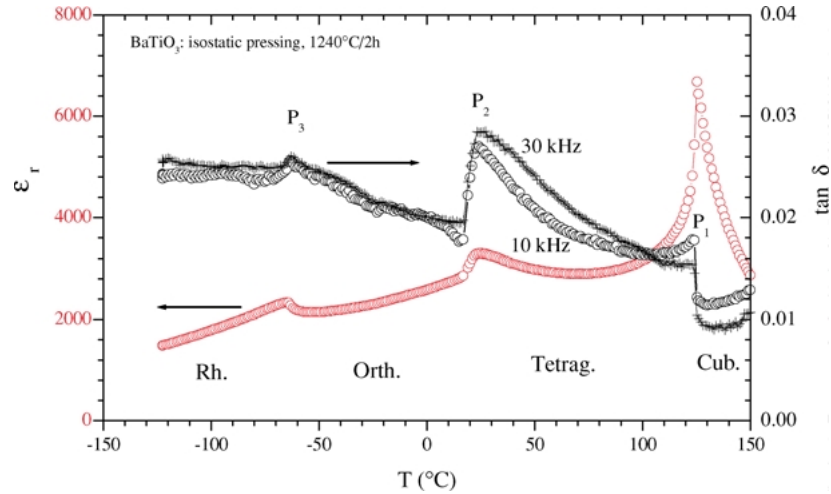

Fig. 5. Permittivity and dielectric loss as a function of temperature at kilohertz frequencies for the same fined-grained ceramic as in Fig. 4.

the three ferroelectric phases. The temperature of the peak increases with increasing of frequency, showing a relaxation behaviour.

The variations of the permittivity response $\varepsilon(T)$, and dielectric loss $\tan\delta(T)$ as a function of vibration frequencies of 1, 3, 10, 100 kHz for the same BaTiO$_3$ sample as shown in Fig. 7 are shown in Fig. 8 during heating run. The $\varepsilon(T)$ curves show three peaks at $-72°$C, $15°$C, and $128°$C during heating, which correspond to the three phase transitions from rhombohedral

to orthorhombic to tetragonal, and to cubic phases. It is interesting to point out that there are two peaks (R_r^e, R_o^e) in the dielectric loss curves, located respectively at the rhombohedral and orthorhombic phase, and the temperatures of the both peaks, T_p, are shifted to higher temperature with increasing frequencies.

In order to rule out a possible contribution of pyroelectricity, which may contribute additional loss to the peak when temperature is varying, the dielectric losses at constant temperature are measured as a function of
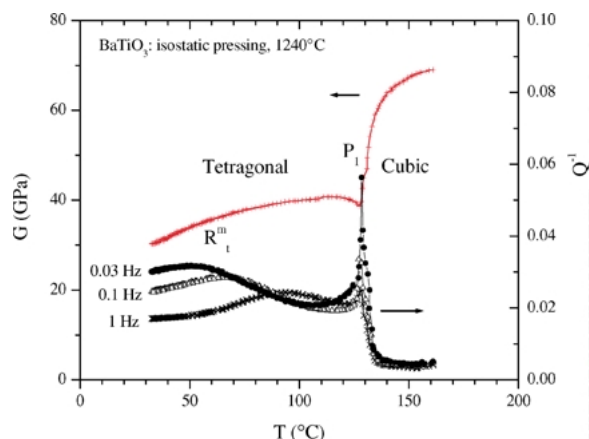
Fig. 6. Shear modulus G and mechanical loss Q^{-1} in the tetragonal phase at low frequencies for the fined-grained ceramic prepared by isostatic pressing.

frequency. The peak frequency, f_p, has been observed clearly shift to higher value with increasing temperature in the tetragonal phase as shown in Fig. 9. The peak frequency, f_p, at different temperatures is shown in the Table 1. The relaxation time, τ, can also be written according to the Arrhenius equation. For all the relaxation peaks, the Arrhenius relationship between peak temperatures and vibration frequencies is plotted in Fig. 10, The activation energy, H, and the relaxation time, τ_0 of peaks R's are determined for all the peaks, the results are summarised in Table 2.

Table 1. Peak frequency of BaTiO$_3$ sintered at 1300°C/2 h in the T-phase.

T(°C)	48.2	58.1	68.8	79.2	89.4	99.9
f_p (kHz)	60.56	100.0	120.5	196.0	313.1	446

Table 2. Activation parameters of the relaxation peaks in the BaTiO$_3$ ceramics.

	$R_r^e + R_r^m$	$R_{r,o}^m + R_{o,t}^e$	$R_o^m + R_t^m$	R_t^m
τ_0 (s)	2×10^{-13}	9×10^{-14}	4×10^{-14}	3×10^{-13}
H (eV)	0.29	0.47	0.68	0.92

3.4. Influences of Vacuum Annealing at High Temperature

In order to check if oxygen vacancies have any influence on the variation of the relaxation peaks, a series of thermal treatments have been carried out *in situ* during the mechanical loss measurements [4, 6]. The results of the $Q^{-1}(T)$ and $G(T)$ in the tetragonal phase for the frequency of 0.1 Hz for the material with large grain are shown in Fig. 11. The height of the peak is drastically reduced and the temperature of the peak T_P shifts towards low temperature (from 104°C to 68°C) after an annealing at high temperature of 950°C for 6 h in vacuum (2 Pa), and then the height of the peak has been observed to be partially recovered and the T_P shifts from 68°C to 82°C after *in situ* air annealing at a lower
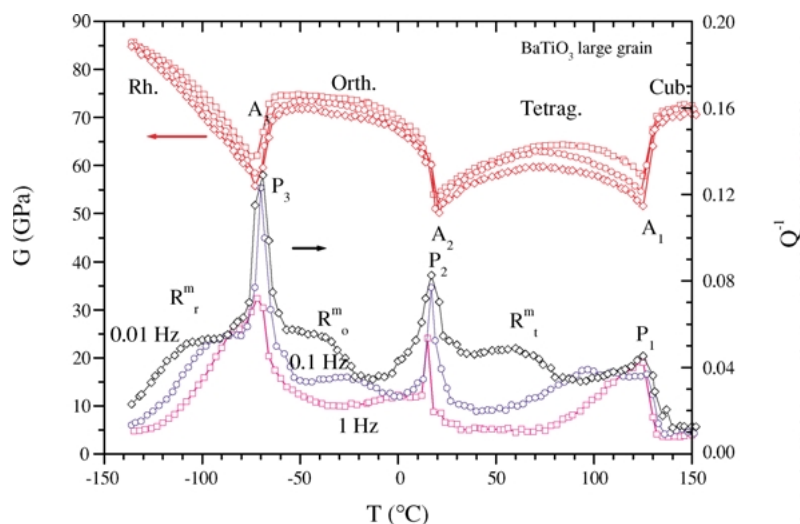

Fig. 7. Shear modulus G and mechanical loss Q^{-1} as a function of temperature at low frequencies for the large grain ceramic prepared by isostatic pressing.
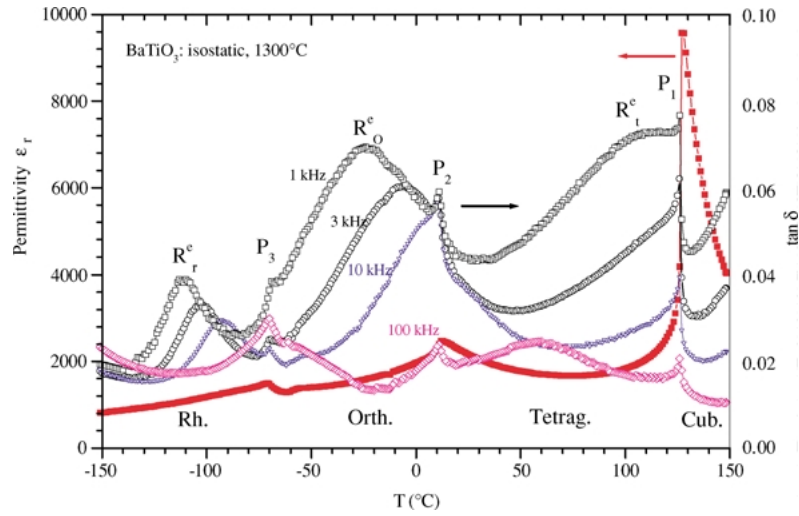
Fig. 8. Permittivity and dielectric loss as a function of temperature at kilohertz frequencies for the same large grained ceramic as in Fig. 7.
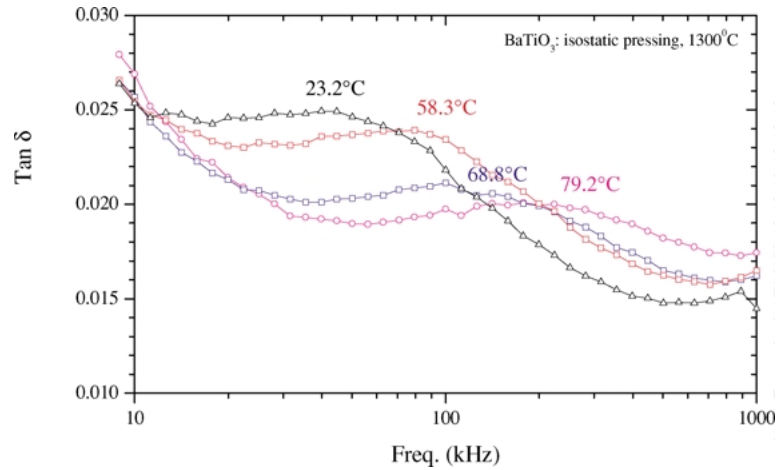

Fig. 9. Isothermal variation of dielectric loss as a function of frequencies in the tetragonal phase for large grained BaTiO$_3$ ceramic prepared by isostatic pressing.

temperature of 650°C for 2 h. All those results show that the relaxation process has been certainly influenced by the point defects induced during high temperature annealing in vacuum.

4. Discussion

4.1. Characteristics of the Relaxation Peaks

First we can summarize the characteristics of the relaxation peaks as follows.

1. The peak temperature is of frequency dependent.
2. A large variation of frequency induces a large shift of the temperature of the peak, so that a relaxation peak can be observed continuously in two or even three ferroelectric phases.
3. The height of the peak changes when the relaxation peak crosses a phase transition.
4. Annealing in vacuum at high temperature induces a decrease of the height and temperature of the peak, and further annealing in air can restore the initial relaxation peak.
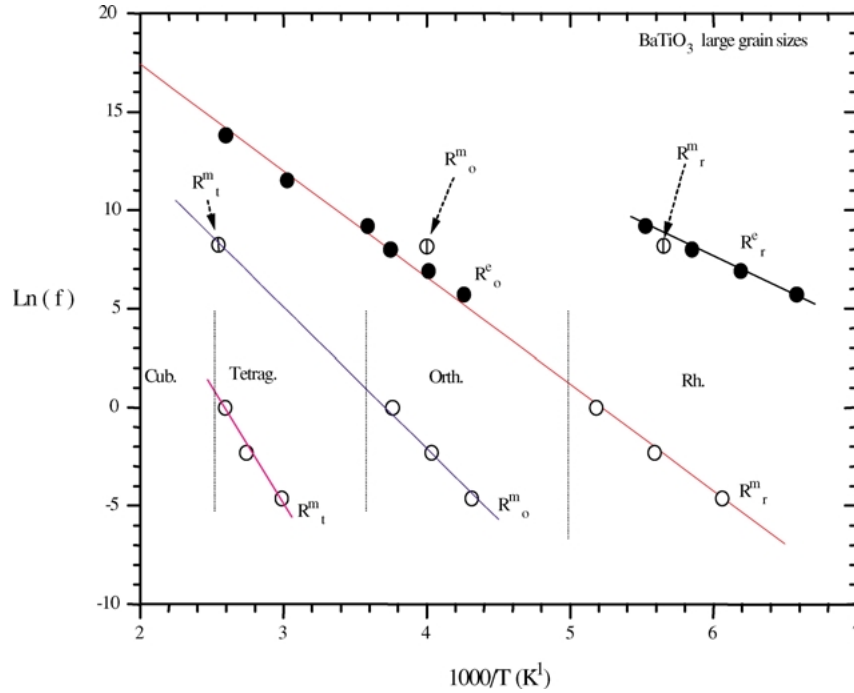
Fig. 10. Arrhenius plot of the relaxation peaks in large grained BaTiO$_3$ ceramic. The full circles data correspond to dielectric loss peaks at higher frequencies range, the open circles data correspond to mechanical loss peaks at lower frequencies range, and the dotted circles data correspond to the mechanical loss at kilohertz frequency range.

5. No such a kind of relaxation peak exists in the paraelectric phase.

All these experimental results show the relaxation peaks should be partly associated with domain wall motion, partly with the oxygen vacancies in the materials. In the following section, we will discuss possible signification of the relaxation peak on the domain wall structures, and then we will investigate the effect of oxygen vacancies on the relaxation peaks.

4.2. Multi-Relaxation Peaks Associated to Different Domain Structures

Arlt et al. [25, 27, 28] have pointed out the domain structure is different in ceramics from that in single crystal because the domain structure in ceramic is formed under clamped condition, while it is free in single crystal. The domain density depends on the grain size g. Larger than a critical grain size the twin lamellae increase proportionally to $\sqrt{g}$, and the shape of the grain adjusts to the surroundings in two dimensions. Above another larger critical grain size more complex

interfaces are created, which allow stress relief in three dimensions. For example, in the tetragonal phase, the etch patterns can be described by two kinds of domain configurations. One of them is made up of 90° and 180° domain walls (so-called α-type structure). The other type has a more complex structure which is a mixed net of trapezoidal areas of 90° walls, 0° (walls), and head to side walls with positive or negative polarisation charge (so-called β-type structure), the detail model see [25].

Recently, Eng et al. [29] have shown more complicated domain walls structures using voltage-modulated scanning force microscopy (SFM). For example, the α-type structure and β-type structure can exist in the same grain, and domain walls are not straight lines but with a bent structure, which could stems from strain mismatch and corresponding stress relief at the sample surface. In large grain ceramic there always exist certain configurations of domain walls responding to the mechanical and electrical excitation in the ferroelectric phase. So the relaxation peaks R_T, R_O, and R_R could be observed in the tetragonal, orthorhombic, and rhombohedral phases. The disappearance of multi-relaxation
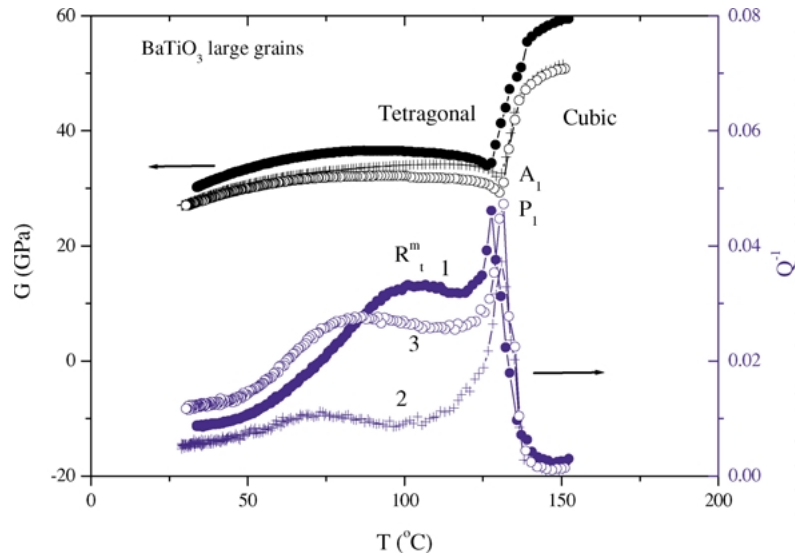
Fig. 11. Influence of thermal treatment on the mechanical loss in the tetragonal phase for large grain ceramic. Curve 1: As-received sample, curve 2: After vacuum annealing at 950°C for 6 h, curve 3: After air annealing at 650°C for 2 h.

peaks and very low intensity of peak R's in the small grain sizes ceramics may be due to the strong pinning effect of grain boundaries on the motion of domain wall. In the meantime, various domain structures could correspond to a number of domain wall motions. This could be the reason why there are multiple relaxation processes in $BaTiO_3$ with large grain size.

4.3.   Possible Memory Effect of Domain Structures

The experimental results also show that two relaxation peaks can pass from one phase to other in the ferroelectric phases without change in the Arrhenius slope (Fig. 10), with activation energy of 0.47 and 0.68 eV, respectively. People may argue that different relaxation peaks correspond to different types of domain wall pinning effects, for example, oxygen vacancy-acceptor impurities dipoles, electron diffused into domain walls, pinning at grain boundaries etc. The constant activation energy might simply mean that one of these processes has the same activation energy in all the ferroelectric phases. This may be a possible explanation for the multiple peaks. However, if this is the case, the multi-peaks should be observed in the fine-grained $BaTiO_3$ ceramic, for at least, the pinning at grain boundaries might give a peak because of a large portion of grain boundaries in the fine-grain ceramic.

In fact, the experimental results show that only one single peak has been observed in the fine grain $BaTiO_3$ ceramic, which has a very simple domain structure of 90° domain walls, but multi-peaks exist in the large grain $BaTiO_3$ ceramic with complicate domain structures. Furthermore, the peak located in the tetragonal phase with activation energy of 0.87 eV in the fine-grained material can be considered as the same mechanism for the peak located in the same ferroelectric phase with activation energy of 0.92 eV in the large grain $BaTiO_3$ ceramic. So, we can associate such peak to this simple domain wall structure.

As discussed in the above section, it is more reasonable to contribute the multi-relaxation peaks to multiply domain structures. Figure 10 shows that there are three peaks located in the tetragonal phase for different excitation frequencies, with activation energy of 0.92, 0.68, and 0.47 eV. We may suggest that these peaks are associated with (1) simple 90° domain walls, (2) α-type structure, and (3) β-type structure, respectively. Surely the most of domain walls have different orientations in different ferroelectric phases [30]. But, the microscopic observation by Oh et al. [31] has shown that the domain walls of $BaTiO_3$ at room temperature are very clear straight lines, and the width of the domain was rather thick, such configuration remains in the low temperature orthorhombic phase. Furthermore, with increasing temperature, domain wall becomes

unclear and disappears only *above* the Curie temperature. This means that some parts of domain structures in one ferroelectric phase could remain in the other phase, even if the crystalline structure is changed from the rhombohedral to orthorhombic, or from orthorhombic to tetragonal phases. It seems that the domain structures have a certain memory effect. Our observation of relaxation peaks existing in different ferroelectric phases can be regarded as a support that the domain walls configurations may have a "memory effect".

4.4. Peak Mechanism of Interaction of Domain Wall and Oxygen Vacancies

The relaxation peaks could be due to the interaction between domain walls and oxygen vacancies. The values of relaxation time τ_0, of this work, are similar to the value of the Debye frequency ν_D^{-1} (about 10^{-13} sec.), and all the relaxation peaks could be attributed to a single atomic diffusion process [5]. Lewis et al. [32] have reported diffusion activation energies of barium vacancies V_{Ba}'' as 2.8 eV, and oxygen vacancies $V_O^{\bullet\bullet}$ as 0.44–0.68 eV. Shirasaki et al. [33] reported that the activation energy of oxygen vacancy in undoped $BaTiO_3$ was 0.59 eV by a solid-gas exchange technique in the cubic phase. Such results of diffusion activation energy of $V_O^{\bullet\bullet}$ are very similar to the activation energy of the dielectric and mechanical loss peaks observed in the present paper.

Therefore, the R peaks could be attributed to the domain wall motion controlled by diffusion of oxygen vacancies. Certain impurities, such as $Fe^{3+,2+}$, Sr^{2+}, Ca^{2+}, K^+, Na^+, always exist in the undoped $BaTiO_3$ ceramics to substitute of Ti^{+4}, Such impurities with negative charges are compensated by the oxygen vacancy. In this way the oxygen vacancies always exist in the material.

Postnikov et al. [7] have proposed that the shear stress σ causes an increase in the polarisation of the domain oriented in the direction of tension, and a decrease in the polarisation of those oriented in the direction of compression. The domain wall is shifted by such stress. The accompanying change of polarisation causes a bound electrical charge to appear at the domain wall. These bound charges induce an electrical field in the grain. The mobile charges associated with point defects will diffuse in the electrical field in order to achieve equilibrium, establishing the equilibrium takes time, and though the converse piezoeffect this induces

an additional anelastic deformation. For small concentrations of mobile charges, as in undoped ceramic, they obtained the height of mechanical loss peak

$$Q_{max}^{-1} = \frac{2(d_{33} - d_{31})^2 C_o L^2}{\pi^4 \varepsilon_r^2 \varepsilon_o^2 kTs} \tag{4}$$

where C_o is the density of point defects, L is width of domain, s is the elastic compliance, ε_o is the permittivity in vacuum. The activation energy of the relaxation is the diffusion energy of point defect and the relaxation time can be written as

$$\tau = \frac{L^2}{\pi^2 D} \tag{5}$$

where D is the diffusion coefficient.

As shown in Eq. (5) the height of the peak in the mechanical loss is proportional to the square of the width of domain. SEM observation shows that the width of domain is about 10 μm in large grain ceramic, which is about 5 times larger than that in the fine-grain ceramic (about 0.2 μm) [4]. So the height of the peak in large grain ceramic could be 25 times higher than that in the fine grain ceramic, supposing other parameters be the same. In fact, the difference between the effective width of domain in the large and fine grain materials should be smaller than the value of 25, but it is certainly that the effective width of domain is larger in the large grain materials than that in the fine-grain materials as observed in the microscopy. This consists with the experimental result for the peak in the tetragonal phase. The relaxation peak is about several times higher in the large grain material than that in the fine-grain material.

4.5. Effect of Excess Oxygen Vacancies Pinning on Domain Wall Motion

Now we will discuss the influence of oxygen vacancies on the relaxation peak. Concerning the effect of high temperature annealing in vacuum, it is accepted that the oxygen vacancies and free electrons can be induced as follows

$$O_o \Leftrightarrow \frac{1}{2}O_2 + V_o^{\bullet\bullet} + 2e. \tag{6}$$
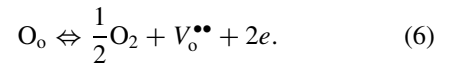
The oxygen vacancies induced by high temperature annealing in vacuum could be located preferably at domain walls because of the domain walls have distortion

of unit cells with low energy barrier for the oxygen vacancies. These oxygen vacancies have certain pinning effect on the domain walls, so the peak height is reduced after high temperature annealing in vacuum; and a further high temperature annealing in air can recover the peak height. Such a pinning effect of the excess oxygen vacancies on the domain wall motion has been directly observed in the high resolution TEM by Tan et al. [34], and also by the mechanical loss measurement in perovskite structure PZT ceramics by He et al. [35].

However, a vacuum annealing at lower temperature (just above the Curie temperature, T_c) is not efficient enough to introduce oxygen vacancies into the lattice, so there is no change on the relaxation peak [36]. But, the oxygen vacancies induced by the acceptor impurities are usually located in the crystal unit cells and near the substitution atoms to forming a dipole in order to keep electrical neutrality of the material. The relaxation peaks are mainly due to the diffusion of oxygen vacancies induced by the acceptor impurities in an electrical field induced by the variation of polarisation of the material under mechanical and/or electrical excitation.

5. Conclusions

Correlation between microstructures in undoped $BaTiO_3$ ceramics and the mechanical and dielectric losses has been demonstrated in a wide range of frequencies from 0.01 Hz to 10 MHz in the temperature from $-150°C$ to $150°C$.

In addition to the phase transition loss peaks in the material, a number of relaxation loss peaks (R's) in the ferroelectric phases in large grain materials have been observed. Such relaxation peaks are sensitive to the domain structure and grain sizes. Which is *a direct evidence* of limiting effect of grain boundaries on motion of domain wall in fine-grain materials when the grains are smaller than 1 μm.

Furthermore, the same relaxation processes exists in the different ferroelectric phases. This is an original experimental result, and it may indicate *a possible memory effect* of domain structures, i.e., one kind of domain structures formed in one phase can remain in other phase. Meanwhile, the reduced height of the relaxation peak after the phase transition implies a smaller activated volume of the domain walls due to the phase transition.

All of the relaxation peaks can be analysed by a *thermal activated Arrhenius relationship*, and could be explained by the domain walls motion controlled by diffusion of oxygen vacancies in the ferroelectric phases. The activation energy of the relaxation peaks of 0.30, 0.47, 0.68 and 0.92 eV could be interpreted as the *diffusion energy of oxygen vacancies* in the R-, O-, and T-phases. Excess oxygen vacancies induced by high temperature vacuum annealing can *pin the domain walls motion*.

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