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Anelastic relaxation associated with the motion of domain walls in barium titanate ceramics

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The mechanical loss (Q^{-1}) and shear modulus (G) were measured as a function of temperature in the range 130 K < T < 430 K for $BaTiO_3$ ceramics by an inverted pendulum at low frequencies ranging between 1–0.01 Hz. The Q^{-1} (T) and $G(T)$ curves exhibit the three phase transitions observed in $BaTiO_3$. Each phase transition induces a loss peak and an anomaly in the elastic modulus. Moreover, three other loss peaks (R) are located below the phase transition temperature. These peaks can be described by an Arrhenius relationship, and the activation energies are determined as 0.92, 0.68, and 0.45 eV for the peak located in the tetragonal-, orthorhombic-, and rhombohedral-phase, respectively. These peaks are due to the interaction between the domain walls and the diffusion of oxygen vacancies in the domains.

1. Introduction

Ferroelectric $BaTiO_3$ ceramics are widely used as multilayered capacitors, non-linear positive-temperature-coefficient resistors, and piezoelectric transducers [1]. In all these applications the mobility and motion of domain walls plays a decisive role. For instance, for a capacitor with an X7R-specification, which means that the variations of the dielectric constant ε_r must be within 15% of the ε_r value at 25 °C in the temperature range − 50 to 125 °C. Commonly, Nb and Co are added to $BaTiO_3$ in order to stabilize the permittivity and to reduce the dielectric loss [2, 3]. The microstructure of such ceramics has a core–shell structure for smoothing the variation of permittivity ε_r at the phase transition of the para–ferroelectric T_{Curie}, of the tetragonal–orthorhombic T_{O-T}, and of the orthorhombic–rhombohedral T_{R-O}. It also limits the mobility and motion of the domain walls. Therefore, it is very important to obtain a clear picture of the domain wall motion in undoped $BaTiO_3$ ceramics with different grain sizes and also to obtain a knowledge of the influence of the dopant ion on the motion of the ferroelectric domains.

It is interesting to note that in a study using a flexural mode of vibration in the kilohertz range [4, 5], the mechanical loss and the Young's modulus of undoped coarse grained $BaTiO_3$ ceramics showed that each phase transition induces a mechanical loss peak (P) and a very sharp anomaly in the elastic modulus (A). In addition an extra mechanical loss peak (R) is also observed in each ferroelectric crystalline phase. The loss peak located at the orthorhombic phase is confirmed by dielectric measurement [5]. The R peaks are considered to be connected with the motion of domain walls. Such a correlation between the R peak and the domain walls has been reported for other ferroelectric ceramics, such as Sr-doped lead zirconate titanate (PZT) [6], potassium dihydrogen phosphate (KDP) [7], $La_{1-x}Nd_xP_5O_{14}$ (LNPP) [8], triglycine sulfate (TGS) [9], and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [10], by mechanical and dielectric loss and permittivity measurements. It has also been studied in alloys with twinned structures such as A15 [11] and Mn–Cu alloys [12].

However, the present authors have not found any other reports in the literature concerning the peak created by the domain wall motion as a function of temperature in $BaTiO_3$ ceramics [13–24]. Moreover, there are several different models concerning the creation of the loss peak by the movements of the domain walls. Postnikov *et al.* [6] have proposed that the loss peak may be caused by an interaction between electrically charged point defects and immobile 90° domain walls. Gentner *et al.* [25] also proposed a model based on the interaction of 90° domain walls with the point defects, whose energy-level arrangement is controlled by an order parameter which varies continuously within the walls. This theoretical calculation shows a weak frequency dependence of the dielectric loss. Subsequently, Arlt and Dederiches [26] developed a model describing the loss in ferroelectric ceramics by means of a damped motion of 90° domain walls. Snead and Welch [11] proposed that the mechanical loss is proportional to the tetragonal deformation

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$(1\text{-}c/a)^2$ on the basis of movement of domain walls in A15 alloys. Recently, Huang *et al.* [27] and Wang *et al.* [28] considered the interaction among domain walls and the variation of the density of domain walls with temperature and proposed that the loss peak is due to viscous movement of domain walls. They also state that an Arrhenius relationship cannot be used for describing the variation of peak temperature as a function of frequency.

The aim of the present paper is to investigate the motion of domain walls by using mechanical loss and elastic modulus measurements at different vibration frequencies in $BaTiO_3$. Due to this study on the appearance conditions of the relaxation peak, it should be possible to highlight details of domain wall motion and verify whether or not a specific kind of domain wall motion obeys an Arrhenius relationship for a thermally activated process.

2. Experimental procedure

The barium titanate powder (Elmic BT 100: 0.7–1.0 μm particle size, Ba : Ti = 0.996 ± 0.004) supplied by Rhone-Poulenc was mixed with suitable organic binders. After drying and deagglomeration, the powders were pressed uniaxially at 30 MPa to make prismatic bars (8 × 8 × 50 mm) and then pressed isostatically at 300 MPa. The compacts were sintered in air for 2h at 1513 K or 1573 K with a heating/cooling rate of 300 K per h. The compacts were sliced into rectangular plates (1 × 5 × 40 mm). The sample was mounted at its ends and excited for torsional oscillations around its vertical oriented longitudinal axis. The dynamic modulus is written as

$$G^* = G\exp(j\phi) = G' + jG''$$

where ϕ is the lag angle between the strain and the stress. The $Q^{-1}(T)$ is measured by the ratio of G''/G', and the shear modulus $G(T)$ is equal to G'. The mechanical loss $Q^{-1}(T)$ and shear modulus $G(T)$ were measured during the heating, cycle with the exceptions of a few cases measured during cooling.

3. Results

Fig. 1a shows the variations of the shear modulus $G(T)$ as a function of a vibration frequency of 0.01, 0.1 and 1 Hz for an undoped $BaTiO_3$ sample sintered at 1573 K for 2 h with a large grain size (about 40 μm). The $G(T)$ curves show three very sharp anomalies during heating: A3 (200 K), A2 (293 K) and A1 (400 K), which correspond to the following three phase transitions: A3: rhombohedral to the orthorhombic phase, A2: orthorhombic to the tetragonal phase, and A1: tetragonal to the cubic phase.

These anomalies are respectively associated with three narrow peaks P1, P2, and P3 on the $Q^{-1}(T)$ curves that are shown in Fig. 1b. These results confirm the experimental results obtained by use of a flexural mode of vibration in the kilohertz range [3,4]. Moreover, the $Q^{-1}(T)$ curves show three large peaks designated R1, R2, and R3, located in the temperature ranges that correspond to the tetragonal, orthorhombic and rhombohedral structured phases, respectively. The R3 peak is very easily identified as being a thermally activated process, because the shifts of the $G(T)$ curves with frequency in the rhombohedral phase correspond to the shifts of the R3-peak with frequency. For the orthorhombic and tetragonal phases, the variations of $G(T)$ are complicated by the phase transitions $T_{R\text{-}O}$ and $T_{O\text{-}T}$. However, the shifts of the R1 and R2 peaks with the vibration frequency still suggest that both peaks could be described as a thermally activated process.

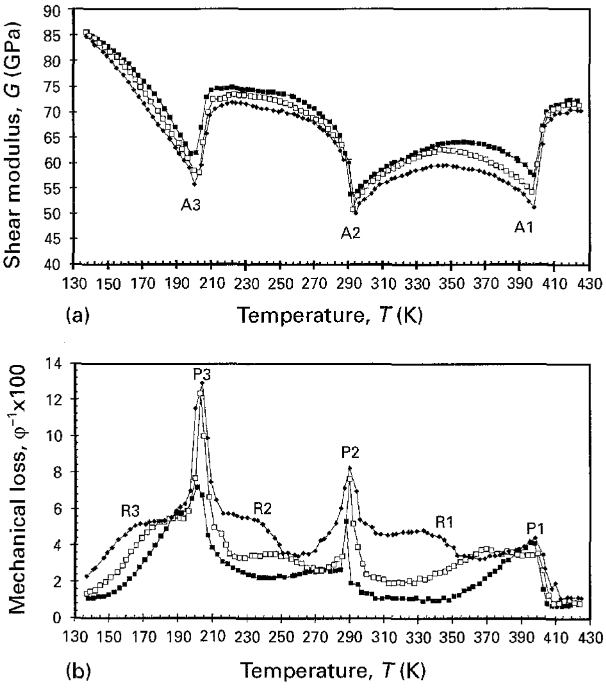

Figure 1 Variations of (a) the shear modulus G, and (b) the mechanical loss Q^{-1} as a function of temperature for an undoped coarse grained $BaTiO_3$ ceramic. The vibration frequency (f) is (◆) 0.01, (□) 0.1 and (■) 1 Hz. The heating rate is 0.25 K per min.

Fig. 2 (a and b) shows the $G(T)$ and $Q^{-1}(T)$ data for undoped $BaTiO_3$ sintered at a temperature of 1513 K for 2 h with small grain sizes (about 1 μm). The three phase transitions show similar anomalies in the elastic modulus (A1 : 395 K, A2 : 295 K and A3 : 210 K) and similar internal friction peaks (P1, P2 and P3). However, the R-peaks can no longer be observed.

The temperatures of the peaks depends on the vibration frequency. According to the Arrhenius equation, the relaxation rate can be written as

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

where T is the absolute temperature and k is the Boltzmann constant, H is the activation energy and τ_0 is the inverse of the frequency factor. For a Debye peak the condition for a peak is that $\ln(\omega\tau) = 0$. This gives

$$\ln(\omega\tau_0) + \frac{H}{kT_p} = 0 \qquad (2)$$

where T_P is the temperature of the peak $\omega = 2\pi f$ where f is the vibration frequency.

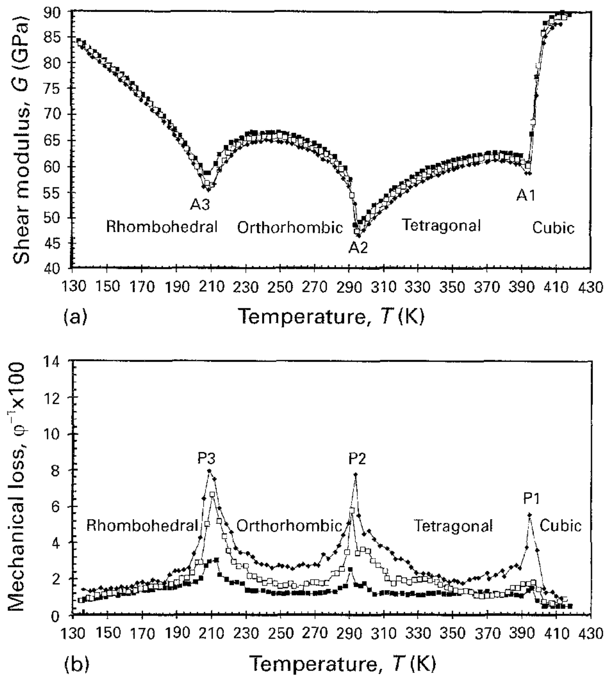

Figure 2 Variations of (a) the shear modulus G, and (b) the mechanical loss Q^{-1} as a function of temperature on undoped $BaTiO_3$ with small grains. $f =$ (◆) 0.01, (□) 0.1 and (■) 1 Hz.

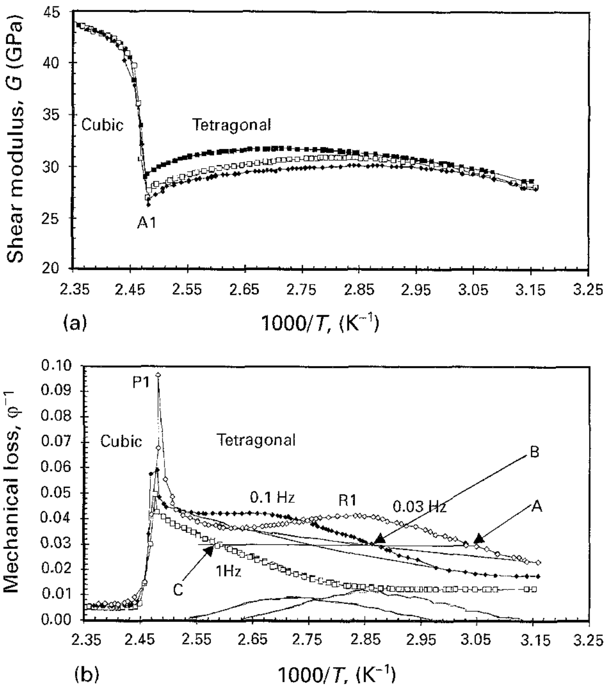

Figure 3 Results of (a) the $G(1/T)$, and (b) the $Q^{-1}(1/T)$ versus vibration frequency for frequencies of (◆) 0.03, (□) 0.1 and (■) 1 Hz for an undoped coarse grained $BaTiO_3$ ceramic. The cooling rate is 0.2 K per min.

However, the shape and the temperature of the R peaks are not only influenced by the vibration frequency, but also by the height of the phase transition peaks, which increases as the vibration frequency decreases [29]. Thus, in the orthorhombic and tetragonal phases, the height of the R2 and R1 peaks for a frequency of 0.01 Hz are strongly increased by their presence on the high-temperature side of the phase transition peaks P3 and P2, respectively. However, in the rhombohedral phase the R3 peak is easily identified because no phase transition occurs at lower temperature than $T_{O\text{-}R}$.

In order to obtain well defined R1 and R2 peaks a higher frequency than 0.01 Hz should be used. Fig. 3 (a and b) shows the $G(1/T)$ and $Q^{-1}(1/T)$ results for the undoped coarse gained $BaTiO_3$. The vibration frequencies are 1, 0.1 and 0.03 Hz. The R1 peak is very well formed for $f = 0.03$ Hz, and is still clear for $f = 0.1$ Hz, but for $f = 1$ Hz it appears to have disappeared. However, the mechanical loss for 1 Hz is shifted to higher temperatures as the frequency increased from 0.03 Hz. Equation 2 can be rewritten for two vibration frequencies as [30]

$$\ln\left(\frac{f_1}{f_2}\right) = \frac{H}{k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3}$$

The variations on the low-temperature-side of the R1 peak from 0.03–0.1 Hz (AB) and from 0.1–1 Hz (BC) in $1/T$ axis can be estimated by Equation 3, the rate of the variations $1/T$(0.03–0.1 Hz) over $1/T$(0.1–1 Hz) is about 0.59. The rate of the variation of ln (0.1/0.03) over ln (1/0.1) is equal to 0.52. This means that at 1 Hz the increasing component to the loss with temperature is on the low-temperature side of a peak. The whole peak cannot be observed because the ferroelectric–paraelectric phase transition takes place at almost the temperature of the peak for the 1 Hz vibration. By using an exponential function for the high-temperature background, the true R1 peak can be obtained by subtracting the background as is shown in Fig. 3 (a and b). The peak temperatures are determined to be 348 K (for 0.03 Hz), 365 K (for 0.1 Hz) and 395 K (for 1 Hz), however, before the subtraction the values were 353, 370 and 399 K, respectively. The activation energy and the pre-exponential factor for the peaks are 0.93 eV, 1.90×10^{-12} s, and 0.90 eV, 4.10×10^{-12} s for before and after the subtraction of the background. The heights of the peak Q_m^{-1} are 0.011 and 0.009 and the half-widths of the peak $\Delta(T^{-1})$ are 2.96×10^{-4} and 2.76×10^{-4} K^{-1} for the 0.03 and 0.1 Hz vibrations. It is now possible to test whether or not the peak is a single Debye process. For a Debye peak the width $\Delta(T^{-1})$ is given by [30]

$$\Delta(T^{-1}) = 2.635\, k/H \tag{4}$$

If there is a distribution of relaxation processes then the peak will be broad and the ratio $\gamma = \Delta(T^{-1})/(2.635/H)$ will be larger than 1. For the R1 peak, the γ value estimated by using $H = 0.90$ eV is presented in Table I. The average value of γ which is about 1 indicates that the R1 peak is essentially a single-relaxation time process.

For other samples with coarse grains, the H and τ_0 of the R peaks were determined for several thermal cycles. The average value of H obtained for the R peaks were;

$$\begin{aligned} &\text{R1: } H = 0.92 \pm 0.04 \text{ eV}, &&\tau_0 = 3.0 \times 10^{-13} \text{ s} \\ &\text{R2: } H = 0.68 \pm 0.05 \text{ eV}, &&\tau_0 = 0.4 \times 10^{-13} \text{ s} \\ &\text{R3: } H = 0.45 \pm 0.03 \text{ eV}, &&\tau_0 = 3.2 \times 10^{-13} \text{ s} \end{aligned} \tag{5}$$

The relationship between the peak temperatures and vibration frequencies are plotted in Fig. 4. For

TABLE I Activation parameters for the R1 peak

Frequency (Hz)	T_p (K)	Q_m^{-1}	γ
0.03	348	0.011	1.17
0.1	365	0.009	1.10
1	395		

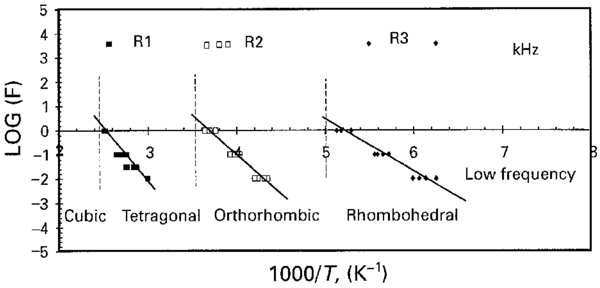

Figure 4 Arrhenius plot log *f* versus $1/T_P$ for the mechanical loss peaks for a $BaTiO_3$ sample with large grains.

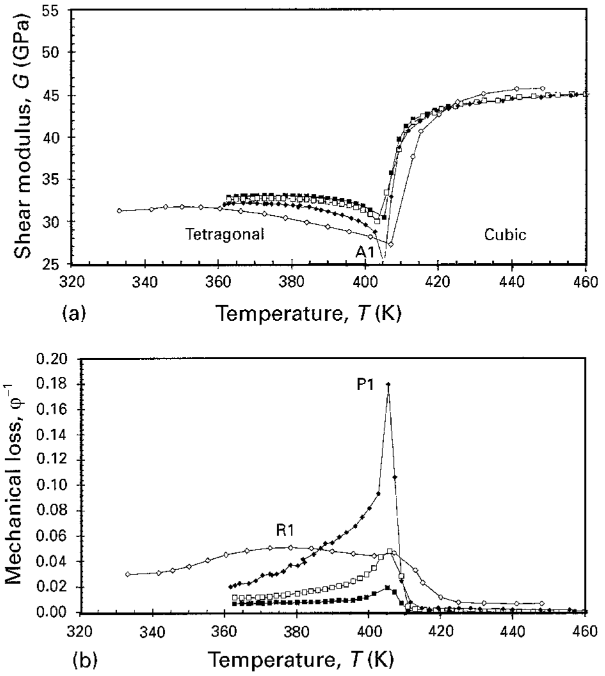

Figure 5 Influence of *in-situ* annealing in vacuum on the variations of (a) the shear modulus *G*, and (b) the mechanical loss Q^{-1} as a function of temperature for an undoped coarse grained $BaTiO_3$ ceramic. The vibration frequency (*f*) is (◆) 0.01, (□) 0.1 and (■) 1 Hz. The cooling rate is 0.4 K per min and the heating rate is 1.0 K per min. The symbol (◇) represents data taken at 0.1 Hz during the heating.

comparison purposes the R peak temperatures at kilohertz frequencies are also presented in Fig. 4. The R peak observed in each crystalline phase at kilohertz and also at lower frequencies cannot be described by the same thermal activated relaxation process. This will be discussed later.

Fig. 5 shows the $G(T)$ and $Q^{-1}(T)$ values obtained during the cooling of an undoped coarse grained $BaTiO_3$ ceramic after *in situ* annealing in vacuum at 873 K for 30 min. As a comparison, the $G(T)$ and $Q^{-1}(T)$ values obtained during the heating run are also given in Fig. 5 for the vibration frequency of 0.1 Hz. During the heating there is a broad mechanical loss peak R1, in addition to a narrow peak corresponding to the paraelectric to ferroelectric phase transition. However, after the *in situ* annealing at 873 K in vacuum, there is no indication of the R1 relaxation peak. This demonstrates that the appearance of the R1 relaxation peak is not only connected with the ferroelectric domain walls but also with some kind of point defect diffusion process. The possible identity of these defects will be discussed in detail in the next section.

4. Discussion

4.1. The conditions under which the R peaks appear

The R relaxation peaks are observed only in ceramics sintered at high temperatures that contain large grains (a size of about 40 μm) with numerous 90° domain walls. For a ceramic sintered at 1513 K which shows a fine grain size (about 1 μm) homogeneous structure, there is no R peak. Thus the R peaks can be attributed to the motion of domain walls in large grained ceramics, since such a motion is limited by grain boundaries in fine grained ceramics. The other three anomaly-peak pairs (A1, P1), (A2, P2), and (A3, P3) can be obviously attributed to the three structural phase transitions in $BaTiO_3$ ceramics.

The appearance of the R peaks is also influenced by an *in-situ* annealing in vacuum at high temperature as is shown in Fig. 5. A survey of the literature on the defect chemistry of undoped $BaTiO_3$ shows that the equilibrium defect chemistry is dominated by impurities over a wide range of temperature and oxygen partial pressures. Chan *et al.* [31] have pointed out that the naturally occurring impurities for undoped large-grained $BaTiO_3$ are predominantly of the acceptor type because of the relative natural elemental abundances, and that the acceptor impurity is charge compensated by oxygen vacancies ($V_{O}^{\cdot\cdot}$). If a sample is annealed at a high temperature and a low oxygen partial pressure then the valence state of the acceptors will be changed [32, 33]. This valence change is always connected with the creation or annihilation of doubly ionized oxygen vacancies required for charge compensation. The increase of the vacancy concentration is approximately one-half of the impurity concentration ($[A^1] = 2[V_O^{\cdot\cdot}]$). The excess oxygen vacancies will segregate at the domain walls [34] which may cause pinning of the motion of the domain walls since the peak disappears after the vacuum annealing.

4.2. Analysis of the activation parameters

The activation energy *H* is determined to be 0.92, 0.68 and 0.45 eV for the R1, R2 and R3 peaks and the pre-exponential factor τ_0 is about 10^{-13} s for all the relaxation peaks. From the value of *H*, the R peaks could be attributed to an atomic diffusion process. Concerning the value of τ_0^{-1}, which is similar to the value of the Debye frequency ν_D (about 10^{14} Hz), this suggests that the motion of the domain walls could be connected with an atomic diffusion process.

In barium titanate the most mobile point defect is an oxygen vacancy. Lewis *et al.* [35] have calculated the diffusion activation energies for $V_{\mathrm{T}_\mathrm{i}''''}$(15 eV), $V_{\mathrm{B}_\mathrm{a}''}$(3.4 eV), and $V_{\mathrm{O}^{\cdot\cdot}}$ (0.62 eV). These results are comparable to the experimental results of $V_{\mathrm{B}_\mathrm{a}''}$(2.8 eV), and $V_{\mathrm{O}^{\cdot\cdot}}$ (0.44–0.68 eV). Shirasaki *et al.* [36] reported that the activation energy of an oxygen vacancy in undoped $\mathrm{BaTiO_3}$ was 0.59 eV which was determined in the cubic phase by a solid–gas exchange technique. These results for the diffusion activation energy for a $V_{\mathrm{O}^{\cdot\cdot}}$ are very similar to the activation energy of the R3 and R2 mechanical loss peaks. It is reasonable therefore to attribute these R peaks to the diffusion of oxygen vacancies.

However, for the R1 peak ($H = 0.92$ eV), which is almost the same as the enthalpy of oxidation with formation of two holes ($H_\mathrm{p} = 0.92$ eV) reported in reference [31]. In the measurements of mechanical loss and elastic modulus, the temperature range was 130–430 K for heating, or 430–25 K for cooling. Even if the oxygen partial pressure was low as in the case of the vacuum, the temperature range was not high enough for changes in the valence state of the acceptor impurities. Thus oxygen incorporation is possible in undoped $\mathrm{BaTiO_3}$ with the presence of an extrinsic concentration of $V_{\mathrm{O}^{\cdot\cdot}}$ being controlled by the acceptor impurity content. As discussed previously, the R1 peak disappears after annealing in vacuum at a high temperature. This could be due to the release of oxygen. Another possible mechanism for the R1 peak could be the oxidation reaction described as

$$V_{\mathrm{O}^{\cdot\cdot}} + 1/2\mathrm{O}_2 \rightleftharpoons \mathrm{O}_\mathrm{O} + 2h^{\cdot}$$

The notation is that of Kröger and Vink [37]. In summary, the R relaxation peaks may be connected with both domain wall and oxygen incorporation and the diffusion of oxygen vacancies in the ferroelectric domain.

4.3. Motion of domain walls

As concerns the spatial structures of domain walls, Arlt and Sasko [38] and Arlt and Peusens [39] pointed out that in ferroelectric $\mathrm{BaTiO_3}$ the domain is different from that in a single crystal because the domain structure of a grain is formed under clamped conditions, whilst a single crystal is free. The domain density depends on the grain size g. There is a critical grain size above which the twin lamellae increases proportionally to $g^{1/2}$. The shape of the grain adjusts to the surroundings in two dimensions. Above a larger critical grain size more complex interfaces are created which allow stress relief in the third dimension [40]. In the tetragonal phase the etch patterns can be described by two kinds of domain configurations. Thin layered domains separated by 90 ° walls are piled up to form sloped stacks. Neighbouring stacks are bounded by two types of boundaries. 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 polarization charge (so-called β-type structure). The excitation produced by the external stress means that the 180 ° walls, 90 ° walls, the mixed walls and the boundaries between the various configurations will move and thus the grain can be deformed and polarized. This could be the origin of the anelastic behaviour of the motion of the domain walls. At suitable experimental conditions the specific kind of domain wall motion could induce a mechanical loss peak. This is the case for the ceramic sintered at higher temperature (1573 K) with coarse grains (about 40 μm) and with numerous 90 ° domain walls, in which the domain configurations can be described by the above model. However for the ceramic sintered at 1513 K, scanning electron microscopy (SEM) shows a more homogeneous structure of fine grain size (about 1 μm), in which the domain configurations are composed of simple thin layered domains separated by 90 ° walls.

The motion of domain walls can be divided into two mechanisms: migration and gliding. The migration of domain walls is a motion whose direction is perpendicular to the wall, whereas the gliding of domain walls is a motion which is directed parallel to the walls. In fact, the motions of domain walls are complex not only because the single 90 ° domain wall has two kinds of movements (migration and gliding) but also because the spatial domain configuration has two types of configurations (α and β-type structure). The domain walls and spatial domain configurations become much more complex as the material structure changes from tetragonal to orthorhombic and finally to rhombohedral symmetry [41]. The relaxation peaks R1, R2 and R3 could be assigned to the motion of domain walls in the tetragonal, orthorhombic and rhombohedral phase, respectively. The disappearance of the R peaks may be due to the strong pinning effect that grain boundaries have on the domain walls [40].

Postnikov *et al.* [6] considered the piezoelectric effect in a fine grain with a lamellae domain configuration. They proposed that the shear stress σ causes an increase in the polarization of the domain oriented in the direction of tension and a decrease in the polarization of those oriented in the direction of compression. The excess polarization created by the stress is expressed as

$$\Delta P = (d_{33} - d_{31})\sigma \tag{6}$$

where d_{ij} is the piezoelectric constant. The domain wall is moved by such a stress. Due to the change of polarization, a bound electric charge appears at the domain wall with the density

$$\rho = (2)^{1/2}\Delta P = (2)^{1/2}(d_{33} - d_{31})\sigma \tag{7}$$

These bound charges induce an electric field in the grain. The mobile charges associated with the point defects will diffuse in the electric field in order to achieve equilibrium. However, establishing the equilibrium requires time and through the inverse piezoeffect this induces an additional anelastic deformation. For small concentrations of mobile charges, as in the case of an undoped ceramic, Pestnikov *et al.* [6] derived the height of the mechanical loss peak as

$$Q^{-1}_{\max} = \frac{2(d_{33} - d_{31})^2 c_o L^2}{\pi^4 \varepsilon_r^2 \varepsilon_o^2 k T^s} \tag{8}$$

where c_0 is the density of point defects, L is the width of the domain, s is the elastic compliance and ε_o is the permittivity in a vacuum. The activation energy is taken as the diffusion energy of a point defect and the relaxation time can be written as

$$\tau = \frac{L^2}{\pi^2 D} \tag{9}$$

where D is the diffusion coefficient. They proposed that the mobile point defects which cause the relaxation peak in PZT are stoichiometric Ti and Zr vacancies resulting from an excess of Pb in the synthesis. However, the activation energy of the peaks is small (0.4 and 0.8 eV for the 140 and 280 °C peaks in PZT ceramics). In $PbZrO_3$ the migration energy of a cation vacancy obtained from electric conductivity measurements is 1.31 eV [43], which is higher than that of the mechanical loss peaks. The relaxation peaks cannot therefore be due to cation vacancies but instead to oxygen vacancies. In the same way, the relaxation peaks observed at low frequency in $BaTiO_3$ ceramics are caused by the diffusion of oxygen vacancies which is controlled by the migration of domain walls. As shown in Equation 8 the height of a mechanical loss peak is proportional to the square of the width of a domain. SEM observations show that the width of a domain is about 1 μm in a coarse grained ceramic which is about 5 times that in the fine grained ceramic (about 0.2 μm) [44]. So the height of a loss peak in a coarse grained ceramic could be 25 times higher than that in a fine grained ceramic, if all other parameters are equal. In fact, the mechanical loss peaks exist only in the coarse grained ceramic (see Figs 1 and 2).

It may be possible to explain the peaks observed at kilohertz frequencies, by the above model, if the relaxation peaks located in the tetragonal phase or orthorhombic phase at kilohertz frequencies are considered as the shift of the relaxation peak located in the orthorhombic phase or in the rhombohedral phase measured at low frequencies. This explanation can be verified by the high frequency measurement of mechanical and dielectric losses.

5. Conclusions

In undoped coarse grained $BaTiO_3$ ceramics there are three mechanical loss (R) peaks in addition to three phase transition (P) peaks. The R peaks can be explained by the interaction of domain walls and the diffusion of oxygen vacancies in each crystalline phase in the ferroelectric state. Such a motion of domain walls can be described by an Arrhenius relationship. The activation energy of the R1, R2, and R3 peaks is determined to be 0.92, 0.68, and 0.45 eV, which is the diffusion energy of an oxygen vacancy in the tetragonal, orthorhombic and rhombohedral phases, respectively. The mechanism should be studied by a combination of mechanical and dielectric measurements.

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