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Oxygen Vacancy Relaxation and Domain Wall Hysteresis Motion in Cobalt-Doped Barium Titanate Ceramics

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Mechanical and dielectric loss measurements were carried out in the $BaTiO_3$ ceramics doped with Co at frequencies between 0.01 Hz and 1 MHz as a function of temperature from $-150°$ to 150°C. The relaxation peak observed in the ferroelectric phase with an activation energy of 0.27 eV is assumed to be related to the motion of oxygen vacancies. This peak could be because of the reorientation of an electrical dipole made of oxygen vacancies and Co^{3+} ions in the lattice. Furthermore, another loss peak located just below the Curie temperature T_c could be interpreted as hysteretic motion of the domain walls in a regime where the domain wall density is changing.

I. Introduction

In the manufacture of multilayer capacitors with the X7R specification, the grain size of the $BaTiO_3$ ceramic is controlled at about 1 μm by doping with cation additions such as Nb and Co, in order to stabilize the variation of permittivity as a function of temperature.[1] The dopants inhibit the grain growth during sintering, and form a so-called ‘‘core-shell’’ structure inside the grain to limit the motion of domain walls. Measurements of mechanical loss and Young’s modulus in the kilohertz range on the $BaTiO_3$-based ceramics show that Nb and Co dopants result in attenuation of mechanical loss and smoothing of elastic modulus anomalies at the phase transitions.[2–4] The Nb dopant reduces the mechanical loss in the tetragonal phase, and Co reduces the mechanical loss in the orthorhombic phase. The combination of Nb and Co gives a smooth variation of mechanical loss and elastic modulus versus temperature, which is the basis of the X7R specification.

However, Co doping also induces oxygen vacancies in the material to preserve electrical neutrality. Even in undoped $BaTiO_3$ ceramics with large grain size, the relaxation peak in the ferroelectric phase can be affected by the oxygen vacancies. The peak in the tetragonal phase is suppressed by vacuum annealing, showing clearly the impact of oxygen vacancies on the motion of domain wall.[5,6] Furthermore, in the application of tunable microwave devices of $(BaSr)TiO_3$-based ceramics,[7] oxygen vacancies also exist and, in the films prepared by pulsed laser deposition, for example, this can cause a change in the lattice parameters.[8] In all cases, the mobility of the oxygen vacancies is one of the most important factors for controlling the stability of the dielectric properties.[9–15] At ambient application temperatures, normal diffusion measurements are ineffective in tracing the motion of the oxygen vacancies. However, the measurement of the mechanical loss (at frequencies between 0.01 and 10^3 Hz) and the dielectric loss (at frequencies of 10^3–10^6 Hz) as a function of temperature between $-150°$ and 150°C can be used to indicate the motion of the oxygen vacancies in the materials, their motion being indicated by relaxation peaks. The objective of this paper is to understand the participation of oxygen vacancies in the relaxation behavior, and the influence of Co doping on the phase transformations and domain wall motion in fine-grained $BaTiO_3$ materials.

II. Materials and Experimental Techniques

Barium titanate powder (Elmic BT 100: 0.7–1.0 μm particle size, $Ba/Ti = 0.996 \pm 0.004$) was provided by Rhone-Poulenc (Rhone-Poulenc, France). Cobalt carbonate was added to the barium titanate powder in an alcoholic suspension in appropriate proportions to obtain 0.6 and 1.0 at.% Co-doped $BaTiO_3$, and the ratio of Ba/(Ti+Co) was then reduced by the Co doping. The suspension was mixed by vibration milling with agate balls for 2 h together with suitable organic binders. After drying and deagglomeration, the powders were uniaxially pressed at 30 MPa to make prismatic bars, which were then isostatically pressed at 300 MPa. The compacts were sintered in air for 2 h at 1300°C using a heating and cooling rate with 300°C/h. Undoped barium titanate ceramics were also prepared by sintering for 2 h at temperatures between 1240° and 1325°C, in order to vary the sintered grain size. The sintered samples were then sliced into rectangular plates (1 mm × 5 mm × 40 mm).

Room-temperature X-ray diffraction was carried out in a Rigaku–Geiger–Flex diffractometer with a graphite [0002] monochromator using Cu$K\alpha$ radiation. The $BaTiO_3$ ceramics doped with 0.6 and 1.0 at.% Co have a tetragonal perovskite structure with a distortion (c/a) of 1.006. The distortion (c/a) in the undoped $BaTiO_3$ was 1.009 and 1.007 for the samples sintered at

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1300° and 1240°C, respectively. Scanning electron microscopy observations were made on samples polished to 1 μm using diamond paste and etched in acid (5 vol% HCl, 0.5 vol% HF, and 94.5 vol% H_2O).

The relaxation and domain wall motion phenomena were studied using mechanical vibration at low frequencies between 0.01 Hz and 4 kHz, and by electric excitation at higher frequencies of 1–100 kHz. An inverted pendulum technique was used to measure the mechanical loss and shear modulus at low frequency. The samples were mounted at the ends and excited for torsion oscillations around a vertically oriented longitudinal axis. A heating rate of 0.25°C/min was used. The dynamic modulus can be written as

$$G^* = G\,\exp(\mathrm{j}\phi) = G' + \mathrm{j}G'' \tag{1}$$

where ϕ is the phase lag angle between the strain and the stress. The mechanical losses $Q^{-1}(T)$ are calculated by the ratio of G''/G', and the shear modulus $G(T)$ is equal to G'. The mechanical loss and Young's modulus at kilohertz frequencies have been obtained by a flexural transverse vibration of the sample at resonance, using a heating rate of 0.5°C/min.[2] For the dielectric measurements, the samples used were plates of 1 mm × 5 mm × 5 mm, cut from the same sample used for the mechanical measurements. Two opposite faces of the samples were electroded by gold evaporation or by air-dried silver paste. Permittivity and dielectric loss were measured using an automated impedance analysis system (HP4192A) for 5 Hz$<f<$13 MHz. The heating rate was about 0.25°C/min, and the excitation electrical field was 1 V/mm.

III. Results

The microstructure of the $BaTiO_3$ ceramics doped with 0.6 at.% Co is shown in Fig. 1(a). A similar microstructure was observed for the ceramic doped with 1.0 at.% Co. The Co inhibits the grain growth of the ceramics. The grain size is homogeneous at approximately 1 μm and domain walls are rarely observed. The relative density of the samples is about 97% for both the 0.6 and 1.0 at.% Co-doped $BaTiO_3$ ceramics. Furthermore, a fine-grained microstructure is also observed for the undoped $BaTiO_3$ ceramic, which was sintered at 1240°C, Fig. 1(b). The grain size of these samples is approximately 1 μm, the relative density is 94%, and simple 90° domain wall structures can be identified in some grains at room temperature.

In order to study the effect of Co doping in the $BaTiO_3$ ceramics, it is instructive to compare the results of the mechanical loss with those of the undoped $BaTiO_3$ ceramics. The mechanical loss and Young's modulus for the fine-grained microstructure of the undoped $BaTiO_3$ ceramic shows the phase transition in the material in the kilohertz frequency range; see Fig. 2. There are three phase transition peaks on the curves of mechanical loss. The anomalies in the elastic shear modulus of A_1, A_2, and A_3 show the phase transitions in the material: A_1, tetragonal to cubic; A_2, orthorhombic to tetragonal; and A_3, rhombohedral to orthorhombic. No indication of a relaxation peak was observed. In contrast, however, for materials with large grain sizes (about 40 μm), sintered at 1300°C, the mechanical loss curve shows not only the peaks P_1, P_2, and P_3 for the three phase transitions but also additional peaks, noted as R_r^m and R_o^m, as shown in Fig. 3. The letter R is chosen for such a 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, and the sub-exponent r and o indicates the peak located in the rhombohedral and orthorhombic phase. Detailed investigation carried out in Cheng *et al.*[16] shows that the peaks R_r^m and R_o^m are thermal-activated relaxation processes, which could be explained by the interaction between different domain walls and diffusion of oxygen in the domains. The results in Figs. 2 and 3 clearly demonstrate the influence of grain size on the loss behavior of the materials. There is no peak attributable to the motion of domain wall motion in the fine-grained materials.

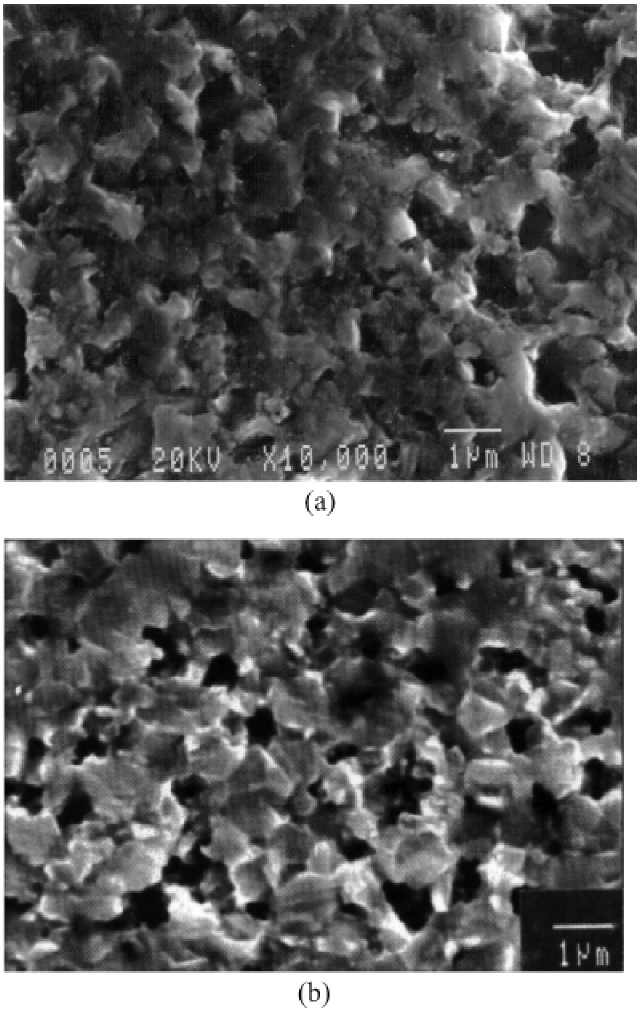

Fig. 1. Microstructures of $BaTiO_3$ ceramics doped with (a) 0.6 at.% of Co and (b) undoped.

The variations of the mechanical loss Q^{-1} and shear modulus G at low frequencies (0.01, 0.1, 1 Hz) for the $BaTiO_3$ fine-grained ceramics doped with 1 at.% of Co are shown in Fig. 4. There are three phase transition peaks on the curves of mechanical loss. No indication of a relaxation peak is observed. The anomalies on the elastic shear modulus of A_1, A_2, and A_3 indicate the phase transitions in the material.

The mechanical loss Q^{-1} and Young's modulus E curves of the $BaTiO_3$ ceramics doped with 0.6 and 1.0 at.% Co at 4 kHz frequency range are shown in Fig. 5. When the concentration of Co is increased, the anomalies A_3 and A_2 shift to high temperatures from −93° to −52°C and from 5° to 20°C, respectively. In

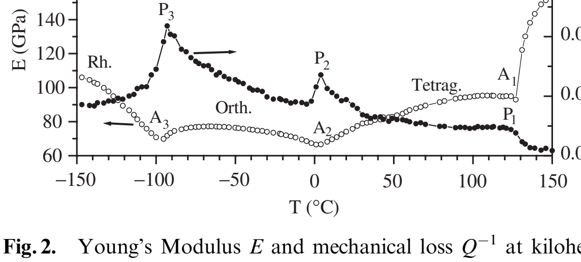

Fig. 2. Young's Modulus E and mechanical loss Q^{-1} at kilohertz vibration range in undoped $BaTiO_3$ ceramic with fine grain.

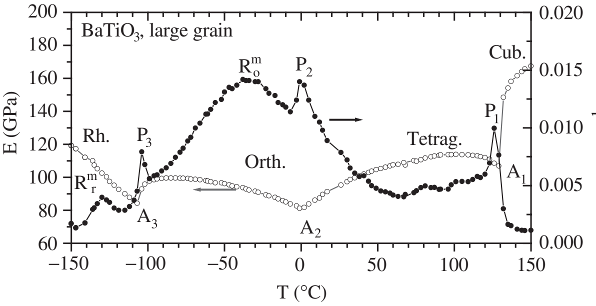

Fig. 3. Young's Modulus E and mechanical loss Q^{-1} at kilohertz vibration range in undoped BaTiO$_3$ ceramic with large grain.

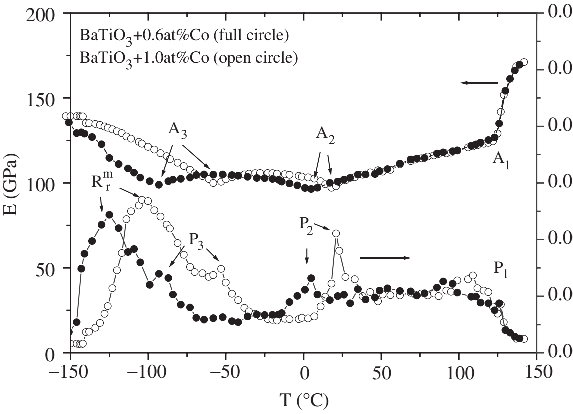

Fig. 5. Influence of Co doping on Young's Modulus E and mechanical loss Q^{-1} of the BaTiO$_3$ ceramics in the kilohertz vibration range. ●, 0.6 at.% Co; o, 1.0 at.% Co.

addition, there is a large loss peak located in the rhombohedral phase, noted as R_r^m. The height of the peak R_r^m seems to vary with the concentration of the Co in the material, and the temperature of the peak is clearly changed with the concentration of the Co in the material. Such a peak was not observed in the undoped BaTiO$_3$ ceramic with a similar fine-grained microstructure.

The temperature dependence of the permittivity $\varepsilon(T)$ and dielectric loss tan $\delta(T)$ for excitation frequencies of 3, 10, 30, 100 kHz of the BaTiO$_3$ ceramics doped with 1 at.% Co are shown in Fig. 6. The $\varepsilon(T)$ curves show that there are three peaks, A_1, A_2, and A_3, corresponding to the three phase transitions in the material. On the dielectric loss curves, there are two peaks noted as R_r^e and R_t^e (exponent e denotes the electrical measurement) observed in the rhombohedral and the tetragonal phases, respectively. The peak temperature T_p for both peaks shifts to higher temperatures with increasing measurement frequency. The peak R_r^e is also observed in the BaTiO$_3$ ceramic doped with 0.6 at.% Co. The loss peak R_r^e can be analyzed by the Arrhenius-type equation for the relaxation time:

$$\tau = \tau_0 \exp(H/kT) \tag{2}$$

where the H is the activation energy, and τ_0 is the relaxation time. The parameters H and τ_0 are estimated to be 0.27 eV and 2.6×10^{-13} s, respectively, as shown in Fig. 7. Careful analysis of Fig. 5 indicates that there may be a loss peak in the tetragonal phase region of the mechanical loss data measured in the kilohertz range, but the peak is not well shaped because the resonant frequency of the sample changed with temperature.

The variation of the temperature of the peak R_t^e with the frequency is shown in Table I. However, these data cannot be described by either a standard Arrhenius relationship, or the relationship for the phase transformation given by

$$\tau = \tau_0/(T - T_c)^\beta \tag{3}$$

where T_c is the phase transition temperature, and β is a phase transition parameter. Huang *et al.*[15] have proposed a modified relationship as follows:

$$\tau = \tau_0 \exp[H/k(T - T_c)] \tag{4}$$

Suppose that at the peak temperature, T_p,

$$\ln(\omega\tau) = 0$$

This gives

$$\begin{aligned} &\ln(\omega\tau_0) + H/k(T_p - T_c) = 0 \\ &\ln(2\pi f) = -\ln \tau_0 - H/k(T_p - T_c) \end{aligned} \tag{5}$$

The fitting parameter T_c can be adjusted until a linear relationship between $\ln(2\pi f)$ and $1/(T_p - T_c)$ is obtained. The values of the correlation coefficient R as a function of T_c are given in Table II, where it can be seen that for the best fit (largest R value), the parameter $T_c = 419$ K (146°C). The corresponding apparent activation energy $H = 0.016$ eV, and relaxation time $\tau_0 = 0.77$ ms are obtained (Fig. 8).

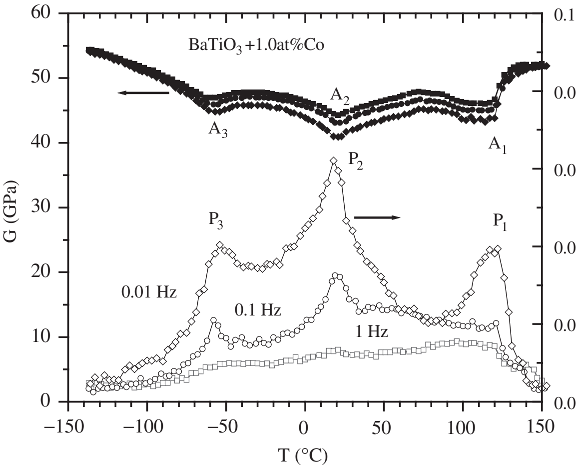

Fig. 4. Variations of mechanical loss Q^{-1} and shear modulus G with temperature on 1 at.% Co-doped BaTiO$_3$ for low frequencies of 0.01, 0.1, and 1 Hz.

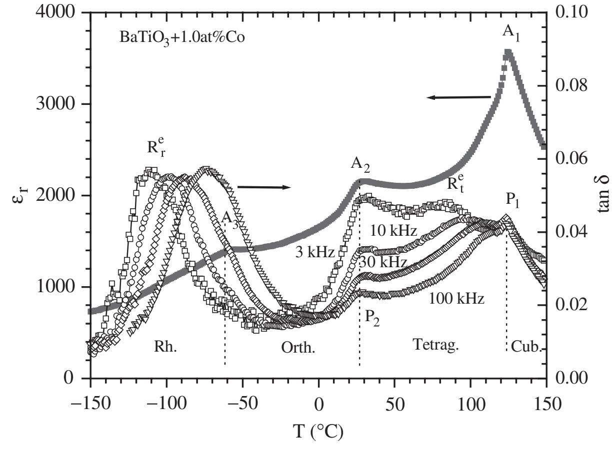

Fig. 6. The temperature dependence of the permittivity (□) and dielectric loss (open symbols) of the BaTiO$_3$ ceramic doped with 1 at.% Co at excitation frequencies of 3–100 kHz. The results of the permittivity are all the same in the measured frequency range; for clarity, only the results for the frequency of 10 kHz are shown in the figure.

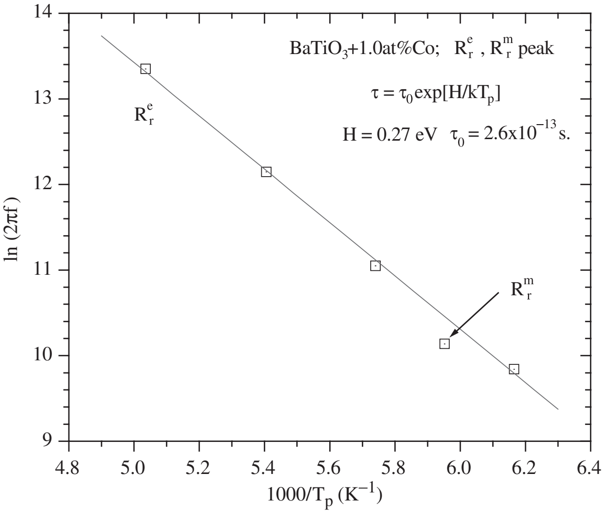

Fig. 7. Arrhenius plot for the dielectric loss peaks and mechanical loss peak for $BaTiO_3$ doped with Co.

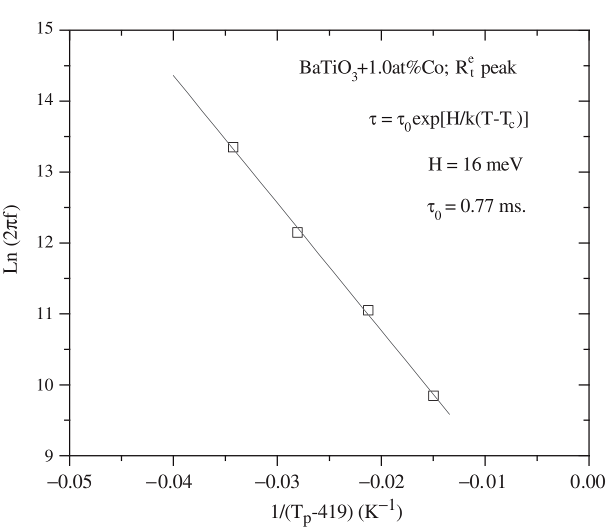

Fig. 8. Activation parameters plot for the loss peak located in the tetragonal phase in Co-doped $BaTiO_3$ ceramic.

Table I. Variation of Peak Temperature T_p of the Peak R_t^e as a Function of Frequency

Frequency (Hz)	3000	10 000	30 000	1 00 000
T_p (°C)	79.2	98.9	110.4	116.8

IV. Discussion

The experimental results of mechanical and dielectric losses in the frequency range from 0.1 Hz to 100 kHz have shown that, in fine-grained Co-doped $BaTiO_3$ ceramic, there is a relaxation peak that is not observed in undoped materials with similar grain sizes. Furthermore, the relaxation peaks because of the motion of domain walls appear only for the larger grain size $BaTiO_3$ materials.[16] It is interesting to note that the relaxation peaks, R_r^m and R_r^e, for the Co-doped materials are observed in similar temperature ranges and for a similar excitation frequency range in both the dielectric and mechanical loss measurements. Therefore, the peaks of R_r^m or R_r^e could be because of the same mechanisms, and could be related to the effect of the Co dopant in the $BaTiO_3$ fine-grained materials. In the following section, we will first discuss the possible mechanisms of the relaxation peak, R_r^m or R_r^e, located in the rhombohedral phase, and then try to study the peak R_t^e located in the tetragonal phase.

(1) Oxygen Vacancy Relaxation Peak in Co-Doped $BaTiO_3$ Ceramics

It is well known that the Co^{3+} ion doped into $BaTiO_3$ lattice will substitute at Ti sites. The Co^{3+} ions possess acceptor character, with the charge deficiency compensated by vacancies in the oxygen lattice as follows:[17]

$$2\text{BaO} + \text{Co}_2\text{O}_3 \rightarrow 2\text{Ba}_{\text{Ba}} + 2\text{Co}_{\text{Ti}} + 5\text{O}_0 + \text{V}_0^{\bullet\bullet} \tag{6}$$

It has been proposed by Ihrig[17] that there is a tendency for the Co^{3+} and $V_0^{\bullet\bullet}$ to associate in the Co-doped $BaTiO_3$ ceramic. The diffusion energies of the oxygen vacancies in barium titanate materials have been reported to be 0.46±0.13 eV[18] and 0.44–0.68 eV.[19] The smallest value of diffusion energy ($H = 0.33$ eV) is similar to the present result of 0.27 eV obtained in the Co-doped $BaTiO_3$ ceramics. So we can tentatively attribute the activation energy $H = 0.3$ eV as the diffusion energy of oxygen vacancies in the ferroelectric phases. The relaxation peak observed by the mechanical and dielectric loss measurements can thus be assumed to be because of diffusion of oxygen vacancies in the ferroelectric phases leading to the reorientation of electrical dipoles of Co^{3+} and $V_0^{\bullet\bullet}$.

(2) Viscous Motion of Domain Walls

In order to study the loss peak R_t^e located near the Curie temperature, the first intention was to make a comparison with the high-frequency polar relaxation mode in pure and iron-doped barium titanate demonstrated by Maglione *et al.*[20] However, the low-frequency peak observed here is not a pure relaxation process, and cannot be described by the normal Arrhenius relationship. Furthermore, it cannot be attributed only to the phase transition, because its peak temperature and relaxation frequencies do not follow a critical law at T_c. In fact, there is another loss peak located at the Curie temperature. It should also be questioned as to why this peak does not appear clearly in the mechanical loss measurement. As already shown in Fig. 8, this peak is not a pure activated process, and the peak temperature and peak height are sensitive to the measurement frequencies. In the dielectric loss measurement, the excitation frequency can be kept constant during temperature variation, but the resonance frequency of the mechanical vibration cannot be kept constant as it is dependent on elastic modulus, which changes with temperature. This could be one of the reasons this peak is not clearly identified in the mechanical loss measurement.

However, there is still an indication of high mechanical loss in the temperature range just below the T_c as shown in Fig. 5. So, it is therefore proposed that the R_t^e peak could be correlated with the phase transformation and domain wall motion in the material. Huang *et al.*[15] have proposed a model of viscous motion of domain walls to describe similar loss peaks below the Curie temperature. They have considered variation of density of domains and obtained an expression for the relaxation time, τ, the mechanical loss, Q^{-1}, and dielectric loss, D, as follows:

$$\tau = A_0 \exp(-H/k(T_c - T)) \tag{7}$$

Table II. Coefficients R as a Function of T_c

T_c (°C)	153	151	149	147	146	145	144	143	141
R	0.99872	0.99897	0.99917	0.99930	0.99933	0.99932	0.99929	0.99921	0.99892

$$Q^{-1} = (c' 2N_0 \varepsilon_{st}^2 / J' k_0)\omega\tau/(1+\omega^2\tau^2) \tag{8}$$

$$D = (2N_0 P_0^2 / C k_0)(T_c - T)\omega\tau/(1+\omega^2\tau^2) \tag{9}$$

where A_0 is constant, c' is the shear modulus, N_0 is the density of domain walls, ε_{st} is the spontaneous shear strain, J' is the elastic compliance, k_0 is the constant of recovering force for the domain wall motion, P_0 is the initial spontaneous polarization vector, and C is the Curie parameter for the permittivity, χ, where

$$\chi = C/(T_c - T) \tag{10}$$

In fact, the model is a combination of phase transition and motion of domain walls. As shown in Fig. 8, the relaxation time of the peak located just below the Curie temperature in the Co-doped $BaTiO_3$ material could be fitted by Eq. (7). Then, it is possible to speculate that the peak R_t^e observed in Co-doped $BaTiO_3$ ceramics is a hysteretic motion of the domain walls in a regime where domain wall density is changing.

V. Conclusions

Mechanical and dielectric loss measurements were carried out in the $BaTiO_3$ ceramics doped with Co at frequencies between 0.01 Hz and 1 MHz as a function of temperature from $-150°$ to 150°C. The relaxation peak observed in the ferroelectric phase with an activation energy of 0.27 eV is assumed to be related to the motion of oxygen vacancies. This peak could be the reorientation of electrical dipole composed of oxygen vacancies and Co^{3+} in the lattice. Furthermore, another loss peak located just below the T_c could be interpreted as hysteretic motion of the domain walls in a regime where the domain wall density is changing.

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