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Correlation among oxygen vacancies and its effect on fatigue in neodymium-modified bismuth titanate ceramics

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Abstract

Pure and Nd-modified $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics are prepared using the conventional solid state reaction method and their dielectric properties and mechanical properties are investigated. This shows that the activation energy of oxygen vacancies is enhanced whereas the concentration of oxygen vacancies is reduced when Bi^{3+} ions are partially substituted by Nd^{3+} ions. The *Cole–Cole* fitting to the dielectric loss reveals a strong correlation among oxygen vacancies, which is found to be proportional to the concentration of oxygen vacancies. The strong correlation reduces the activation energy of oxygen vacancies efficiently. Therefore, we conclude that the enhancement of activation energy originates from the diluted oxygen vacancy concentration and that the diluted oxygen vacancy concentration is the basic aspect of the excellent fatigue resistance in Nd-modified $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ materials.

1. Introduction

Ferroelectric materials have been extensively studied for their promising usage in nonvolatile ferroelectric random access memory (NvFRAM) devices. Among these ferroelectrics, lead zirconate titanate (PZT) [1–3] is known to be the most important candidate. However, the poor fatigue resistance as well as the lead toxicity associated with PZT and other lead oxide-based ferroelectrics is problematic. Therefore, lead-free ferroelectric materials with excellent fatigue resistance are desired. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) materials are considered as lead-free ferroelectrics for their strong anisotropy of the spontaneous polarization (P_s) along the *a*-axis ($\sim 50 \mu\text{C cm}^{-2}$) and *c*-axis ($\sim 4 \mu\text{C cm}^{-2}$) [4], low processing temperature and high Curie temperature. However, polycrystalline BiT thin films have a reduced remanent polarization

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(P_r) of approximately $10 \mu\text{C cm}^{-2}$ and they suffer from severe polarization suppression after $\sim 10^6$ read/write switching cycles [5]. Recent studies have revealed that La-doped BiT as well as Nd-modified BiT material show excellent fatigue resistance with a large P_r [6–8]. Many mechanisms based on chemical stability, surface configuration and domain walls have been put forward as explanations [9–12], but the issue is not yet clear. Detailed information about the fatigue mechanisms still warrants further investigations. Park *et al* [9] suggested that the fatigue property is related to the chemical stability of the perovskite layers to oxygen vacancies. Warren *et al* [12] argued that fatigue is caused by the diffusion of oxygen vacancies to the domain walls and their subsequent pinning.

Thus, we can see that oxygen vacancies play an important role in determining the fatigue property of ferroelectric materials and that information about oxygen vacancies in a material is helpful to understand its fatigue behaviour [13]. In this paper, the different behaviours of oxygen vacancies in both pure and Nd-modified BiT materials were investigated using dielectric measurements and the internal friction method. Considering the complexity, we limit ourselves to the simple case in ceramics where the bulk effect is dominant over that of the contact surface.

2. Experiments

Pure and Nd-modified BiT ($\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}$) bulk ceramics were prepared using the conventional solid state reaction method starting with metal oxide Bi_2O_3 (99%, 5% excess), Nd_2O_3 (99%), and TiO_2 (99%) powders. The mixed powders were calcined at 900°C for 5 h and sintered at 1050°C for 3 h. The rectangular-shaped ceramics were polished to a uniform thickness of 0.3 mm and were then plated with platinum in vacuum by rf sputtering, forming a uniform circular electrode of radius 1.5 mm. The dielectric properties were measured using an HP4194A impedance analyser in the frequency range from 100 Hz to 1 MHz in a vacuum chamber between 300 and 650 K (measured by a thermal couple attached to the bottom electrode with a cooling rate of about 2.0 K min^{-1}). The mechanical properties were measured by a free-free bar apparatus in a vacuum chamber in the temperature range from 300 to 650 K at a kilohertz frequency.

3. Results and discussions

Figures 1(a) and (b) show the temperature dependence of the dielectric loss of pure and Nd-modified BiT ceramic found with a quenched-in process, respectively. The measuring frequency range is from 100 Hz to 1 MHz. As shown, dielectric loss peaks were detected in both samples and all of these peaks tend to broaden and uniformly shift toward higher temperatures, accompanying a slight increase of the peak height, with the increase of measuring frequencies. This indicates that the dielectric loss peak is of relaxation type. One set of peaks in the dielectric loss was explained by Shulman *et al* [14] in terms of a Debye-type relaxation resulting from an ion-jump mechanism that occurred preferentially in the *ab*-plane. In YBCO ceramics [15], jumps of oxygen vacancies between two unequal lattice sites $\text{O}_A(1/2, 0, 0)$ and $\text{O}_B(0, 1/2, 0)$ have induced a high IF peak. BiT and BNT ceramics have unequal oxygen positions (like YBCO). Thus, we assume that the dielectric loss peak is related to the migration of oxygen vacancies among those unequal oxygen positions in ferroelectric ceramics. This conclusion will be further confirmed by the calculated activation energy as follows.

Since the peak was related to the motion of oxygen vacancies, the famous Arrhenius relation can be used here to describe this thermal activation process. As a result, using the

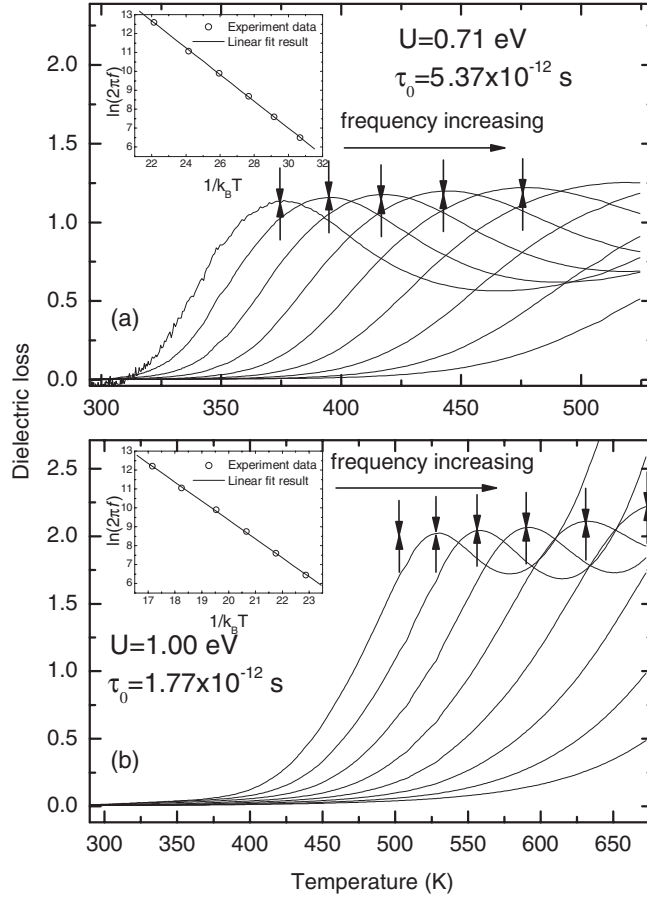


Figure 1. Temperature dependence of the dielectric loss of (a) pure and (b) Nd-modified BiT ceramic. The measuring frequencies are 10^2 , $10^{2.5}$, 10^3 , $10^{3.5}$, 10^4 , $10^{4.5}$, 10^5 , $10^{5.5}$, and 10^6 Hz, respectively. The inset shows the plots of $\ln(2\pi f)$ versus $1/k_B T$, and the activation energy of oxygen vacancies in these two kinds of ferroelectric materials is measured from the slope.

Arrhenius relation,

$$\tau = \tau_0 \exp(U/k_B T) \quad (1)$$

and the extreme value relation,

$$\omega\tau = \sqrt{\varepsilon_s/\varepsilon_\infty} \quad (2)$$

where U is the activation energy, τ_0 is a constant, k_B is the Boltzmann parameter and $\omega = 2\pi f$, the relationship between the measuring frequency and the dielectric loss peak temperature can be expressed as

$$\ln(2\pi f) = -U/k_B T + \ln(\sqrt{\varepsilon_s/\varepsilon_\infty}/\tau_0) \quad (3)$$

ε_s and ε_∞ are defined as the value of ε when ω equals zero and infinity, respectively. Using equation (3), the peak temperature value under different frequencies of pure and Nd-modified BiT ceramics was well fitted as shown in the inset of figures 1(a) and (b). The slopes of the linear fits in the insets of figures 1(a) and (b) yield the activation energies of oxygen vacancies in both ceramics. The fitted value of activation energies and relaxation times of

oxygen vacancies are 0.71 eV, 1.00 eV and 5.37×10^{-12} s, 1.77×10^{-12} s, respectively. They are quite reasonable compared with the value of activation energy for oxygen vacancy jumping in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ [16], where U is equal to 0.97 eV, and in SrTiO_3 [17] for the oxygen vacancy jumping, where U is 0.25 eV. In YBCO ceramics [15], the activation energy caused by jumps of oxygen vacancies between two unequal lattice sites $\text{O}_A(1/2, 0, 0)$ and $\text{O}_B(0, 1/2, 0)$ is about 1.03 eV, in agreement with typical values of 1.0 eV in other perovskites and related oxide structures [18]. Thus, the calculated activation energy further confirmed that the dielectric loss peak is associated with the migration of oxygen vacancies among those unequal oxygen positions in ferroelectric ceramics.

It is interesting to note that the activation energy increased by about 44% with the introduction of Nd element. The enhancement indicates that the chemical stability of the BiT ceramic was improved and the oxygen vacancy will need more energy to overcome the elevated potential barrier to jump and consequently pin the domain walls. Therefore, the probability of oxygen vacancies diffusing to the domain walls to pin the domain wall decreased, i.e., the higher the activation energy, the lower the probability of pinning, and the better the fatigue property. The enhancement of the activation energy could be the main reason for the excellent fatigue resistance in Nd-modified BiT materials.

However, the origin of this enhancement is still ambiguous and further discussion concerning the spectrum of dielectric loss is necessary. Debye theory, developed for the molecule's rotation, is often used to fit a vacancy hopping process in the elastic energy loss plot [19, 20]. During the century, this method has been extended in many elegant ways [21, 22]. Since the dielectric loss peak is directly related to the motion of oxygen vacancies, which belongs to a relaxation process, the well known Debye theory [20]

$$\tan \delta = \frac{\Delta}{T} \text{Im} \left[\frac{1}{1 + (i\hat{\omega}\tau)} \right] \quad (4)$$

where $\hat{\omega} = \omega\sqrt{\varepsilon_\infty/\varepsilon_s}$ $\tan \delta$ is the tangent of the loss angle and Δ is the strength of relaxation, can be used to describe this relaxation process. This equation is often used to fit the Debye peak in a mechanical loss plot, whose maximum occurs when $\omega\tau = 1$. When this equation is used to describe the dielectric loss peak, ω must be replaced by $\hat{\omega} = \omega\sqrt{\varepsilon_\infty/\varepsilon_s}$, whose maximum occurs when $\hat{\omega}\tau = 1$. But strictly speaking, this is not exact, because we cannot deduce the exact form of equation (4) from the Debye equation $\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty\omega^2\tau^2}$ in dielectric physics. Generally, it would be more accurate to fit the imaginary part of the dielectric constant instead of the tangent loss using Debye theory. Unfortunately, it is hard to determine peak positions (peak temperature and peak height) in the plot of the imaginary part versus temperature. Therefore, we have to focus on the fitting of the tangent loss plot.

The fitting result using Debye theory is not very satisfying (and is not shown here). Thus we turned to the *Cole–Cole* relation, which is deduced by Cordero *et al* [23, 20]:

$$\tan \delta = \frac{\Delta}{T} \text{Im} \left[\frac{1}{1 + (i\hat{\omega}\tau)^\alpha} \right] = \frac{\Delta}{T} \left[\frac{(\hat{\omega}\tau)^\alpha \sin(\frac{\pi}{2}\alpha)}{1 + (\hat{\omega}\tau)^{2\alpha} + 2(\hat{\omega}\tau)^\alpha \cos(\frac{\pi}{2}\alpha)} \right] \quad (5)$$

where α is the broadening factor, having a value between zero and unity. The α value is equal to $1 - \alpha$ in [23]. When $\alpha = 1$, the *Cole–Cole* relation changes to Debye theory. Assume that the relaxation time is in accordance with the Arrhenius relation as expressed in equation (1). The activation energy of the oxygen vacancies of the two materials adopted here is equal to the value obtained in figure 1. Figure 2 shows the *Cole–Cole* fitting result of dielectric loss as a function of temperature for both pure and Nd-modified BiT ceramics (the background was subtracted with a linear fit method) with 100 Hz measuring frequency. It is obvious that the fitted data are in very good agreement with the experimental data except for the head and tail

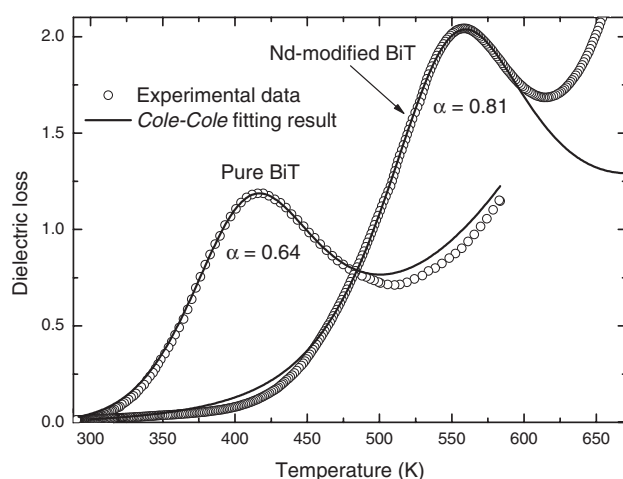


Figure 2. Dielectric loss as a function of temperature for both pure and Nd-modified BiT ceramics (the background is subtracted) with the measuring frequency of 100 Hz. The solid curves give their fitting result using the *Cole–Cole* relation. The activation energy adopted here is consistent with the result obtained in figure 1.

of each peak. The discrepancy in the high temperature region of each peak is caused by the first-order para–ferroelectric transition at Curie temperature. The values of α obtained from the fitting result for pure and Nd-modified BiT ceramics are 0.69 and 0.76, respectively.

The small α value suggests the existence of a strong correlation among those relaxation units [24], namely oxygen vacancies in our experiment. Thus, the movement of oxygen vacancies in ferroelectrics is not an individual behaviour but a collective one. Since oxygen vacancies are charged defects, it is unavoidable that interactions exist among them during their relaxation under an external electric field. Moreover, due to space-limiting factors, the motion of an oxygen vacancy is predicatively affected by its neighbourhood. These correlations among oxygen vacancies more or less make them demonstrate a collective behaviour during their movement.

It has been known for 20 years that increasing the number of oxygen vacancies in perovskites causes a self-ordering into planar structures [25–27]. Previous studies of oxygen vacancy ordering in perovskites include a $\text{Ba}_2\text{In}_2\text{O}_5$ study by Zhang and Smyth [25] and studies of calcium titanate/ferrites by Grenier *et al* [26] and most recently Becerro *et al* [27]. In these systems it is observed that in dilute amounts oxygen vacancies are uncorrelated point defects, but that with increasing vacancy concentrations the vacancies cluster, initially in one-dimensional chains whose lengths increase with vacancy concentration, and above a certain vacancy density in planes of specific geometries. Scott *et al* [28] has developed oxygen-vacancy ordering as a fatigue mechanism in perovskite ferroelectrics, in which oxygen vacancies order into two-dimensional planar arrays capable of pinning domain wall motion. Therefore, based on the previous studies on oxygen vacancy, we propose that oxygen vacancies in ferroelectrics form ‘clusters’ due to the existence of a strong correlation among them. These ‘clusters’ are distributed heterogeneously in the whole ceramic. The activation energy of such ‘clusters’ is smaller than that of uncorrelated point defects. Thus, the activation energy of oxygen vacancies is efficiently reduced through this ‘cluster’ mode. During the fatigue process, it is easier for oxygen vacancies to diffuse out and pin the domain walls through this ‘cluster’ mode than through the point defect mode.

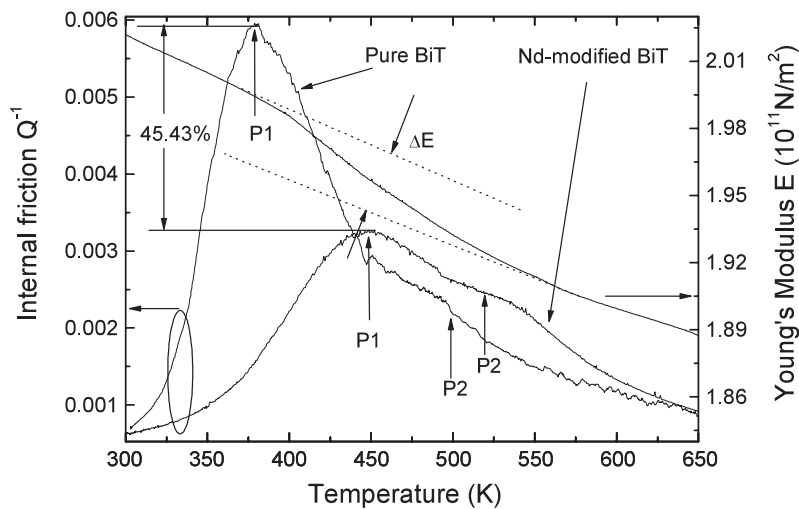


Figure 3. Internal friction of pure and Nd-modified BiT ceramic as well as Young's modulus of Nd-modified BiT as a function of temperature ranging from 300 to 650 K. Each material has two IF peaks marked P1 and P2, respectively. The peak height of P1 is decreased by 45.43% with the introduction of the Nd element.

The α value of pure BiT ceramic is about 10% lower than that of Nd-modified BiT ceramic, which indicates that the correlation of oxygen vacancies in pure BiT ceramic is stronger than that in Nd-modified BiT ceramics. Therefore, the motion of oxygen vacancy 'clusters' in pure BiT ceramics is easier compared with that in Nd-modified BiT ceramics as they pin the domain walls. Thus, the enhancement of the activation energy of oxygen vacancies originates from the weak correlation among oxygen vacancies in the modified BiT ceramics due to the introduction of Nd.

It is well known that the internal friction technique is very sensitive to the motion of point defects, domain walls and other imperfections, similarly to dielectric measurement [19, 29]. In order to determine the concentration of oxygen vacancies and to find out the relations between concentration and the correlation of oxygen vacancies, we consequently performed measurements of internal friction on these two kinds of materials. Figure 3 shows the internal frictions of pure and Nd-modified BiT ceramics as well as the Young modulus of Nd-modified BiT as a function of temperature. As shown, the internal friction (IF) peak of P1 decreases and the peak temperature increases when Nd is introduced into BiT ceramics and when the Young modulus decreases with temperature. Around 450 K, a modulus defect corresponding to the IF peak of P1 in Nd-modified BiT can be found, which is the characteristic of relaxation behaviour according to anelastic theory [19].

The P1 peak is caused by defects in the samples and the peak height is in proportion to the concentration of defects, e.g., oxygen vacancies in our samples according to point defect relaxation theory [19]. Thus, the decrease of the peak height implies the decrease of the concentration of oxygen vacancies in Nd-modified BiT ceramics. This is quite reasonable; Park *et al* [9] has demonstrated that, in BiT material, the oxygen ions near the Bi ions are unstable due to the volatility of the Bi ions. With the volatilization of Bi, oxygen vacancies are produced in the perovskite during the sample preparation. These charged defects could pin the domain walls, thus fatigue appears. Various amount of La substituents, or other rare-earth ions, like Nd, could reduce the quantity of volatile Bi, and consequently the produced oxygen vacancies. Using Raman spectra, Melgarejo *et al* [30] and Osada *et al* [31] have demonstrated

that with Nd or La doping the Bi mode at the perovskite A site exhibits a substantial hardening, whereas the Bi mode at the Bi_2O_2 layer is negligibly changed. Thus, A-site substitution can only affect the perovskite layers.

Therefore, we demonstrate that there is an identical relation between the concentration of oxygen vacancies and the correlation among them based on the result obtained from our experiments, namely, that the higher the concentration of the oxygen vacancies, the stronger the correlation among them.

Shulman *et al* [14] has previously demonstrated that niobium substitution at B sites could suppress the generation of oxygen vacancies in BiT materials. In this paper, we found that Nd substitution at A sites could also affect the concentration of oxygen vacancies. Based on our experiment, with the introduction of Nd element in BiT materials, the following two results were found: (1) the concentration of oxygen vacancies reduced; (2) the activation energy of oxygen vacancies was enhanced. The above two points are generally known to be the two aspects of the excellent fatigue resistance in Nd-modified BiT materials. However, it is found that there is an identical relation between the concentration of oxygen vacancies and the correlation among them and that the enhancement of the activation energy originates from the dilution of the concentration of oxygen vacancies. Thus, we propose that the diluted oxygen vacancy concentration is the basic aspect of the excellent fatigue resistance in Nd-modified $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ materials.

The increase in peak temperature of P1 in figure 3 indicates an enhancement in activation energy of oxygen vacancies in Nd-modified BiT ceramics, which is consistent with the result obtained by dielectric measurement.

In addition, another internal friction peak (P2) was detected in both pure and Nd-modified ceramics as shown in figure 3, which does not appear in dielectric measurements. The peak temperature and height are not significantly changed by the introduction of Nd. This peak has been attributed to the interaction between 90° domain walls and oxygen vacancies in ceramics [29].

In summary, the behaviour of the oxygen vacancies in pure and Nd-modified BiT ceramics was investigated using the dielectric measurement and the internal friction technique. It is found that the activation energy of oxygen vacancy was increased whereas the concentration of oxygen vacancies was decreased with the introduction of Nd. The *Cole–Cole* relation was used to fit the dielectric loss peak for both the pure and the Nd-modified BiT ceramics and a strong correlation among oxygen vacancies was considered to exist commonly in all ferroelectrics. The introduction of Nd to BiT ceramics efficiently diluted the concentration of oxygen vacancies and consequently enhanced the activation energy by weakening the correlation among oxygen vacancies. Thus, the dilution of the oxygen vacancy concentration is proposed to be the basic aspect of the excellent fatigue resistance in Nd-modified BiT materials.

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