JCS-Japan

May
vol.126

Journal of the Ceramic Society of Japan

2018

FULL PAPER

Effect of oxygen vacancies on intrinsic dielectric permittivity of strontium titanate ceramics

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We prepared oxygen-deficient strontium titanate ceramics and measured the THz dielectric spectra to discuss the effect of oxygen vacancies on the intrinsic dielectric permittivity. In the presence of oxygen vacancies, the lattice volume of strontium titanate increased. First-principles calculation revealed that the expansion of the lattice originated from repulsion between the oxygen vacancies and cations, causing a decrease in the covalency of the Ti–O bonding. THz dielectric measurement using a far-infrared spectroscopic ellipsometer made it clear that the Slater-type phonon mode hardened and then the intrinsic permittivity of strontium titanate decreased in the presence of oxygen vacancies.

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Key-words: Strontium titanate, Oxygen vacancy, Dielectric property, Ionic polarization, THz response, Ellipsometer, First-principles calculation

[Received November 27, 2017; Accepted January 31, 2018]

1. Introduction

Perovskite-type oxides are the most important materials in dielectric, ferroelectric, and piezoelectric applications.^{1)–6)} Since the dielectric and piezoelectric properties of perovskite-type oxides depend heavily on the constituent elements, microstructures, defects, etc., various approaches such as modification of the chemical composition,⁷⁾ engineering of the domain or grain boundary structure,^{8)–17)} and defect control^{18)–27)} have been studied to improve the properties. In this study, we focused on the influence of oxygen vacancies in perovskite-type oxides. Characteristics such as the dielectric permittivity, piezoelectric coefficient, elastic coefficient, resistivity, remanent polarization, and coercive electric field depend on the concentration of oxygen vacancies, and the precise control of oxygen vacancies is therefore required.^{18)–29)} For example, the control of oxygen vacancies in barium titanate (BaTiO₃) systems is one of the most important issues in the development of multilayer ceramic capacitors (MLCCs) since BaTiO₃ ceramics are co-fired with base metal inner electrodes in a reducing atmosphere.^{28)–31)} Generally, the insulation reliability and lifetime of MLCCs deteriorate and the dielectric permittivity of BaTiO₃ decreases with increasing the concentration of oxygen vacancies. The dielectric permittivity of BaTiO₃ is mainly determined by dipole and ionic polar-

izations, and the decrease in permittivity due to oxygen vacancies may therefore be understood as a decrease in dipole and ionic polarizations.^{28),29)} Dipole polarization of BaTiO₃ originates from the 90° domain-wall motion induced by the external electric field,³²⁾ and decreases in dipole polarization are caused by the pinning of 90° domain walls. On the other hand, ionic polarization is related to the lattice vibrations (phonons), and decreases in ionic polarization may be understood as hardening of the soft mode. However, the Slater-type soft mode of BaTiO₃ is known to be the overdamped phonon mode, which is difficult to be observed directly using conventional methods.³³⁾ For this reason, no direct evidence for hardening of the soft mode has not been reported yet. In contrast, the intrinsic permittivity of strontium titanate (SrTiO₃) can mainly be explained by ionic polarization alone, and the Slater-type soft mode of SrTiO₃ is the underdamped mode,^{34)–36)} suggesting that hardening of the soft mode caused by oxygen vacancies may be directly observed in a THz dielectric spectrum. We recently reported the THz dielectric spectra of nonstoichiometric strontium titanate ceramics with different Sr/Ti atomic ratios to discuss the effect of atomic vacancies on ionic polarization.³⁷⁾ The Slater-type soft mode hardened in the presence of the atomic vacancies, and the hardening was thought to be due to a reduction in the covalency of the Ti–O bonding.

In this study, reduced strontium titanate ceramics with various concentrations of oxygen vacancies were prepared, and the THz dielectric spectra of oxygen-deficient strontium titanate ceramics were measured to discuss the effect of oxygen vacancies on the intrinsic permittivity of

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[‡] Preface for this article: DOI <http://doi.org/10.2109/jcersj2.126.P5-1>

strontium titanate. In addition, first-principles calculation was carried out in order to understand the electronic and bonding states of oxygen-deficient strontium titanate ceramics.

2. Experimental procedure

Oxygen-deficient strontium titanate ceramics were prepared using the solid-phase method. SrCO_3 (Wako Pure Chemical Industries, 99.9%) and TiO_2 (Toho Titanium HT1311, 99.9%) powders were weighed and mixed by ball milling for 24 h. After calcination at 1100°C for 2 h, the powder was milled again and pressed into disks by cold isostatic pressing at 200 MPa. The green compacts were sintered at 1350°C for 4 h in air atmosphere. After sintering, the samples were annealed at 1000°C for 6 h under various oxygen partial pressures controlled by mixing H_2 , N_2 water vapor, and O_2 . The relative densities of the obtained samples were over 98%. Powder X-ray diffraction (XRD; Bruker AXS D8 Advance) was performed to analyze the crystal structure of the samples. The lattice parameters were determined by the Rietveld method (Bruker TOPAS 2.1).

The THz dielectric spectra of the samples were measured using a far-infrared spectroscopic ellipsometer. The measurement principles and the details of the ellipsometer are described in previous reports.^{33),34),38)} Ionic polarizations originating from three kinds of optical phonon modes, i.e., the Slater, Last, and Axe modes, were measured directly to discuss the effect of oxygen vacancies in strontium titanate ceramics.

In addition to the experimental approach, first-principles calculation was carried out using the Vienna Ab-initio Simulation Package (VASP) code.^{39),40)} The density functional theory (DFT) calculation was performed using the projector-augmented wave (PAW) method⁴¹⁾ and the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange–correlation potential.⁴²⁾ The plane-wave cutoff energy was 500 eV and $3 \times 3 \times 3$ k-point mesh was set in the Brillouin zone. To express a structure containing oxygen point defects, a model consisting of $2 \times 2 \times 2$ supercell (8 perovskite unit cells) was constructed, and then one of the 24 oxygen atoms was replaced with an oxygen vacancy. This model corresponds to an oxygen vacancy concentration of 4.16% and a chemical composition of $\text{SrTiO}_{2.875}$. Geometry optimization was performed using a conjugate-gradient algorithm. The partial charge density was calculated and visualized using VESTA software.⁴³⁾

3. Results and discussion

Figure 1 shows the photos of the strontium titanate ceramics annealed under various oxygen partial pressures (P_{O_2}). The sample color changed from light ochre to dark grey with increasing oxygen partial pressure, suggesting that the concentration of electron carriers increased with the generation of oxygen vacancies in the sample. The sample annealed under P_{O_2} of 10^{-5} – 10^{-13} atm did not indicate insulation properties, and therefore intrinsic

Fig. 1. Strontium titanate ceramics annealed under oxygen partial pressures of (a) 1, (b) 10^{-5} , and (c) 10^{-13} atm.

Fig. 2. Lattice constant of strontium titanate ceramics as a function of oxygen partial pressure.

dielectric permittivities could not be measured using a conventional capacitance method. From the XRD measurement, it was confirmed that all the samples had a perovskite-type cubic phase that contained no impurities. **Figure 2** indicates the lattice constants of the samples. The lattice constant increased with decreasing oxygen partial pressure in the annealing process, i.e., the crystal lattice of strontium titanate expanded due to the presence of oxygen vacancies. To discuss the lattice expansion and bonding state of the oxygen-deficient strontium titanate ceramics, first-principles calculation was carried out. Although the XRD measurement indicated that the oxygen-deficient strontium titanate had cubic Pm-3m symmetry, the local symmetry around an oxygen point defect is tetragonal P4/mmm. (Since oxygen point defects are not arranged in one direction when the vacancy concentration is not especially high, the average symmetry observed by XRD measurement is Pm-3m.) To obtain constancy with the experimental results, geometry optimization of the DFT calculation was performed by fixing the point group to cubic. After only the part coordinates of atoms were relaxed by fixing the cell shape and volume, the cell volume was relaxed by fixing the part coordinates and the cell shape. As a result, the lattice constants of SrTiO_3 and $\text{SrTiO}_{2.875}$ were estimated at 0.39395 and 0.39447 nm, respectively. The lattice expansion due to oxygen vacancies was confirmed by DFT calculation. **Figure 3** shows the total and projected density of states (DOS) for SrTiO_3 and $\text{SrTiO}_{2.875}$. Oxygen p-orbitals make the primary contribution to the valence band and the top of the valence band is created by the O 2p-orbital. The bottom of the conduction

Fig. 3. Total and projected density of states for (a) SrTiO_3 and (b) $\text{SrTiO}_{2.875}$. E_f indicates the Fermi energy.

band is formed by the Ti 3d-orbital. This orbital makes the main contribution to the conduction band at around the lowest portion. Since the valence of Ti decreases in the presence of oxygen vacancies, the lowest portion of conduction band changes^{(44)–(46)} and the conduction band minimum of $\text{SrTiO}_{2.875}$ is lower than that of SrTiO_3 . The DOS suggests that $\text{SrTiO}_{2.875}$ exhibits metallic properties. It is noted that the O 2p-orbital makes a small contribution to the lowest portion of conduction band. Ti 3d-orbital also contribute to the lower half of valence state spectrum. It is known that the admixture of the Ti 3d-orbital and O 2p-orbital indicates the covalency between Ti and O ions.^{(45)–(47)} The admixture of Ti 3d-orbital and O 2p-orbital decreased in the presence of oxygen vacancies, meaning that the covalency of the Ti–O bonding was weakened by the oxygen vacancies. **Figure 4** shows the partial charge density distribution of the Ti 3d-orbital and O 2p-orbital constituting the valence band. For the oxygen-deficient strontium titanate, repulsion between the oxygen vacancies and cations ($\text{V}_\text{O}^{\bullet\bullet}\text{--Sr}^{2+}$ and $\text{V}_\text{O}^{\bullet\bullet}\text{--Ti}^{4+}$) contributes to the expansion of the lattice. In addition, the difference in the covalency of Ti–O bonding is clearly seen as electron density between Ti and O ions. In the presence of oxygen vacancies, the overall electron density is low and the electron distribution around O and Ti ions is not much distorted in the direction of Ti–O bonding. It was certainly

visualized that the covalency of the Ti–O bonding is weakened in the presence of oxygen vacancies.

To understand the effect of oxygen vacancies on the intrinsic dielectric permittivity, we estimated the ionic polarization by measuring the complex permittivities of the samples in the THz frequency region. **Figure 5** shows the THz dielectric permittivities measured using the far-infrared spectroscopic ellipsometer. The responses of the Slater, Last, and Axe modes,^{(34),(35)} which are all optical phonon modes of SrTiO_3 at room temperature, were clearly observed for all samples. The Slater mode, which is the soft mode of SrTiO_3 , represents the mutual oscillation between the Ti ion and the rigid O_6 octahedra. The Last and Axe modes indicate the oscillation of the Sr ion against the TiO_6 octahedral framework and the bending of the O_6 octahedra, respectively. It is known that the dielectric dispersion of SrTiO_3 in the THz region is well described by the damped harmonic oscillator model;^{(34)–(36),(48),(49)}

$$\begin{aligned}\varepsilon^*(\omega) &= \varepsilon'(\omega) - i\varepsilon''(\omega) \\ &= \varepsilon_\infty \prod_{j=1}^n \frac{\omega_{j\text{LO}}^2 - \omega^2 + i\gamma_{j\text{LO}}\omega}{\omega_{j\text{TO}}^2 - \omega^2 + i\gamma_{j\text{TO}}\omega},\end{aligned}\quad (1)$$

where ε_∞ is the complex permittivity due to electric polarization, $\omega_{j\text{TO}}$ and $\omega_{j\text{LO}}$ are the resonance frequencies of the j th transverse optical (TO) and longitudinal optical (LO) modes, and $\gamma_{j\text{TO}}$ and $\gamma_{j\text{LO}}$ are the damping factors of the

Fig. 4. Partial charge density distribution of Ti 3d-orbital and O 2p-orbital constituting the valence band for (a) SrTiO_3 and (b) $\text{SrTiO}_{2.875}$. a_0 indicates the Born radius.

Table 1. Mode frequencies of strontium titanate ceramics annealed under various oxygen partial pressures

Mode	Mode frequency (THz)		
	$PO_2 = 1 \text{ atm}$	$PO_2 = 10^{-5} \text{ atm}$	$PO_2 = 10^{-13} \text{ atm}$
Slater (TO)	2.75	2.80	2.84
Slater (LO)	5.13	5.16	5.15
Last (TO)	5.16	5.18	5.19
Last (LO)	14.4	14.5	14.4
Axe (TO)	16.3	16.3	16.3
Axe (LO)	(24.5)	(24.3)	(24.0)

TO and LO modes, respectively. Therefore, we analyzed the phonon states of the samples by fitting the THz dielectric permittivity using Eq. (1). The results of the analysis are listed in Table 1.

First, we discuss the Slater mode. The TO mode frequency of the Slater mode depended strongly on the oxygen partial pressure, while the LO mode frequency was almost the same value. The Slater TO mode frequency increased with increasing the concentration of oxygen vacancies. Since the Slater mode is strongly influenced by the covalent bonding of Ti–O, it is considered that the increase in the Slater mode (hardening of the soft mode) is related to the decrease in the covalency of the Ti–O bonding. Note that the decrease in the effective ion mass is also considered as a reason for the increase in the Slater mode frequency. Next, we discuss the Last mode. Both the

TO frequency and LO frequency were almost constant regardless of oxygen partial pressure. Since Sr is strongly ionic and the covalent bond of Sr–O is extremely weak, the covalency of Sr–O is hardly affected by oxygen vacancies. This may be the reason why the frequency of the Last mode, which is related to the Sr–O bonding, did not change in the presence of oxygen vacancies. In the Axe mode as well, the TO mode frequency was almost independent of the concentration of oxygen vacancies. In contrast, the LO mode frequency may appear to depend on the concentration of oxygen vacancies; however, the data on the LO mode are not reliable because the mode frequency exists outside the measurement range of above 21 THz. The Axe LO mode should therefore not be discussed in detail. Figure 6 indicates the contribution of each optical phonon mode to the intrinsic permittivity, which encompasses the totality of electronic and ionic polarizabilities. The contribution of the Slater mode was largest among the modes, and the permittivity originating from the Slater mode depended on the concentration of oxygen vacancies. In the presence of oxygen vacancies, the Slater soft mode hardened, and the intrinsic permittivity decreased as a result.

4. Conclusions

In this study, we fabricated oxygen deficient strontium titanate ceramics and discussed the effect of oxygen vacancies on the intrinsic dielectric permittivity by mea-

Fig. 5. THz dielectric permittivities of strontium titanate ceramics annealed under oxygen partial pressures of (a) 1, (b) 10^{-5} , and (c) 10^{-13} atm.

Fig. 6. Contribution of each optical phonon mode to dielectric permittivity.

suring the ionic polarization. The intrinsic permittivity decreased in the presence of oxygen vacancies in strontium titanate. The reduction of the intrinsic permittivity was mainly explained by the hardening of the Slater-type phonon mode (soft mode of SrTiO_3), which is strongly related to the covalency of the Ti–O bonding. In the presence of oxygen vacancies, the covalency of the Ti–O bonding was weakened, and then the Slater mode hardened. This way of thinking should be applied not only to SrTiO_3 but also to other perovskite-type materials such as BaTiO_3 .

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