Materials Science and Engineering B 161 (2009) 55–60

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Wide range dielectric spectroscopy on perovskite dielectrics

Takashi Teranishi*, Takuya Hoshina, Takaaki Tsurumi

Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:
Received 18 June 2008
Received in revised form 6 October 2008
Accepted 21 November 2008

Keywords:
Dielectric dispersion
Relaxor
Ferroelectrics
Size effect
Ferroelectric domain
Barium titanate

ABSTRACT

Wide band dielectric spectra from the kilohertz to terahertz range were discussed for $SrTiO_3$ (ST) and $BaTiO_3$-based ceramics. The dielectric permittivity of $BaTiO_3$ (BT) is determined by the ionic polarization of the Slater mode as well as the dipole polarization of domain-wall vibrations in micro-sized domains. $(Ba_x,Sr_{1-x})TiO_3$ (BST) shows relatively high dielectric permittivity with a low dielectric loss up to GHz region, while $Ba(Zr_xTi_{1-x})O_3$ (BZT) shows a high permittivity with dielectric relaxation at MHz range. The dielectric dispersion in the BZT was due to the dipole fluctuation in polar nano-regions (PNR) in relaxors. The change of dielectric spectrum from BT to BZT was interpreted by the change from normal ferroelectrics to relaxors *via* ferroelectrics with diffuse phase transition (DPT-ferro.). Wide band dielectric spectra were also measured for BT ceramics with different grain and domain sizes to elucidate the size effect observed in BT ceramics. The low-frequency permittivity increased with decreasing grain size when the grain size was above 1 μm. It was found that the dipole polarization due to the domain-wall motion was enhanced with increasing domain density. We demonstrated wide band dielectric spectroscopy is a powerful tool to investigate the polarization mechanism of dielectric and ferroelectric materials.

1. Introduction

Perovskite ferroelectrics have been widely used for various dielectric devices in current electronic circuits. For example, $BaTiO_3$ (BT) is a base material of multi-layered ceramic capacitors (MLCCs) [1–2] because of its high permittivity while $SrTiO_3$ (STO) has the dielectric property of $\varepsilon_r = 290$, $Qf = 3{,}000$ GHz [3] and expected as a dielectric material in GHz region. The permittivity of BT at low frequencies is enhanced by the replacement of Ti ions with Zr ions at the B-site of the perovskite structure. $Ba(Zr_xTi_{1-x})O_3$ ($x > 0.2$, BZT) shows high dielectric permittivity with the relaxor behaviors and also used for the dielectric layers in the MLCCs [4]. On the other hand, $(Ba_x,Sr_{1-x})TiO_3$ ($x \approx 0.5$, BST), where Ba ions at the A site of BT are replaced with Sr ions, shows relatively high permittivity with low losses up to GHz region and expected for applications of microwave tunable capacitors, phase shifters and so on.[5–8] The dielectric properties of these ferroelectrics likewise depend on the A-site or B-site modifications in the perovskite crystals but the microscopic origin determining the dielectric properties is not fully understood so far.

In the perovskite dielectrics, the ionic and dipole polarizations dominantly determine the dielectric property in the frequency range used for practical applications (kHz – GHz region). The ionic polarization is directly concerned with the phonon behaviors. The dipole polarization is governed by the domain-wall vibrations of ferroelectrics [9,10] as well as the thermal fluctuation of dipoles in the polar nano-regions (PNR) in relaxors [11,12] and diffuse phase transition ferroelectrics (DPT-ferros.) [13,14]. Dipoles such as ferroelectric domain-walls and PNRs fluctuate by static electric field. But these fluctuations of dipoles become to be not able to follow the electric field, that generates the dielectric relaxation at high frequency [11,15,16]. To understand the microscopic origin of the dielectric properties, it is necessary to measure the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) as a function of frequency in a wide frequency range from kHz to THz and distinguish the contributions of the ionic and dipole polarizations in the dielectric responses.

Plenty of studies have been done historically to analyze phonons in the perovskite crystals using several techniques such as Raman or Infrared spectroscopy (IR-spectroscopy) and neutron diffractions. However, most of these studies did not relate the phonon behaviors to the dielectric properties in the low-frequency range important for the applications. Simada [17] Tamura et al. [18] and Chen et al. [19] have studied IR-reflectivity of $Ba(Mg_{1/3},Ta_{2/3})O_3$ (BMT) ceramics using a harmonic-oscillator phonon model and discussed the relationships between phonons and microwave dielectric properties. Kamba and co-workers [20,21] have been reporting many results obtained by THz spectroscopy to clarify the relation between the phonon behaviors and dielectric properties of various oxide dielectrics. These studies are actually opening a new window to understand the structure – property relationship in oxide dielectrics. However, most of these studies focused only on the analysis of ionic polarization in THz (IR) region. We believe that

---

* Corresponding author. Tel.: +81 3 5734 2517; fax: +81 3 5734 2514.
E-mail address: teranishi.t.aa@m.titech.ac.jp (T. Teranishi).

0921-5107/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2008.11.039

the continuity from the dipole polarization in kHz – GHz region to the ionic polarization should be incorporated into the analysis for obtaining accurate and reliable results.

In ferroelectric ceramics, it is known that the dielectric permittivity depend on the grain size. This phenomenon is called the size effect in ferroelectrics and many researchers reported the size dependence of the permittivity for $BaTiO_3$ ceramics [22–25]. It was generally recognized that the permittivity of $BaTiO_3$ ceramics increased with decreasing grain size in micron level while that decreased in submicron level. Arlt et al. [22] reported that the 90° domain size decreased with decreasing grain size and the permittivity increased by the contribution of 90° domain-wall. However, the mechanism of domain contribution has not fully clarified. Wide range dielectric spectra should give a confirm evidence of domain contributions to the size effect of BT ceramics.

In this paper, we are going to review our recent studies [15,26,27] done to understand the difference of dielectric properties among ST, BT, BZT and BST, and the size effect of BT using wide range dielectric spectra.

2. Evaluation of complex dielectric permittivity up to THz region

The detail of experimental technique to determine the wide range dielectric spectra in microwave region has been reported previously [28–31]. From kHz to 10 MHz, the complex permittivity was determined from the capacitance and the loss tangent ($\tan\delta$) of ceramic plates measured with an impedance analyzer (4294A, Agilent Tech.). In the dielectric measurements up to a few GHz, the micro-sized planer electrode method [32,33] was employed. The admittance between the source and ground ports in micro-sized planer electrodes was measured with an impedance analyzer (E4991A, Agilent Tech.) or a vector network analyzer (37397C, Anritsu, Japan). The complex permittivity of the ceramics was determined with the help of electromagnetic field simulation (Sonnet 10.52, Sonnet Software Inc.). In the THz region, IR-reflectivity of the ceramics was measured with a Fourier-transform far-IR spectrometer (FARIS-1, JASCO) at room temperature.

The dielectric dispersion due to the dipole polarization was analyzed using the following empirical expression [34]:

$$\frac{\varepsilon*(\omega)-\varepsilon_{\infty 1}}{\varepsilon_0-\varepsilon_{\infty 1}}=\sum_{i=1}^{n} g_i[1/(1+i\omega\tau_i)] \tag{1}$$

where $\varepsilon_{\infty 1}$ is the permittivity due to the ionic polarization, ε_0 is the low-frequency permittivity, ω is the angular frequency and g_i is the distribution of relaxation time (τ_i). On the other hand, the dielectric dispersion due to the ionic polarization was analyzed using the following four-parameter-semi-quantum (FPSQ) model [35]:

$$\varepsilon*(\omega)=\varepsilon_{\infty 2}\prod_{j=1}^{n}\frac{\omega_{jLO}^2-\omega^2+i\gamma_{jLO}\omega}{\omega_{jTO}^2-\omega^2+i\gamma_{jTO}\omega} \tag{2}$$

where $\varepsilon_{\infty 2}$ is the permittivity due to the electronic polarization, n is the number of optical phonon mode, ω_{jLO} and ω_{jTO} are the angular frequencies of j-th longitudinal optical (LO) and transverse optical (TO) modes respectively, γ_{iLO} and γ_{iTO} are the damping factors of j-th LO and TO modes, respectively. The relation between the ε^* and the IR-reflectivity $R(\omega)$ is given by

$$R(\omega)=\left|\frac{\sqrt{\varepsilon*(\omega)}-1}{\sqrt{\varepsilon*(\omega)}+1}\right|^2 \tag{3}$$

We have combined Eqs. (1) and (3) to fit the observed permittivity from kHz to GHz region and IR-reflectivity in THz region. The following $F(x_i)$ was minimized to determine the optimum x_i using non-linear least-squares calculation:

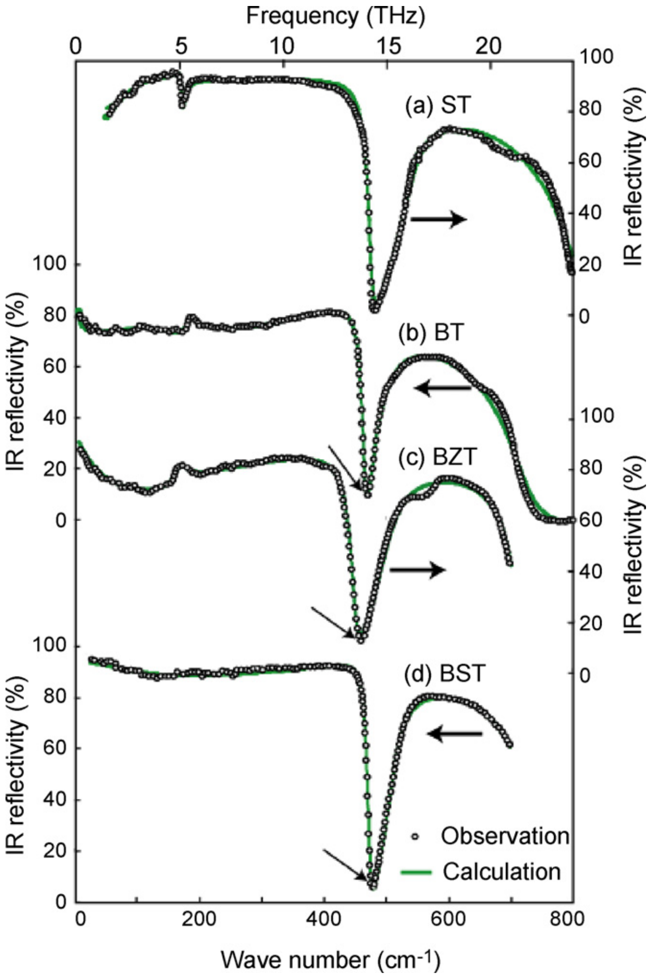

Fig. 1. IR-reflectivity of the ST and BT-based ceramics.

$$F(x_i)=(\varepsilon*_{obs}(\omega)-\varepsilon*_{cal}(\omega))^2+(R_{obs}(\omega)-R_{cal}(\omega))^2 \tag{4}$$

where x_i is the parameters in Eqs. (1) and (2) and suffixes 'obs' and 'cal' indicated observed and calculated values.

3. Dielectric dispersions of perovskite dielectrics

Ceramics samples of BT, BZT ($x = 0.25$), BST ($x = 0.6$) and ST with relative densities above 97% were prepared by a conventional solid-state reaction process. No secondary phase was observed in the X-ray diffraction analyses in the ceramics. These ceramics were used for the measurements of wide range dielectric spectra after polishing the surfaces. The dielectric permittivity (ε) *vs.* temperature (T) curves of the BST and BZT ceramics indicated that the temperatures at the ε-maxima (T_m) of the both ceramics were consistently about 5 °C.

Fig. 1 shows the IR-reflectivity data of the BT, BZT ($x = 0.25$), BST ($x = 0.6$) and ST ceramics as a function of wave number. The observed results were in excellent agreement with those calculated by minimizing the function $F(x_i)$ in Eq. (4). Wave numbers of phonons obtained to fit the IR-reflectivity using a least-squares method were listed in Table 1. The wave numbers of the soft phonon modes in the ST and BT were respectively 93.3 and 15.1 cm^{-1}, which were consistent with the reported values [36,37].

Fig. 2 shows the wide range dielectric spectra of the ST and the BT-based ceramics. The agreements between the observations and