Broadband spectroscopy of dielectrics and oxygen-ion conductors

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The frequency response of the permittivity of oxides is described by the dielectric dispersion of four contributions: the interfacial, dipole, ionic, and electronic polarizations. Our recent studies related to the broadband dielectric and conductivity spectroscopy of oxides are reviewed herein. Two methods, i.e., the micro-sized planar electrode and ring resonator techniques, were developed to measure the microwave dielectric properties of specimens having a large permittivity. Using these methods, we developed the complex permittivity of a paraelectric SrTiO3 (ST) single crystal up to a few GHz. We also investigated the polarization contribution to the microwave tunability, T, of ferroelectric Ba0.8Sr0.2TiO3 (0.8-BST). The apparent tunability of 0.8-BST was determined by the domain wall density; a higher domain wall density resulted in a larger dipole polarization. A modified Kohlrausch–Williams–Watts model was used for the dipole relaxation function. Ionic polarization was analyzed using the four-parameter semi-quantum phonon dispersion model. The dielectric function combining these two relationships was used for broadband spectroscopic analysis of the dielectrics. The dipole and ionic polarizations and electronic contributions were simultaneously quantified for the ferroelectric BaTiO3 ceramic and ST single crystal. The broadband conductivity spectrum of 8 mol% yttria-stabilized zirconia, a fast oxygen-ion conductor, was also acquired to quantify all conduction contributions, i.e., the interfacial, grain boundary, and bulk contribution.

1. Introduction

In oxides, the dielectric response to frequency is interpreted as dielectric dispersion, which consists of four polarization contributions: interfacial, dipole, ionic, and electronic polarizations. Figure 1 shows a schematic diagram of dielectric dispersion in oxides. The frequency to which dielectric materials are exposed is determined by the driving frequency of the application, with different relaxation frequencies spanning the range from low (kHz to MHz) to light (THz) via microwave (GHz). Interfacial polarization is derived from the charge transfer of electrons and carrier ions between grain boundaries and bulk–electrode interfaces, which leads to an enormous apparent dielectric constant, ε\text{interface}, ranging from 10^3 to 10^5, as well as to large dielectric losses. Dipole polarization of normal ferroelectrics originates in the vibrations of the ferroelectric domain walls. This polarization contributes to an ε\text{dipole} permittivity of 10^3 to 10^4 in the MHz and GHz ranges. In relaxor ferroelectrics, the fluctuations of dipoles in polar nanoregions (PNRs) yield a large polarizability. The permittivity in the THz range, i.e., in the far-infrared region, is governed by ionic polarization, which is attributed to optical phonons. In ferroelectrics, the soft phonon mode dominates the ionic polarization, giving rise to an ε\text{ionic} permittivity ranging from 10–10^3. Electronic polarization is derived from a strained electronic cloud in an electric field, giving rise to a relatively small polarizability and an ε\text{electronic} permittivity of ca. 10 in the ultraviolet region. The dipole, ionic, and electronic contributions to polarization are interpreted as intrinsic contributions in dielectrics, whereas the interfacial contribution is regarded as an extrinsic effect due to its large dielectric loss.

Quantitative analysis of these polarizations will provide an understanding of the relationship between the apparent dielectric properties and microscopic polarization behaviors of oxide dielectrics. It is necessary to measure the broadband dielectric spectrum [ε(ω) = ε'(ω) – jε''(ω)] continuously from low to THz frequencies to quantify all of the polarization contributions. Kamba, Hlinka, et al. used dielectric spectroscopy over

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a wide frequency range to study dielectric oxides, with a focus on BT-based perovskite ferroelectrics. Using newly developed microwave dielectric measurement methods, we have applied broadband spectroscopy not only to ferroelectric but also to paraelectric oxides to quantify their polarizations. We also used this technique to analyze conductive materials such as fast oxygen-ion conductors. Herein, we review our studies related to measurement of broadband permittivity and the conductivity of oxides.

2. Microwave dielectric measurement

The dielectric constant at low frequencies is often measured by impedance spectroscopy using a plate capacitor configuration. The frequency of the impedance resonance is given by \( \omega_0 = 1/\sqrt{LC} \). The resonance of a ferroelectric plate capacitor \((\varepsilon_r; \text{approx. 2 thousands})\) generally occurs at below a few MHz when the electrode area to thickness ratio, \( S/d \), is ca. \(<0.01-0.1\) m, because of a large capacitance, \( C_0 \), on the order of hundreds of pF to a few nF. We developed an evaluation method using planar electrodes to shift the circuit resonance to a higher frequency.\(^{26,27}\)

With this method, micro-sized planar electrodes with source and ground ports are formed on the surface of a dielectric specimen. The admittance between the source and ground ports is measured, and the complex permittivity of the dielectric specimen is determined using an electromagnetic field calculation. Due to the minute capacitance of the planar electrodes, the impedance resonance frequency shifts to a few GHz. In this way, the complex permittivity of the SrTiO\(_3\) (ST) single crystal (100) was determined up to 1 GHz without exhibiting any impedance resonances (Fig. 2).

A resonance method using a ring-shaped electrode has also been reported for microwave dielectric measurements.\(^{28}\) Ring and elliptical electrodes are generally used as resonator wavelength filters in the microwave circuit.\(^{29,30}\) The ring electrode’s configuration, diameter, width, and thickness were designed using an electromagnetic field calculation. A Cu ring resonator electrode was formed on the sapphire substrate by photolithographic and electroplating techniques. The dielectric specimen was then pressed onto the ring electrode, followed by measurement of the S-parameter. The complex permittivity was determined from the resonance frequency and the half-bandwidth of the resonance peak.

The microwave complex permittivity of the ST single crystal was determined up to ca. 3 GHz using a combination of the above two methods (Fig. 2).\(^{26,28}\) Dielectric relaxation was negligible for ST up to a few GHz, and it displayed an almost constant permittivity \( \varepsilon_r \) of ca. 310. ST is paraelectric and showed no dipole contribution. Thus, these methods can provide the microwave complex permittivity of specimens, even of those with a large dielectric constant.

3. Microwave measurement of ferroelectrics in a DC electric field

The microwave dielectric measurement method described in the previous section was used to analyze tunable ferroelectrics. Barium strontium titanate (Ba\(_{0.8}\)Sr\(_{0.2}\)TiO\(_3\), 0.8-BST) with diffuse phase transition (DPT) ferroelectric compositions, i.e., \( x = 0.4-0.5 \), has been widely applied to microwave tunable modules\(^{31-36}\) such as tunable capacitors, phase shifters, and tunable antenna due to its high tunability and relatively low dielectric loss. Here, tunability, \( T \), is defined as \((\varepsilon_0 - \varepsilon_\infty)/\varepsilon_0 \times 100 \) %, where \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the permittivities without and with applied DC electric fields, respectively. The apparent tunability of ferroelectrics is interpreted as a decrement in dipole, ionic, and electronic polarizations under a direct current (DC) electric field. For DPT ferroelectrics, it is known that a depression of the PNRs fluctuation contributes significantly to tunability, while the freezing of the domain wall motions yields to tunability in normal ferroelectrics.

We investigated the domain contribution to the tunability of normal ferroelectrics Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) (0.8-BST) and related compounds in our previous works.\(^{37,38}\)

The dielectric dispersion function, \( \varepsilon'(\omega) \), due to dipole polarization in ferroelectrics can be analyzed using the Kohlrausch–Williams–Watts (KWW) relationship, which is derived from expanding the Debye function as follows:\(^{39-41}\)

\[
\varepsilon'(\omega) - \varepsilon_\infty = \frac{\varepsilon_{\text{dipole}}}{\varepsilon_0} \int_0^\infty \left[-\frac{d\phi(t)}{dt}\right] \exp[-i\omega t] dt, \tag{1}
\]

where \( \varepsilon_\infty \) is the permittivity at high frequency (i.e., the combination of the ionic and electronic polarizations), \( \varepsilon_{\text{dipole}} \) is the permittivity due to dipole polarization, and \( \omega \) is the angular frequency. The decay function of the polarization, \( \phi(t) \), is estimated as follows:

\[
\phi(t) = \exp[-(t/\tau)\beta] = \exp[-(t/\tau)(1+\beta)], \tag{2}
\]

where \( \tau \) denotes the relaxation time, \( \beta \) denotes the non-Debye degree \((0 < \beta \leq 1, \beta = 1 \text{ for the Debye model}) \) and \( \gamma_0 \) is the weight coefficient for each relaxation time. The micro-sized planar electrode method was used for the analysis, and the complex permittivities of 0.8-BSTs under a DC electric field were determined.

Figure 3 shows the dependence of the microwave complex permittivity in a DC field for 0.8-BST having a ferroelectric...
domain width of ca. 160 nm;37) dielectric spectra are shown for applied DC field intensities of 0, 2.7, 4.0, 5.3 and 6.7 kV/cm. The large dielectric relaxations, over the range of hundreds of MHz to a few GHz, were attributed to dipole polarization originating from domain wall motions. The dipole contribution and that of the combination of the ionic and electronic polarizations to total tunability, \( T_{\text{total}} \), were quantified. Figure 4 shows the calculated \( T \) values for \( T_{\text{total}} \), \( T_{\text{dipole}} \), and \( T_{\text{ionic+el.}} \) as a function of domain width at the maximum applied field strength \( (E = 6.7 \text{ kV/cm}) \).37) The smaller domains, i.e., higher domain densities, resulted in a greater apparent \( T_{\text{total}} \). \( T_{\text{dipole}} \) increased significantly with decreasing domain size, while \( T_{\text{ionic+el.}} \) was less dependent on domain size. In fact, the permittivity due to the domains, \( \varepsilon_{\text{dipole}} \), governs the total permittivity, \( \varepsilon_{\text{total}} \), without an applied DC bias, regardless of the domain size. The \( \varepsilon_{\text{dipole}} \) increased significantly with decreasing domain size, a change attributed to an increase in domain wall density.37) A higher domain wall density therefore induced larger dipole polarization, leading to greater tunability, due to freezing of the larger number of domain vibrations by a DC field. Thus, the density of the domain wall motion is a dominant factor in determining the apparent tunability, whereas the other contributions by the ionic and electronic polarizations are comparably small for BST.

4. Broadband dielectric spectroscopy of dielectrics

The broadband dielectric function for paraelectric oxides is determined by phonon dispersions. The four-parameter semi-quantum (FPSQ) model can be used to describe the phonon dispersion in paraelectrics as follows:42)

\[
\varepsilon^*(\omega) = \varepsilon_\infty \prod_{j=1}^n \frac{\omega_{\text{LO}}^2 - \omega^2 \pm i\gamma_{\text{LO}}\omega}{\omega_{\text{TO}}^2 - \omega^2 \pm i\gamma_{\text{TO}}\omega},
\]

where \( \varepsilon_{\text{electronic}} \) is the permittivity due to the electronic polarization, \( n \) is the number of optical phonons, \( \omega_{\text{LO}} \) and \( \omega_{\text{TO}} \) are the angular frequencies of the j-th LO and TO modes, respectively, and \( \gamma_{\text{LO}} \) and \( \gamma_{\text{TO}} \) are the damping factors of the j-th LO and TO modes, respectively. The infrared (IR) reflectivity \( R(\omega) \) is estimated by the following Fresnel equation related to \( \varepsilon^* \):

\[
R(\omega) = \frac{\sqrt{\varepsilon^*(\omega) - 1}}{\sqrt{\varepsilon^*(\omega) + 1}}.
\]

All FPSQ parameters were optimized by non-linear least-square fitting of the measured and calculated IR reflectivity and dielectric data.

Figure 5 shows the broadband dielectric spectrum from 10 kHz to 100 THz of the ST single crystal (100).26) The contributions of ionic and electronic polarizations to the DC permittivity were determined. Ionic polarization clearly dominated the total permittivity of the ST single crystal compared with electronic polarization. A sharp resonance due to phonon dispersion was observed at ca. 2.7 THz. This resonance was assigned to the soft phonon (Slater) mode, which is the slowest vibrational mode governing the magnitude of the ionic polarization of ST.

In ferroelectrics, the broadband dielectric function is obtained by combining dipole relaxation and phonon dispersion; the FPSQ model [Eq. (3)] was used to estimate \( \varepsilon_\infty \) in Eq. (1). Figure 6 shows the determined broadband dielectric spectrum of the ferroelectric BT ceramic.43) The large dielectric relaxation in hundreds of MHz to a few GHz was attributed to dipole polarization, i.e., domain motions. The analysis simultaneously quantified all the ferroelectric polarizations, i.e., \( \varepsilon_{\text{dipole}}, \varepsilon_{\text{ionic}}, \) and \( \varepsilon_{\text{electronic}} \). We have applied this technique to a variety of dielectric and ferroelectric compounds to quantitatively discuss their polarization behaviors.43-47)

5. Broadband conductivity spectroscopy of oxygen-ion conductors

The conductivity of polycrystalline ion conductors is determined by four contributions: 1) conduction to the electrolyte-electrode interface;1,48) 2) conduction at the grain boundaries;1,48) 3) conduction in the intragrain ion hopping, which is the primary contribution;1,48,49) and 4) ionic displacement by optical phonons.50-52) The magnitude of these four conductions determines the total apparent conductivity. An electrolyte-electrode interfacial effect is observed at very low (kHz) frequencies,
whereas the grain boundary contribution remains up in the MHz range. Intragrain ion migration contributes over broadband frequencies ranging from low frequencies to GHz frequencies, while lattice vibrations remain in the THz region. Ion conductor oxides are utilized at various driving frequencies of the devices. Quantity to the above four conduction contributions determines the rate-controlling resistance to ion migration at any frequency. Broadband conductivity spectroscopy from low to THz was therefore performed to quantify all the conductivity contributions for various ion-conductive materials.\(^5\)

The equivalent circuit for ion conductor ceramics represented in the inset of Fig. 7 consists of the conductance, \(G\), and capacitance, \(C\), for the three contributions. The subscripts ‘interface’ and ‘g.b.’ indicate the electrolyte–electrode interfacial and grain boundary conductions, respectively. Intragrain ion migration is described by the universal dielectric response (UDR).\(^7\) The subscripts ‘UDR + phonon’ denote the combination of the UDR and optical phonons. The bulk complex conductivity, \(\sigma = \sigma’(\omega) + j\sigma”(\omega)\), is described by Eqs. (5) and (6) using the UDR relationship:\(^3\)

\[
\sigma’(\omega) = \sigma_{dc} + \sigma_0 \omega^{s} \n\]
\[
\sigma(\omega) = \tan(\frac{\pi}{2})\sigma_0 \omega^{s} + \omega \varepsilon_\infty \varepsilon_0 \n\]

where \(\sigma_{dc}\) denotes the DC intragrain conductivity and \(\sigma_0\) is a temperature-dependent coefficient. The conductivity increases as a power of frequency with the exponent \(s (s < 1)\). Here, \(\varepsilon_\infty\) is the permittivity of free space and \(\varepsilon_0\) is the high-frequency permittivity due to the optical phonons. The permittivity estimated using the FPSQ model [Eq. (3)] was assigned to \(\varepsilon_\infty\) in Eq. (6). The estimated impedance of the equivalent circuit, \(Z(\omega)\), was then calculated for comparison with the measured impedance.

The broadband conductivity from 0.1 Hz to 100 THz at 600°C of \(8\) mol% yttria-stabilized zirconia (\(8\)YSZ), a fast oxygen-ion conductor, is shown in Fig. 7; circles and rectangles denote the measured conductivities and the conductivities determined by the THz reflectivities, respectively, and the dashed lines are the fitted data. Notably, a depression in \(\sigma’\) was observed at the lowest frequencies (0.1 to 1 kHz). This conductivity depression is responsible for the interfacial and grain boundary resistances. In fact, two broad relaxation peaks attributed to these extrinsic effects were confirmed in the \(\sigma”\) spectra. At above 1 MHz, the total conductivity, \(\sigma_{\text{total}}\), is mostly governed by the contribution of the bulk conductivity, i.e., \(\sigma’_{\text{UDR+phonon}}\). The broadband spectroscopy technique can thus be applied to conductive materials; we have used it to quantify all the conductivity contributions in oxygen-ion conductors.

6. Conclusions

Our recent research related to broadband spectroscopy of dielectrics, ferroelectrics and oxygen-ion conductors was reviewed. Two evaluation techniques, namely the micro-sized planar electrode method and ring resonator method, were developed to determine the microwave dielectric properties of oxides having a large permittivity. The complex permittivity of an ST single crystal having an \(\varepsilon_\infty\) of ca. 310 was successfully determined up to a few GHz. The technique was applied to 0.8-BST tunable ferroelectric to investigate the domain contribution to tunability. A domain size effect was observed for 0.8-BST; a higher domain wall density provided larger dipole polarization, leading to greater tunability.

Broadband dielectric spectra were measured from kHz to THz. The FPSQ model describing the phonon dispersion was used as the broadband dielectric function for paraelectrics, while a combination of the KWW and FPSQ models was used for ferroelectrics. The analyses simultaneously quantified the dipole, ionic, and electronic contributions for the BT ceramic as well as for the ST single crystal. Broadband spectroscopy was also used to characterize \(8\)YSZ, an oxygen-ion conductor, leading to quantification of the interface, grain boundary, and bulk contributions, i.e., the combination of intragrain ion hopping and phonons. These results and those from our previous research indicate that broadband spectroscopy is a powerful tool that may be useful for resolving the microscopic dielectric polarization and ion conduction behavior of oxides.

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