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Journal of the European Ceramic Society 26 (2006) 1807–1810

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THz region dielectric properties of barium titanate fine particles using infrared reflection method

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Abstract

The THz region dielectric properties of barium titanate ($BaTiO_3$) fine particles were measured using the infrared (IR) reflection method. Prior to this measurement, to minimize the scattering light caused by surface roughness, the preparation of the dense 3D colloidal sphere arrays (colloidal crystals) with a flat surface was tried. First, the $BaTiO_3$ fine particles were well dispersed into diethylene glycol as an organic solvent, and this $BaTiO_3$ slurry was dried very slowly at 80 °C. Finally, the dense $BaTiO_3$ colloidal crystals were successfully prepared. The IR reflection method was performed using these dense $BaTiO_3$ colloidal crystals, and their IR reflection spectra were measured from 100 to 1200 cm^{-1}. As a result, by the use of the dense $BaTiO_3$ colloidal crystals, the high intensity reflection spectra of the $BaTiO_3$ fine particles were successfully obtained. The spectra were analyzed using a four-parameter semi-quantum (FPSQ) model, and finally, the THz region dielectric properties were estimated for the $BaTiO_3$ fine particles.

Keywords: Suspensions; Spectroscopy; Dielectric properties; $BaTiO_3$; Capacitors

1. Introduction

Ferroelectric $BaTiO_3$ fine particles have been used as raw materials for electronic devices such as multilayered ceramic capacitors (MLCC). With the miniaturization of electronic devices, the downsizing of MLCC has been developed. As a result, it is expected that the thickness of dielectric layers in MLCC will become less than 0.5 μm. Consequently, the particle size of the $BaTiO_3$ raw materials will decrease to a few 10 nm. However, in ferroelectric fine particles, it was known that ferroelectricity decreases with decreasing particle and grain sizes, and disappears below certain critical sizes; this is called the "size effect" in ferroelectrics.[1–7] Therefore, the size effect in the $BaTiO_3$ is one of the most important phenomena for the industry and science.

To date, some researchers investigated the size effect of $BaTiO_3$ using particles.[3,4,6] Recently, Wada et al. reported a unique particle size dependence that dielectric maximum of 15,000 was observed at 68 nm.[8] This result suggested that the high dielectric constant of 15,000 should be originated from a change of dielectric polarization mechanism, i.e., (a) an appearance of new dipolar polarization at microwave region or (b) a change of the optic phonon behavior at THz region by downsizing of the $BaTiO_3$ particles. Therefore, it is very important to investigate the dielectric properties at THz region. However, there was no report to measure THz region dielectric properties for the fine particles.

In this study, the THz region dielectric measurement of the $BaTiO_3$ particles was tried by using an IR reflection method. For this measurement, high reflection intensity from the $BaTiO_3$ particles must be required. Thus, a new measurement method using the particles was proposed.

2. Experimental procedure

The commercial $BaTiO_3$ powder was used in this study. A hydrothermal $BaTiO_3$ powder with a particle size of 500 nm (Sakai Chemical Industry Co., BT-05) was chosen because of the dielectric constant of around 3000.[8] Using the BT-05 particles, two kinds of samples were prepared. One is a BT-05 powder pellet compacted using a cold isotropic pressing (CIP), and another is a dense BT-05 colloidal crystal prepared from a BT-05 slurry as follows: first, the BT-05 powder was dried

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doi:10.1016/j.jeurceramsoc.2005.09.091

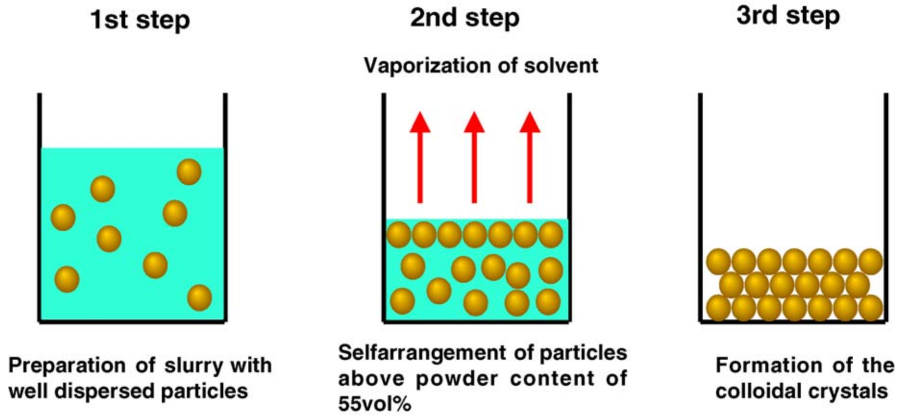

Fig. 1. Schematic concept for preparation of the dense colloidal crystals.

at 180 °C for 24 h in a drying oven, and then mixed well with diethylene glycol $(CH_2CH_2OH)_2O$ (Kanto Chemical Co., Cica-reagent, > 99.0 wt.%) using ball mill for 24 h. Finally, a BT-05 slurry with BT-05 content of 27 wt.% was prepared. The BT-05 slurry was put in a beaker and kept at 80 °C for almost 2 weeks in the drying oven. Through this drying procedure, the dense BT-05 colloidal crystals were prepared as shown in Fig. 1. Keeping of the BT-05 slurry at 80 °C resulted in vaporization of diethylene glycol, and the BT-05 powder content increased with decreasing slurry volume. When the BT-05 powder content was higher than 55 vol%, the BT-05 particles were self-arranged by a transverse capillary force. Finally, this self-arrangement of the BT-05 particles resulted in a formation of the dense BT-05 colloidal crystals.

IR reflection spectra from 100 to 1200 cm^{-1} were measured at 25 °C by using two FTIR spectrometers, i.e., FARIS-1 (JASCO Co., 100–700 cm^{-1}) and FTIR-8600PC (Shimazu, 400–1200 cm^{-1}). As the measurement condition, scanning number of 256 and resolution of 0.5 cm^{-1} were used. Especially, the IR reflection measurement using FARIS-1 was performed in vacuum to neglect the absorption peaks of H_2O in air. A special attachment for a reflection measurement was used as shown in Fig. 2, and the incident and reflection angles to the sample surface were fixed at 11°. Aluminum evaporated film on the glass was used as a reference. These two spectra were connected at 650 cm^{-1}.

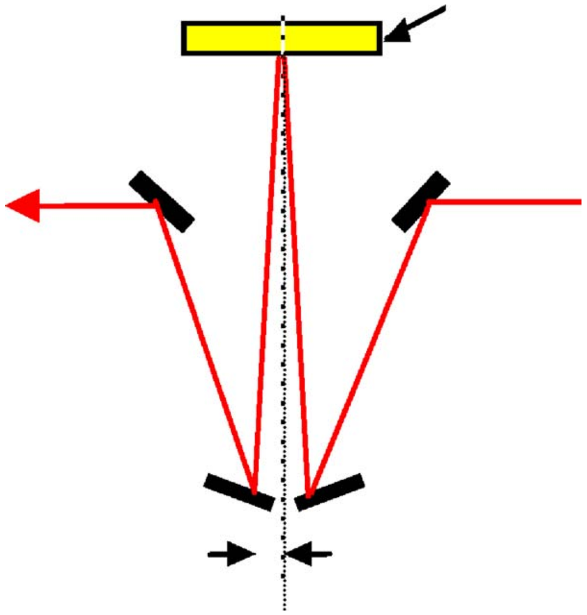

Fig. 2. Schematic sample geometry for the IR reflection measurement.

3. Results and discussion

3.1. Measurement of IR reflection spectra

First, IR reflection spectra were measured using the BT-05 powder pellets, but a reflection intensity using the pellets was too low, and around 1/10 of the reflection intensity from the reference. Thus, the reflection spectra were very noisy and it was impossible to use them as the spectra for a phonon analysis. The surface observation of the BT-05 powder pellets using a laser microscope revealed that this surface was extremely rough. This means that most of the incident light was scattered on the rough surface, and the reflection light became very weak. Thus, to obtain the almost same reflection intensity as that of the incident light, a very flat surface such as mirror-finished surface must be required. For the powder, it is very difficult to make a sample with a very flat surface, but if the particles with much smaller sizes than wavelength of the IR light (>8 μm) can be arranged densely and periodically, it is possible to prepare the very flat surface. In general, it is well-known that the colloidal crystals have a very flat surface.[9] Thus, in this study, preparation of the dense colloidal BT-05 crystals was tried.

To prepare well-dispersed BT-05 slurry, various organic liquids such as, ethanol, 1-propanol and diethylene glycol were investigated as solvents. As a result, it was confirmed that BT-05 particles were well dispersed in 1-propanol and diethylene glycol. Moreover, to control a vaporization rate of organic solvents, temperature of the drying oven was changed from 50 to 90 °C. As a result, for both 1-propanol and diethylene glycol-based BT-05 slurries, it was clarified that the most flat surface was obtained at 80 °C. Moreover, a surface derived from diethylene glycol-based BT-05 slurry was very flat without crack while that from 1-propanol-based BT-05 slurry was also flat but with fine

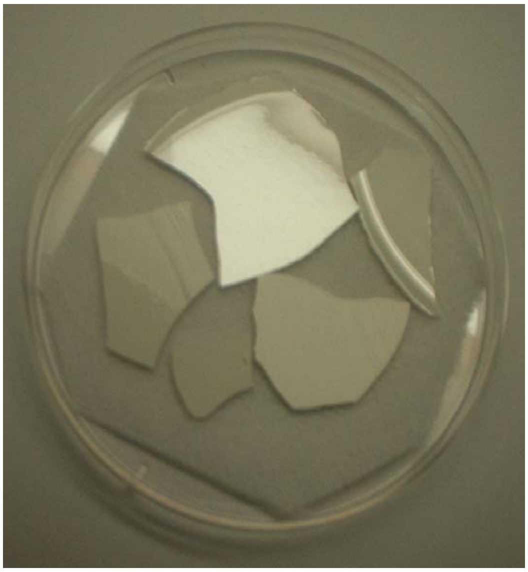

Fig. 3. A photograph of the dense BT-05 colloidal crystals.

cracks. Thus, in this study, the diethylene glycol-based BT-05 slurry was used for the preparation of the dense BT-05 colloidal crystals. Fig. 3 shows a photograph of the dense BT-05 colloidal crystals prepared at 80 °C for 2 weeks. The surface was shining like a mirror. The surface observation using the laser microscope exhibited a very flat surface with an average surface roughness (RMS) of 210 nm. The wavelength used for IR reflection measurement was over 8 μm, and RMS of 210 nm was enough small to regard surface as almost flat. In fact, the integrated IR reflection intensity from this BT-05 colloidal crystal was almost the same as that from the reference in the range below 700 cm^{-1}. Fig. 4 shows the IR reflection spectrum of the colloidal BT-05 crystal measure at 25 °C. This reflection spectrum was almost consistent with that measured using [1 0 0]-oriented $BaTiO_3$ single crystal plate.[10] Therefore, this study revealed that using the dense colloidal crystal, the IR reflection spectra for powder can be obtained with the same quality as the single crystal data.

3.2. Phonon fitting using a FPSQ model

The crystal structure of $BaTiO_3$ is tetragonal with $P4mm$ symmetry at 25 °C. Thus, their optic phonon modes are $3A_1 + B_1 + 4E$, and in these modes, only $3A_1 + 4E$ modes are infrared-active modes.[11] Moreover, three A_1 optic modes are the lattice vibration along c-axis while four E modes are the lattice vibration along a-axis. For the phonon analysis of the BT-05 colloidal crystals, we must consider the random crystallographic orientations because of a use of BT-05 sphere powder. The random orientations suggested that there were a lot of reflections from crystallographic directions except for three principle axes (two a-axis and one c-axis), which means that to analyze these reflections, we must consider the oblique phonons[12] dependent on the angles between the incident light and three principle axis. However, considering the oblique phonons makes a model for the phonon analysis too complicated, and it is very difficult to analyze IR reflection spectrum using this model. Thus, in this study, to simplify an analysis model, the following significant assumption was induced, i.e., all the reflection lights can be regarded as the summation of the reflections from a-axis and c-axis, and a ratio of reflection light from a-axis on that from c-axis is 2:1. Therefore, total reflectance (R) in Fig. 4 can be expressed using the reflectance from a-axis (R_a) and that from c-axis (R_c) as shown in the following equation,

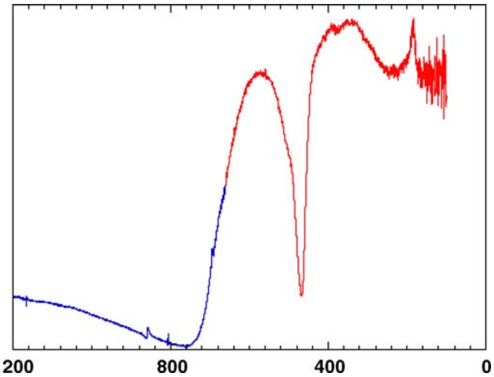

Fig. 4. IR reflection spectrum of the BT-05 colloidal crystal measured at 25 °C.

$$R(\omega) = \frac{2}{3}R_a(\omega) + \frac{1}{3}R_c(\omega) \tag{1}$$

Here, ω means frequency of the IR light. Both R_a and R_c can be calculated using complex dielectric constants along a-axis (ε_a) and c-axis (ε_c), and the following Fresnel formulas,[11]

$$R_a(\omega) = \left|\frac{\sqrt{\varepsilon_a(\omega)} - 1}{\sqrt{\varepsilon_a(\omega)} + 1}\right|^2, \tag{2}$$

$$R_c(\omega) = \left|\frac{\sqrt{\varepsilon_c(\omega)} - 1}{\sqrt{\varepsilon_c(\omega)} + 1}\right|^2. \tag{3}$$

On the other hand, each ε_a and ε_c can be calculated using a modified damping oscillator model. If $BaTiO_3$ is a perfect ionic crystal, complex dielectric constant must be calculated using a classical harmonic damping oscillator model, i.e., in one damping oscillator, a longitudinal optic mode should be related to a transverse optic mode.[11] However, $BaTiO_3$ exhibits both ionic and covalent bonds, which suggested that there is no relationship between longitudinal and transverse optic modes in one damping oscillator. The FPSQ model was proposed for the phonon analysis of the crystals with covalent bonds.[13] Thus, each ε_a and ε_c can be calculated using the FPSQ model as follows,

$$\varepsilon_a(\omega) = \varepsilon_{a\infty} \prod_{j=1}^{4} \frac{\omega_{j\mathrm{LO}}^2 - \omega^2 + i\omega\gamma_{j\mathrm{LO}}}{\omega_{j\mathrm{TO}}^2 - \omega^2 + i\omega\gamma_{j\mathrm{TO}}}, \tag{4}$$

$$\varepsilon_c(\omega) = \varepsilon_{c\infty} \prod_{j=1}^{3} \frac{\omega_{jLO}^2 - \omega^2 + i\omega\gamma_{jLO}}{\omega_{jTO}^2 - \omega^2 + i\omega\gamma_{jTO}}. \tag{5}$$

Here, each $\varepsilon_{a\infty}$ and $\varepsilon_{c\infty}$ is complex dielectric constant by only electric polarization along a-axis and c-axis, respectively. Moreover, each $\omega_{j\mathrm{LO}}$ and $\omega_{j\mathrm{TO}}$ is a resonance frequency of the j-th longitudinal and transverse optic mode, respectively, while

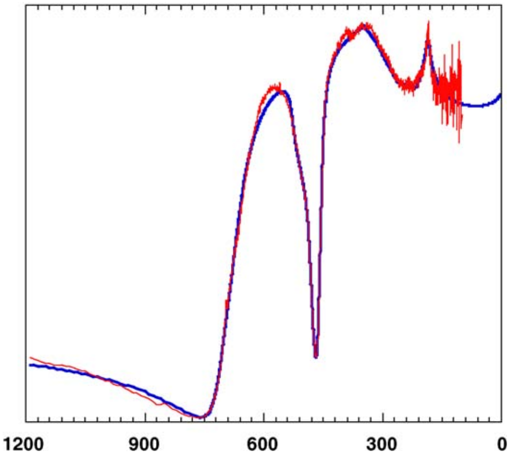

Fig. 5. Fitting result using the FPSQ model for IR reflection spectrum of the BT-05 colloidal crystal measured at 25 °C.

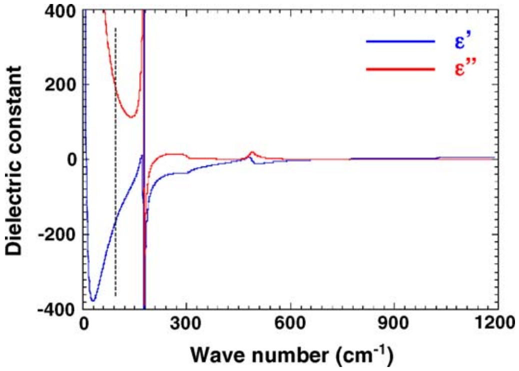

Fig. 6. THz region complex dielectric constants of the BT-05 colloidal crystal measured at 25 °C.

$\gamma_{j\mathrm{LO}}$ and $\gamma_{j\mathrm{TO}}$ is a damping factor of the *j*-th longitudinal and transverse optic mode, respectively.

First, as 30 parameters required for the above calculation, the parameters reported for the $BaTiO_3$ single crystal were used.[10] For the fitting of the IR reflection spectrum (Fig. 4), the non-linear least-squares method was used. Fig. 5 shows the fitting result for the BT-05 colloidal crystals. The calculated reflectance using the FPSQ model was almost consistent with the experimental result. Using the phonon parameters determined in this fitting process and the relation of $\varepsilon = (2/3) \times \varepsilon_a + (1/3) \times \varepsilon_c$, a wavenumber dependence of complex dielectric constant for the BT-05 colloidal crystals was also calculated as shown in Fig. 6. This result suggested that for the $BaTiO_3$ particles, the contribution of three optic modes over 180 cm^{-1} to a GHz region dielectric constant is small in comparison with the soft mode contribution while the dielectric constant of $BaTiO_3$ particles below THz region is determined mostly by the soft optic mode below 180 cm^{-1}.

4. Conclusions

This study revealed that using the dense BT-05 colloidal crystal, high-quality IR reflection spectra for powder was obtained for the first time. Using the modified FPSQ model for the BT-05 colloidal crystal with random crystallographic orientations, 30 phonon parameters were determined, and finally, THz region dielectric properties for the $BaTiO_3$ particles were estimated. Moreover, it was also revealed that the dielectric constant of the $BaTiO_3$ particles below THz region was determined by only the soft optic mode. To analyze the phonon behavior of the soft optic mode, IR reflection spectra must be measured down to 5 cm^{-1} from present 100 cm^{-1}. Much harder work will be required for this measurement in the future.

Acknowledgements

We would like to thank Mr. K. Abe of Sakai Chemical Industry Co., Ltd. for providing high purity BT-05 powders. This study was partially supported by (1) a Grant-in-Aid for Scientific Research (**15360341**) from the Ministry of Education, Science, Sports and Culture, Japan and (2) the Ookura Kazuchika Memorial foundation.

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