

# Dielectric Properties of Silicone Oil Containing Heated Hydrothermal Barium Titanate Powder as Dispersed Phase

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Fluids were prepared by mixing silicone oils with hydrothermal fine BaTiO<sub>3</sub> powders, which were heated at various temperatures. The crystal system of the BaTiO<sub>3</sub> powder transforms from cubic to tetragonal when the powders are heated above 750 °C with release of CO<sub>2</sub>. Electrorheological effects of the fluids show the maximum value when the powders are heated around 800 °C. Dielectric properties of the fluids were measured. The relative permittivity and the dissipation factors also have the maximum values when the powder are heated around 800 °C. We found that the key factors relating to the higher electrorheological effects for disperse systems like our fluids are the dielectric properties of the fluids rather than those of the powder as dispersed phases.

Key words: electrorheological effect, BaTiO<sub>3</sub>, cubic-tetragonal transition, ferroelectricity

## 1. INTRODUCTION

Apparent viscosities of some fluids increase when electric field is applied, and they decrease to their initial viscosities, when the application of electric field is turned off. This phenomenon is called electrorheological effect. The electrorheological fluids are examined to be **applied to transmissions with no gears and dumpers with variable decay constants** [1].

The electrorheological fluids are often prepared by dispersing inorganic powders in electrically insulating liquids [2]. Particles polarize under electric field and attract electrostatically each other so that arrays of the particles are formed in such fluids. The arrays act as resistance to flow and then the electrorheological effect appears. Therefore, the powders having large induced polarization, *e.g.*, ferroelectric fine powders are favorable to be selected to prepare electrorheological fluids according to the mechanism of the electrorheological effect. Fine barium titanate (BaTiO<sub>3</sub>) powder with particle size less than 0.1 μm is prepared industrially by hydrothermal process. However the fine BaTiO<sub>3</sub> powder has cubic symmetry [3], and consequently has no ferroelectricity. The powder has tetragonal symmetry and ferroelectricity, if it is heated above 800 °C [4]. We prepared several fluids using the hydrothermal BaTiO<sub>3</sub> powder heated at various temperatures up to 1200 °C, and measured the

electrorheological effect of the fluids under DC electric field [5]. The electrorheological effect was found to have the maximum value when the powder was heated around 770 °C. The result is against our expectations.

In the present study, we characterized fine BaTiO<sub>3</sub> powders heated at various temperatures and measured the electrorheological effects of the fluids prepared using the powders under AC electric fields. We also measured the relative permittivities and the dissipation factors of the fluids and investigated the electrorheological effects of the fluids in view of the dielectric properties of them.

## 2. EXPERIMENTAL

We used cubic-BaTiO<sub>3</sub> fine powder (BT-01, average particle size: 0.1 μm), which was prepared through hydrothermal process by Sakai Chemical Industry. Weight loss of the powder through heating was measured with a thermobalance (Rigaku, TG8110). The powder was heated at various temperatures for 2 h in air. IR spectra of as-received and the heated powders were measured by diffuse reflectance method with a FT-IR spectrometer (Impact 410, Nicolet). Crystalline phase of as-received and heated powders was determined with an X-ray diffractometer (Rigaku, RINT2500VHF). Densities of these powders were measured with a gas pycnometer (Micromeritics, Accpvc 1330) using He.

We prepared fluids by mixing the BaTiO<sub>3</sub> powders, which was dried at 200 °C for 2 h previously, with silicone oil (Toshiba Silicone, TSF451-500) using a planetary ball mill (Fritch, Pulverisette 5). Volume fraction of the powder is fixed to be 10 % by considering the measured densities of the powders. Dispersion of the BaTiO<sub>3</sub> particles in the silicone oil was confirmed using an optical microscope. Electrorheological effects of the fluids were measured at 30 °C under AC (1 kHz) electric field of 2 kVmm<sup>-1</sup> using a rheometer (Haake, VT500). We defined the increase in yield stress under application of the electric field as the electrorheological effect. Dielectric properties of the fluids were measured using an impedance analyzer (Hewlett Packard, 4194A) equipped with a test fixture (Hewlett Packard, 16452A) in the frequency range of 100 Hz ~ 15 MHz and in the temperature range of 40 °C ~ 150 °C using an oil bath.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the weight loss of as-received BaTiO<sub>3</sub> powder through heating in air. Weight losses of -1.0% and -0.7% are found in the temperature range of 210 °C ~ 400 °C and of 600 °C ~ 800 °C, respectively.

Figure 2 shows the IR spectra of as-received and the heated BaTiO<sub>3</sub> powders. Absorption peaks are found at 1450 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> for as-received powder. The former peak disappears, while the latter peak remains for the powders heated above 800 °C. Hennings *et al.* [6] also reported absorption peaks at 1440 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> for hydrothermally prepared BaTiO<sub>3</sub> powder

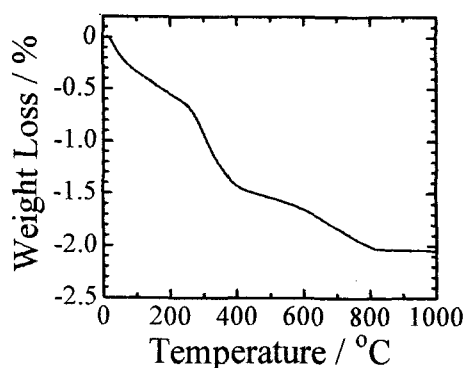


Figure 1 Weight loss of as-received hydrothermal BaTiO<sub>3</sub> powder through heating in air.

heated at various temperatures up to 400 °C. They attributed the former peak and the latter peak to the absorptions due to CO<sub>3</sub> group of BaCO<sub>3</sub> and due to OH group chemically absorbed in BaTiO<sub>3</sub>, respectively. The peaks at 1450 cm<sup>-1</sup> in the present study are also considered to be attributed to the absorption due to CO<sub>3</sub> group of BaCO<sub>3</sub>, so that as-received BaTiO<sub>3</sub> powder contains slight amount of BaCO<sub>3</sub> and releases CO<sub>2</sub> by heating above 800 °C. The peaks at 1640 cm<sup>-1</sup> are considered to be attributed to the absorption due to H<sub>2</sub>O re-absorbed during cooling down after the heating.

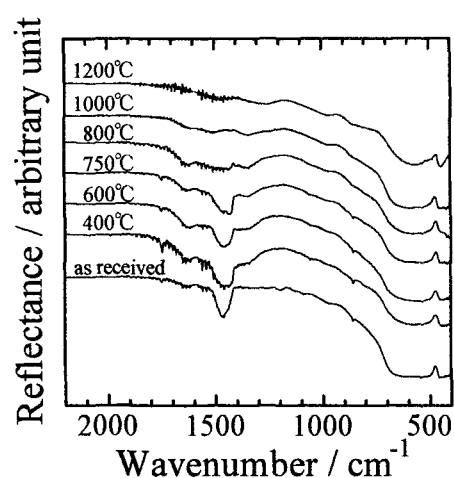


Figure 2 IR spectra of as-received BaTiO<sub>3</sub> powder and the powders heated at various temperatures.

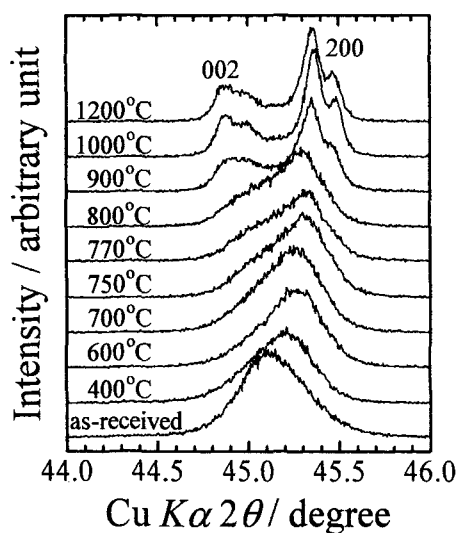


Figure 3 XRD profiles of as-received BaTiO<sub>3</sub> powder and the powders heated at various temperatures.

Comparing the result of TG with that of IR, the decrease in weight from 600 °C to 800 °C is considered to be due to the release of CO<sub>2</sub>.

X-ray diffraction profiles of as-received BaTiO<sub>3</sub> powder and heated powders are shown in Figure 3. Crystal system of as-received powder is cubic. It changes from cubic symmetry to tetragonal one, as heating temperature increases above 750 °C. The heating temperature at which the phase transition occurs as shown in the XRD profiles corresponds well to the temperature at which CO<sub>2</sub> is released as shown in IR spectra. It seems that the phase transition from cubic symmetry to tetragonal one occurs with the release of CO<sub>2</sub>.

Fluids were prepared by mixing the BaTiO<sub>3</sub> powders having the above characteristics and silicone oil. It is expected that electrorheological effect of the fluid increases with the heating temperature, especially, it increases abruptly around the heating temperature at which the BaTiO<sub>3</sub> powder shows the phase transformation from cubic to tetragonal, because relative permittivity of the BaTiO<sub>3</sub> powder is considered to increase abruptly around the temperature. Figure 4 shows the relation between electrorheological effects,

measured under DC [5] and AC electric field, and heating temperature of the BaTiO<sub>3</sub> powder. The electrorheological effects measured under AC electric field are much smaller than those measured under DC electric field. However, the former and the latter electrorheological effects have the maximum values around the heating temperatures of 770 °C and 700 °C, respectively. These two temperatures agree well each other. The heating temperature dependences of the

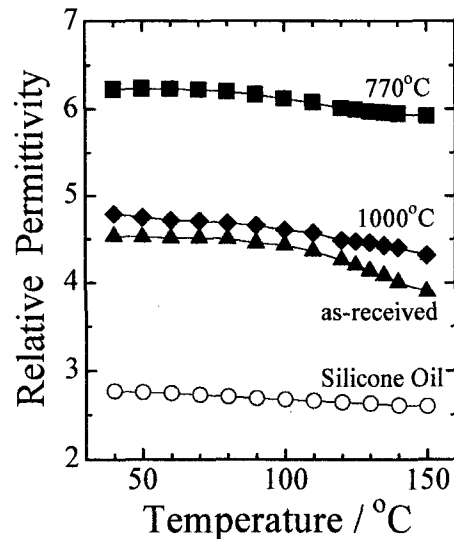


Figure 5 A typical example of temperature dependence of relative permittivity of silicone oil and the fluids prepared in the present study measured under 1 kHz.

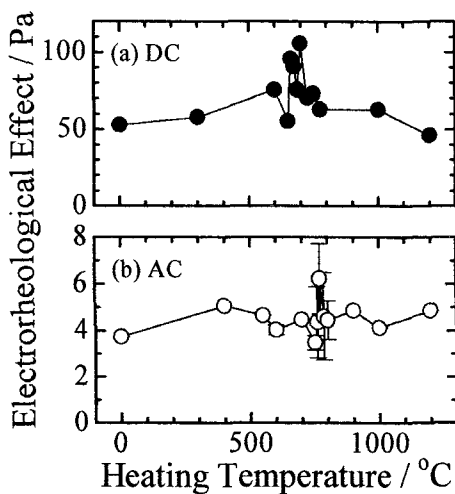


Figure 4 Electrorheological effects of the fluids prepared using as-received BaTiO<sub>3</sub> powder and the powders heated at various temperatures measured at 30 °C under (a) DC electric field of 2 kVmm<sup>-1</sup> at shear rate of 237.5 s<sup>-1</sup> [5] and (b) AC electric field of 2 kVmm<sup>-1</sup> (peak-to-peak voltage, 1 kHz) at shear rate of 265.5 s<sup>-1</sup>.

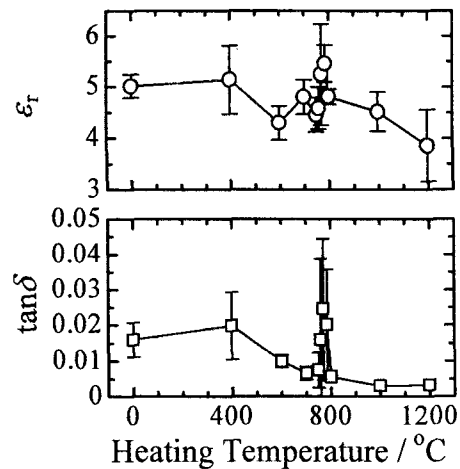


Figure 6 Relative permittivity ( $\epsilon_r$ ) and dissipation factor ( $\tan\delta$ ) of the fluids prepared in the present study. These are measured at 41°C and 1 kHz.

electrorheological effects, in any case, are against our expectation.

Temperature dependences of relative permittivity measured at 1 kHz for the several fluids are shown in Figure 5. It is confirmed by XRD study that tetragonal BaTiO<sub>3</sub> exists in the powders heated above 800 °C. Therefore, it is considered that these powders show ferroelectricity. However, the relative permittivity of the fluid using BaTiO<sub>3</sub> powder heated at 770 °C is the largest among all fluids in the whole temperature range. No peaks but slight inflection points are found around Curie point (130 °C) of tetragonal BaTiO<sub>3</sub> in the temperature dependences of relative permittivities for fluids using the powders heated at 770 °C and 1000 °C. Therefore, these results show that the dielectricities of fluids using BaTiO<sub>3</sub> powder do not reflect that of bulk BaTiO<sub>3</sub>.

Heating temperature dependences of relative permittivity ( $\epsilon_r$ ) and dissipation factor ( $\tan \delta$ ) are shown in Figure 6. The  $\epsilon_r$  and the  $\tan \delta$  show the maximum values around the heating temperature of 800 °C. The temperature agrees well with the temperature at which as-received BaTiO<sub>3</sub> transforms from cubic to tetragonal by the heating. The fluid that contains BaTiO<sub>3</sub> powder being on the way to transform from cubic to tetragonal shows peculiarly large  $\epsilon_r$ , consequently, the electrorheological effect of the fluid also shows the maximum value when the BaTiO<sub>3</sub> powder heated around 800 °C is used.

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