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Simultaneous measurements of dielectric constant and heat flux on the phase transition of a single crystalline $BaTiO_3$

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Abstract

We have developed an apparatus, which can measure heat flux and dielectric constant simultaneously. The heat flux and the dielectric constant of a single crystalline $BaTiO_3$ were simultaneously measured with a temperature resolution of milli-Kelvin to study the detailed behavior of the phase transition. The anomalies are observed between 400 and 402 K both in the heat flux and the dielectric measurements with a close correlation between the heat flux and the dielectric constant. A slow increase and a sudden jump in the dielectric constant were observed in the heating process and at least five thermal anomalies were observed between 400.3 and 401.2 K in the cooling process. The unstable state was observed in the vicinity of Curie temperature keeping at a constant temperature both in the heating and cooling process. The hysteretic behaviors of the phase transition and the unstable state were discussed in terms of two-phase domains in the transition.

Keywords: $BaTiO_3$; Dielectric constant; Heat flux; Hysteresis; Metastable state

1. Introduction

$BaTiO_3$ is known to have a ferroelectric–paraelectric transition at about 400 K with a structural change from tetragonal to cubic symmetry [1–4]. The phase transition of $BaTiO_3$ has been extensively studied in the viewpoint of structural properties [1,3,5], ferroelectric properties [1,4,6–9], thermal properties [10,11], and theoretical interpretations [12–17]. Since the phase transition of $BaTiO_3$ has a character of the first order, the hysteretic behaviors of the transition of $BaTiO_3$ have been detected in the lattice constant [1–3] and ferroelectric properties [4,6–9].

In our previous study [2,11], it was shown from the simultaneous measurements of thermal expansion and heat flux that the phase transition occurred in a single stage in the heating process, but it occurred at several stages at very small temperature intervals in the cooling process. It was also shown that the transition temperature at the heating rate of $0.2\,\mathrm{mK\,s^{-1}}$ was 1.35 or 2.75 K higher than that in the cooling run depending on the direction measured for the single crystalline sample. These hysteretic behaviors are considered to be related to the existence of two-phase mixtures of the low- and high-temperature phases with various shapes of domains [2,11]. In order to investigate such peculiar phenomena, it is desirable to obtain different kinds of information at the same time. We have chosen to make the simultaneous measurement of the dielectric constant and the heat flux for that purpose. Since the phase transition is accompanied by the change from a ferroelectric state to a paraelectric state, the measurement of the dielectric constant is suitable to understand the whole nature of the transition, as has been studied by many investigators [1,6,18–20]. Since the heat flux is a thermal property proportional to a heat capacity, it is suitable to understand the local nature of the transition. It is also desirable to measure the transitional behaviors by changing the heating or cooling rate systematically, since the hysteretic behaviors of the transition are considered to be time-dependent.

In this study we developed a high sensitivity equipment for measuring the dielectric constant and the heat flux simultaneously and studied the phase transition of a single crystalline $BaTiO_3$ near 400 K both in the heating and cooling process.

2. Experimental

The schematic drawing of the high sensitivity apparatus for the simultaneous measurement of the dielectric constant and the

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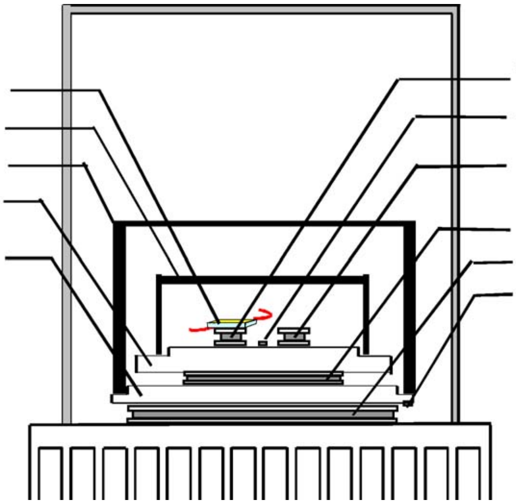

Fig. 1. The schematic drawing of the apparatus: S, sample; TS1-2, Pt resistance thermometer; TM1-4, semiconducting thermoelectric module; B1-2, copper block; C1-2, thermal shield.

heat flux is shown in Fig. 1. The heat flux was measured by using a high sensitivity differential scanning calorimeter, which is similar to the nano-watt stabilized DSC developed by the present authors [21]. In the present case, the sample was fixed with a small amount of Si grease on the surface of the high sensitive temperature sensor TM1, which is made of 18 semiconducting elements connected in series and sandwiched by two thin alumina plates. No material was placed on the reference side of the sensor, TM2. The heat flux was obtained from the difference of the electromotive force between the sensors, TM1 and TM2.

The single crystal sample of $BaTiO_3$ with the size of 3.5 mm × 3.5 mm × 0.8 mm was purchased from MAT and its dielectric constant was obtained by measuring a susceptance between the electrodes on the upper and lower face of the single crystalline $BaTiO_3$ using the HP4263B LCR-meter. A thin layer of Au was deposited on the both sides of the (0 0 1) plane of the $BaTiO_3$ crystal to form a capacitor and then metallic electrodes with the diameter of 0.1 mm were attached to the both faces using Ag paste. The susceptance B was measured at 100 kHz and 0.02 V using the LCR-meter and then the dielectric constant ε and the relative dielectric constant ε_r were obtained using the following equations:

$$\varepsilon = \frac{Bd}{\omega S} = \frac{Bd}{2\pi f S} \tag{1}$$

$$C = \frac{\varepsilon S}{d}, \tag{2}$$

$$B = \omega C, \tag{3}$$

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}, \tag{4}$$

where C is the capacitance, d the thickness of the capacitor, S the area of the capacitor, f the measuring frequency, ω the angular frequency and ε_0 is the dielectric constant of the vacuum. The open-short correction was carried out before the measurement. The heating or cooling rate was controlled by controlling the current of thermoelectric module, TM4, using the Pt resistance thermometer, TS2 as shown in Fig. 1. Since TM4 can pump heat in either direction to heat or cool by changing the direction of the current through it, the measurement in the both direction of heating and cooling is possible with this apparatus. The temperature was controlled with a precision better than 0.1 mK. The temperature of the sample was measured by Pt resistance thermometer, TS1, which was calibrated using the melting point of the standard samples such as Ga, In and benzoic acid within an inaccuracy of 0.1 K.

3. Results

3.1. Heat flux and dielectric constant measurements of $BaTiO_3$

The results of the simultaneous measurements of the heat flux and the relative dielectric constant at a heating and cooling rate of 2 mK s^{-1} are shown as a function of the temperature in Fig. 2. A sharp thermal anomaly and a sharp anomaly in the dielectric constant are seen at about 402 K in the heating run and at about 400 K in the cooling run as shown in the figure. The transition

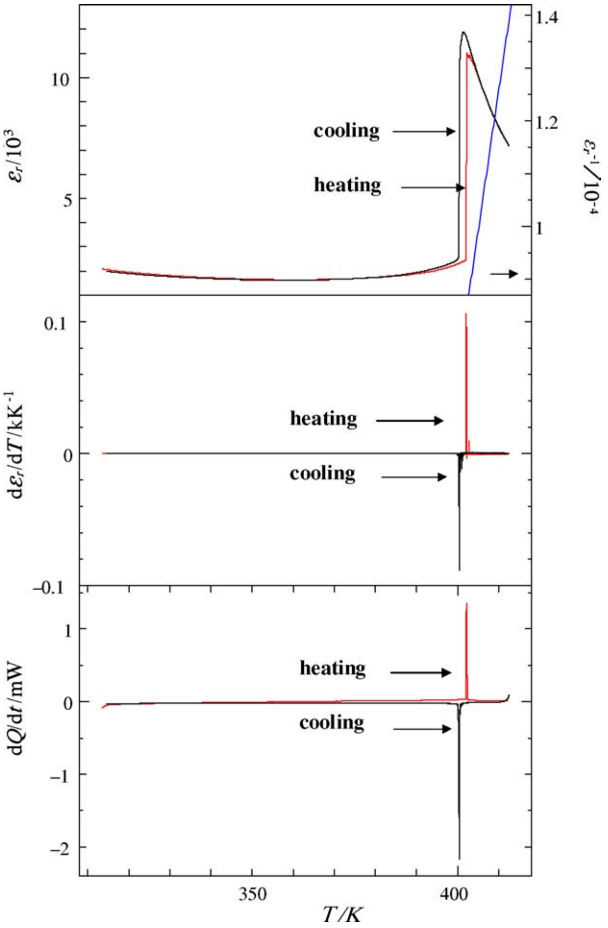

Fig. 2. The results of the simultaneous measurements as a function of the temperature at heating and cooling rate of 2 mK s^{-1}, of relative dielectric constant (ε_r), its reciprocal ($1/\varepsilon_r$), the temperature derivative of the relative dielectric constant ($d\varepsilon_r/dT$), and the heat flux (dQ/dt).

temperature in the heating run is 2.0 K higher than that in the cooling run, showing the hysteretic behavior of the transition being consistent with previous studies [1–4,6,11,18].

The anomalous peak in the dielectric constant decreases above the transition temperature as seen in Fig. 2. The reciprocal of the relative dielectric constant above the transition temperature is also plotted against the temperature in the upper and right part of Fig. 2, where the linear relationship is obtained, showing the paraelectric character in this temperature region [1,6,18].

The temperature derivative of the relative dielectric constant ($d\varepsilon_r/dT$) is taken by calculating the increase of the relative dielectric constant versus the small increase of the temperature, $\Delta\varepsilon_r/\Delta T$ numerically and is shown in the middle of Fig. 2, where the derivative curve is very similar to that of the heat flux. This is considered to be due to the fact that the anomalous heat flux is closely related to the temperature derivative of the dielectric constant. A similar relationship was observed in the relation between the heat flux and the thermal expansion [2,11].

The heat flux and the relative dielectric constant near the Curie point measured at the heating rate of 1 mK s^{-1} are shown in Fig. 3, where a sudden jump in the dielectric constant and a sharp peak in the heat flux are seen. The temperature derivative of the dielectric constant is shown in the middle of Fig. 3, whose curve is very similar to that of the heat flux. It is noted, however, that the peak in the derivative of the dielectric constant is sharper than that of the heat flux. This is considered to be due to the fact that the change in the dielectric constant is directly detected as an electrical signal and the change in the heat flux is detected through the differential heat flow by the temperature sensors, TM1 and TM2, which cause the delay of the response. The heat flux and relative dielectric constant near the Curie point measured at the cooling rate of 1 mK s^{-1} are shown in Fig. 4, where hyperfine multistage transitions are observed both in the dielectric constant and in the heat flux. At least five steps in the dielectric constant and five anomalies in the heat flux were observed being consistent well with the previous results [2,11]. It is noted that the derivative curve of the dielectric constant is very similar to that of the heat flux, although the peaks in the derivative curve of the dielectric constant are sharper than those in the heat flux.

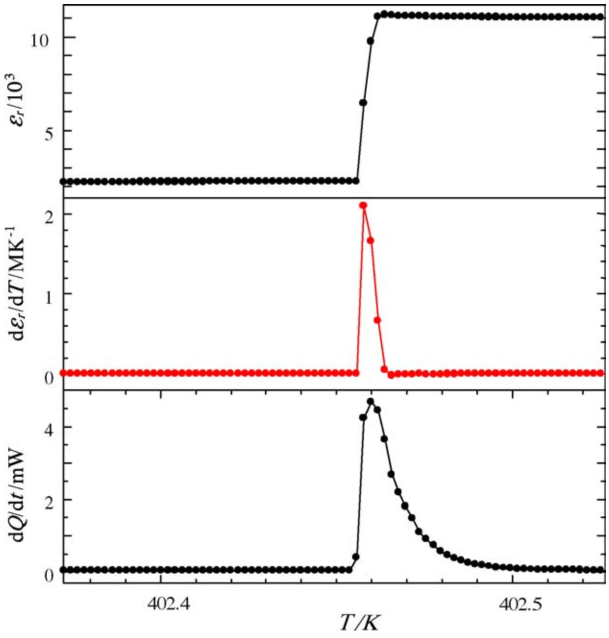

Fig. 3. The simultaneous measurements near the Curie point at the heating rate of 1 mK s^{-1} of the relative dielectric constant (ε_r), the temperature derivative of the relative dielectric constant ($d\varepsilon_r/dT$) and the heat flux (dQ/dt).

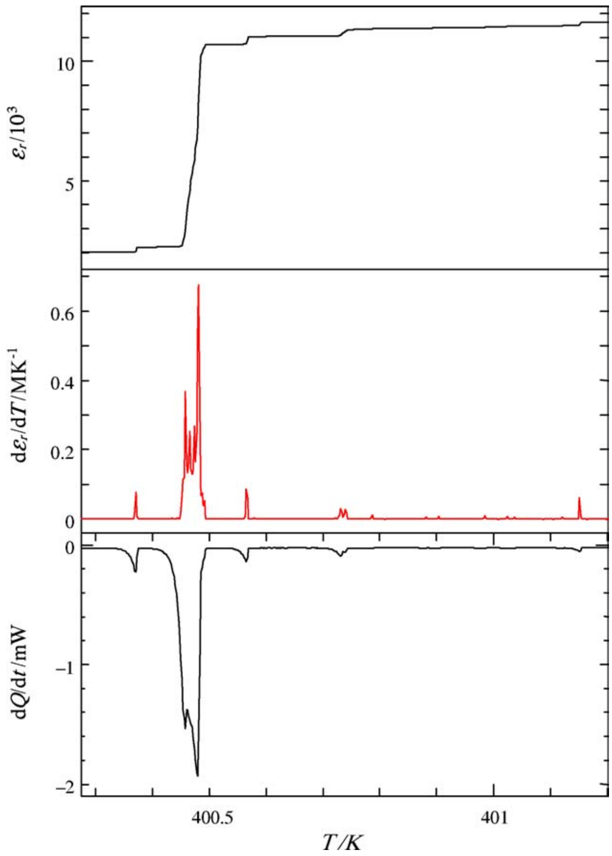

Fig. 4. The simultaneous measurements near the Curie point at the cooling rate of 1 mK s^{-1} of the relative dielectric constant (ε_r), the temperature derivative of the relative dielectric constant ($d\varepsilon_r/dT$) and the heat flux (dQ/dt).

3.2. The dependence of heat flux and dielectric constant on heating rate

The dielectric constant and the heat flux near the Curie temperature measured simultaneously at the heating rate of 0.1, 0.05, 0.02, and 0.01 mK s^{-1} are shown in Fig. 5. At the heating rate higher than 0.05 mK s^{-1}, the dielectric constant shows the sudden jump at about 402.7 K like the case at 1 mK s^{-1} shown in Fig. 3. At the heating rate lower than 0.05 mK s^{-1}, however, the dielectric constant slowly increases until the transition temperature, which becomes lower as the decrease of the heating rate. The heat flux and the derivative curve of the dielectric constant show quite similar peaks at the sudden jump of the dielectric constant. In order to confirm this quantitatively the integral of

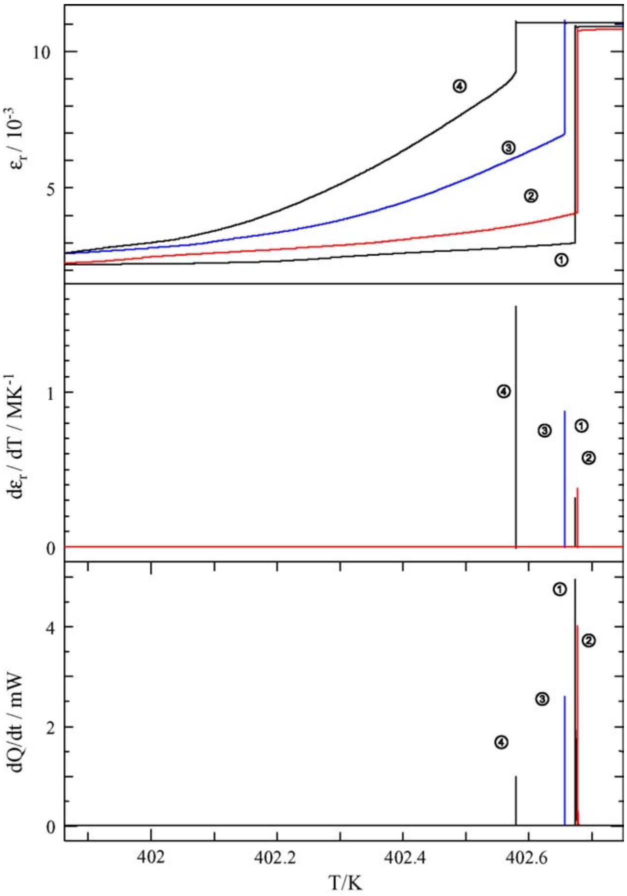

Fig. 5. The simultaneous measurements near the Curie point at the heating rate of ① 0.1, ② 0.05, ③ 0.02, and ④ 0.01 mK s^{-1} of the relative dielectric constant (ε_r), the temperature derivative of the relative dielectric constant ($d\varepsilon_r/dT$) and the heat flux (dQ/dt).

the anomaly in the heat flux, namely the enthalpy change due to the sudden jump was calculated for each run of various heating rates and it is plotted against the jump width of the dielectric constant as shown in Fig. 6, where the linear relationship is seen. This result indicates that the heat flux is proportional to the derivative of the dielectric constant.

The heat flux and the derivative of the dielectric constant show almost no change except for the anomaly at the temperature of the sudden jump in the dielectric constant in the heating process as seen in Fig. 5. These results indicate that the information of the heat flux only cannot describe the whole nature of the phase transition, showing the merit of the simultaneous measurements. If the heating rate would become infinitely slow, the relative dielectric constant would approach the maximum value of 11,000 and the sudden jump of the first order transition would become minimum. Such a dependence of the dielectric constant on the heating rate shows that the phase transition is dependent on time and includes a very slow process.

Such a very slow process may suggest the existence of a metastable or an unstable state in the single crystalline $BaTiO_3$ in the vicinity of the Curie temperature in the heating process as will be discussed next in detail.

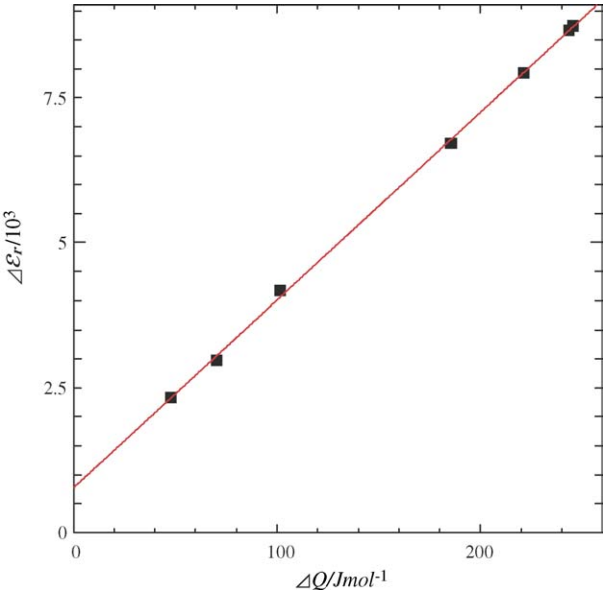

Fig. 6. The relation between the enthalpy change (ΔQ) and the change of the dielectric constant ($\Delta\varepsilon_r$) measured at different heating rates.

3.3. Heat flux and dielectric constant at constant temperatures

Since an unstable state seems to exist in the vicinity of the Curie temperature in the heating process, the simultaneous measurements of the dielectric constant and the heat flux were made at constant temperatures near the Curie temperature.

The sample was heated at the rate of 0.1 mK s^{-1} from 373.2 K, which is in the ferroelectric phase, and it was kept at the constant temperatures of 402.239 and 402.293 K, which are about 0.2 K lower than the Curie temperature measured at the heating rate of 0.01 mK s^{-1} as seen in Fig. 5. The results of the dielectric constant, the derivative of the dielectric constant and the heat flux kept at 402.239 and 402.293 K are shown as a function of time in Fig. 7. The dielectric constant increases with time and the sudden jump is occurred at 17 h at 402.239 K and at 14 h at 402.293 K. The shape of the dielectric constant as a function of time in Fig. 7 is very similar to that at the heating rate of 0.01 mK s^{-1} as a function of temperature in Fig. 5. At the time of the sudden jump in the dielectric constant, the heat flux and the derivative of the dielectric constant show sharp peaks in Fig. 7 like the results shown in Fig. 5. The faster sudden jump obtained at the higher temperature of 402.293 K shows that the unstable state is quickly changed into the stable state at the higher temperature.

Since it is wondered if the unstable state exits in the transition from the high temperature phase to the low temperature phase, a similar experiment was conducted in the cooling process. The sample was cooled at the rate of 0.5 mK s^{-1} from 420 K, which is in the paraelectric phase, and it was kept at the constant temperature of 400.581 K, which is about 0.1 K higher than the Curie temperature measured at the cooling rate of 1 mK s^{-1} as seen in Fig. 4. The results of the simultaneous measurements of the relative dielectric constant, the derivative of the relative dielectric

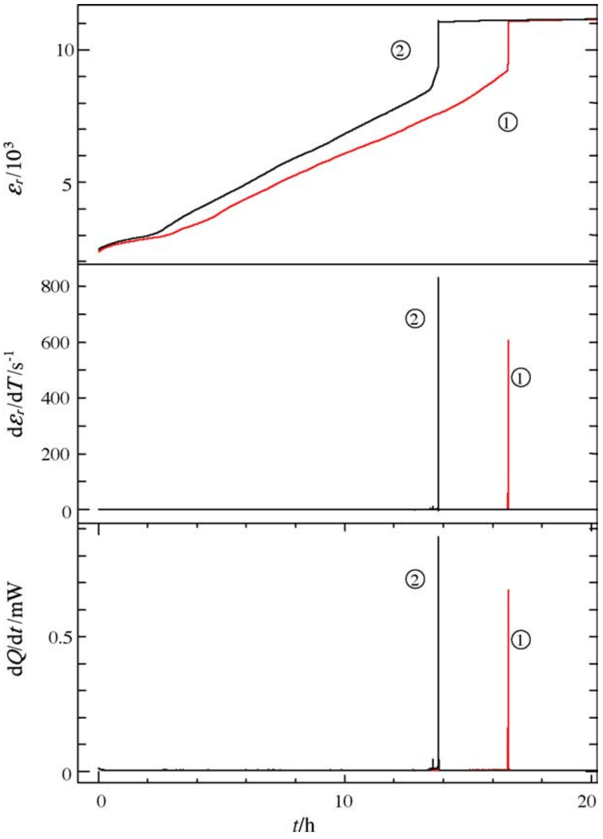

Fig. 7. The results of the simultaneous measurements of relative dielectric constant and heat flux at constant temperatures at ① 402.239 K and ② 402.293 K after heating at 0.1 mK s^{-1} from 373.2 K.

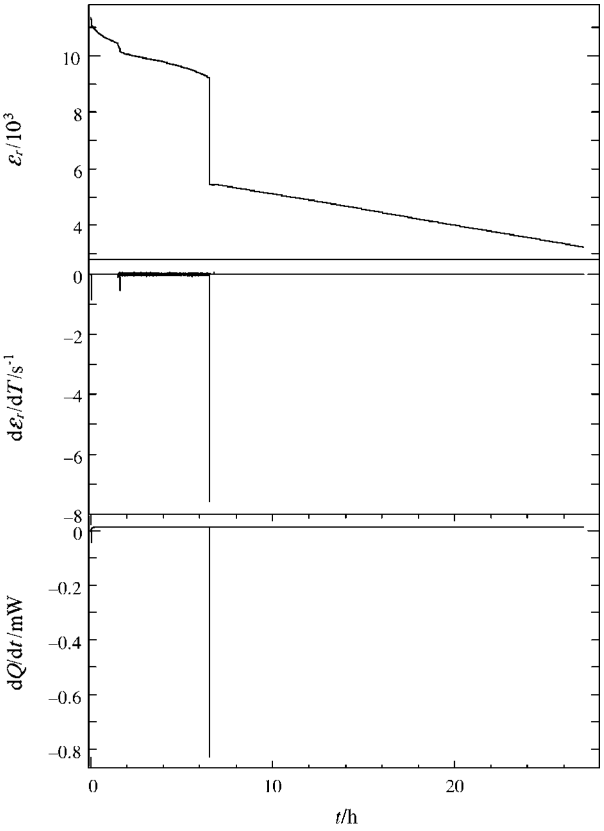

Fig. 8. The results of the simultaneous measurements of relative dielectric constant and heat flux at constant temperatures at 400.581 K after cooling at 0.5 mK s^{-1} from 420.0 K.

constant and the heat flux at 400.581 K are shown as a function of time in Fig. 8. At the time of the sudden jump in the dielectric constant, the heat flux and the derivative of the dielectric constant show sharp peaks in Fig. 8, like the case in the heating process shown in Fig. 7.

4. Discussion

The tetragonal–cubic transition of a single crystalline $BaTiO_3$ with a (0 0 1) plane near 400 K observed by the simultaneous measurements of the heat flux and the dielectric constant showed quite peculiar behaviors depending on the thermal history which are summarized as follows:

(1) The transition temperature in the heating run at the rate of 2 mK s^{-1} is 2.0 K higher than that in the cooling run, showing the hysteretic character of the phase transition. The sudden jump in the dielectric constant was observed in the heating run, while the hyperfine multistage anomalies were observed in the cooling run.

(2) The dielectric constant and the heat flux near the Curie temperature depended on the heating rate. At the heating rate lower than 0.05 mK s^{-1}, the dielectric constant slowly increases until the transition temperature, where a sudden jump characteristic to the phase transition of first-order was observed.

(3) The dielectric constant near the Curie temperature measured at a constant temperature after heating from a low temperature phase increased with time and a sudden jump was observed at some time. Similarly, the dielectric constant near the Curie temperature measured at a constant temperature after cooling from a high temperature phase decreased with time and a sudden drop was observed at some time.

The hysteretic behaviors of the phase transition of $BaTiO_3$ have already been observed in the lattice constant, birefringence and electric polarization by changing the temperature [1,3] and in the observation of ferroelectric domains by changing the direction of the applied field at a constant temperature [1,3,4,6–9]. The hysteretic behaviors of the solid–solid phase transition such as NH_4Cl and KH_2PO_4 were reviewed by Ubbelohde [22]. A single crystalline sample of NH_4Cl and ZrO_2 was shown to be composed of sub-regions of low temperature and high temperature phases in the temperature region of hysteretic, where the coexistence of the low temperature and high temperature phases was confirmed by X-ray diffraction [23,24]. The hysteretic behaviors are explained thermodynamically as due to additional degrees of freedom resulting from the interface energy among the sub-regions. The Gibbs energy of the system at a given temperature is composed of the interface energy among the sub-regions in addition to the sum of the Gibbs energies for constituent low- and high-temperature phases. Therefore, there exist a great number of metastabilities in the temperature region under consideration, which result in hysteretic behaviors [2,22].

Forsbergh [7] investigated the arrangement of domains that arise in single crystals of $BaTiO_3$. The domains are the result of tetragonal (1 0 1) twinning and appear by the formation of wedge-shaped laminar domains between converging (1 0 1) planes. When the crystal was slowly cooled from the region of the Curie temperature, he observed that the laminae frequently advanced in groups in the two perpendicular directions parallel to the edges of the rectangular plate showing a square-net pattern.

The sudden jump in the dielectric constant was observed in the heating run as shown in Fig. 3, while the dielectric constant changed in several steps in the cooling run as shown in Fig. 4. These results are quite consistent with the previous study [2,11]. We found that the heat flux and the thermal expansion curve showed a single anomaly in the heating run and several steps of anomalies in the cooling run, both in the $\langle 1\,0\,0\rangle$ and $\langle 0\,0\,1\rangle$ direction [2,11].

A question may arise here; why the phase transition takes place in a single step in the heating condition, while the phase transition takes place in several steps in the cooling condition? The answer to the question is in the present experimental results. The phase transition does not take place in a single step even in the heating condition in a strict sense. Fig. 5 shows that the dielectric constant starts to increase around 402 K due to the phase transition at the heating rate of 0.01 mK s^{-1}, it increases with the increase of temperature and then it shows a sudden jump at 402.58 K. These behaviors would show that the nucleation and growth of cubic domains take place in mother tetragonal domains around 402 K. Although the degree of the changing speed and the number of steps in the dielectric constant during the transition are different between the heating and the cooling process, the nucleation and growth of the new-phase domains are considered to take place from the mother-phase both in the heating and the cooling process in the temperature range of hysteretic. The spontaneous phase transition obtained at the condition keeping at constant temperatures both from the low- and high-temperature phases as shown in Figs. 7 and 8 supports such an interpretation. Merz [4,6] investigated the nucleation and growth of ferroelectric domains in $BaTiO_3$ as a function of applied electric field and temperature. He observed the hysteretic loop at the Curie point by the application of electric field and observed the formation of many new anti-parallel domains which grew only in the parallel direction, being consistent with the results by Forsbergh [7]. The reason why the degree of the changing speed and the number of steps in the dielectric constant during the transition are different between the heating and the cooling process may be ascribed to the symmetrical problem of the crystal. The structural phase transition from the mother tetragonal phase to the cubic phase is difficult, because the cubic phase is the higher symmetric phase and it is difficult to form the domains of the new phase from the unsymmetrical phase.

A new question may arise here; why it takes such a long time for the transition to occur, since the heating rate of 0.01 mK s^{-1} is not low enough to obtain a nearly equilibrium phase transition? According to the studies by Merz [4,6] and Forsbergh [7], the growth process along the parallel direction may be relatively fast. However, the nucleation process of the new domains may be very slow, since it should create new domain boundaries. Thermodynamically speaking, the nucleation process is an unstable state. The unstable state spontaneously changes into a stable state like the results shown in Figs. 7 and 8. Merz [4,6] investigated the nucleation and growth rate in the crystal of $BaTiO_3$ as a function of temperature near the Curie point. The nucleation and growth rate became faster at higher temperatures because of the activation energy of the nucleation process. The faster transition at the higher temperature of 402.293 K shown in Fig. 7 is considered to be due to the same reason.

5. Conclusions

The simultaneous measurements of the heat flux and the dielectric constant on the tetragonal-cubic transition of a single crystalline $BaTiO_3$ with a (0 0 1) plane near 400 K showed quite peculiar behaviors depending on the thermal history. The transition temperature in the heating run at the rate of 2 mK s^{-1} is 2.0 K higher than that in the cooling run. The sudden jump in the dielectric constant was observed in the heating run, while the hyperfine multistage anomalies were observed in the cooling run.

The dielectric constant and the heat flux near the Curie temperature depended on the heating rate. At the heating rate lower than 0.05 mK s^{-1}, the dielectric constant slowly increases until the transition temperature, where a sudden jump characteristic to the phase transition of first-order was observed.

The dielectric constant near the Curie temperature measured at a constant temperature after heating from a low temperature phase increased with time and a sudden jump was observed at some time. Similarly, the dielectric constant near the Curie temperature measured at a constant temperature after cooling from a high temperature phase decreased with time and a sudden drop was observed at some time.

These results show that $BaTiO_3$ in the vicinity of the Curie temperature has a hysteretic behavior and an unstable state. These behaviors are considered to be resulted from the nucleation and growth process of domains of the new phase from the mother phase in the phase transition.

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