

Simultaneous Measurements of Thermal, Electrical, and Acoustic Properties of BaTiO₃ – New Feature of 403 K Phase Transition¹

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In order to obtain useful information on the transient process of phase transitions in ferroelectrics by various methods including calorimetry, the “mK-stabilized cell” of a small size has been developed. It is based on the heat flux differential scanning calorimeter (DSC) and has a temperature stability better than 1 mK. The “cell” can be used to change the temperature under nearly quasi-static conditions by an infinitesimally small rate not only on heating but also on cooling while passing through the transition points. It enables simultaneous measurements of endothermic heat and exothermic heat along with dielectric constants, displacement currents, etc. with a high degree of temperature resolution. X-ray diffraction measurements for sensing thermal anomalies are also possible by a minor modification of the “cell.” Precise and simultaneous measurements of thermal, electrical, and acoustic properties were carried out at the 403 K phase transition in BaTiO₃ single crystal grown by the top-seeded solution growth method. It has been clarified that the exothermic heat at the transition on cooling has more useful information than the endothermic heat on heating; in the cooling process two thermal anomalies occur separately at T_1 and T_2 although the transition is in a narrow temperature range. It is recognized from other methods that the nature of the

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transition on cooling is not of a single but of multiple steps. Resonant ultrasonic measurements using the "cell" were carried out, after developing a new excitation method. The sample does not have a simple softening approaching the transition point on cooling but has different elastic moduli for the two thermal anomalies at T_1 and T_2 . The dielectric constant also has an intermediate constant value between T_1 and T_2 . The crystal structure in the room temperature phase below the transition point has been determined by X-ray diffraction. In this region, tetragonal and monoclinic structures coordinating with each other exist.

KEY WORDS: BaTiO₃; heat flux DSC; phase transition; quasi-static temperature change; simultaneous measurements; transient process; ultrasonic resonance.

1. INTRODUCTION

The experimental study of phase transitions in ferroelectrics, including calorimetry, is often focused on the transition types classified by the phenomenological Landau theory. However, by the use of innovative measurement techniques, we can get more significant information on the transient process of phase transitions to elucidate the interaction of the constituent particles because the phase transition inevitably causes a decrease of the free energy resulting from the temperature change.

On the other hand, theoretical "first principle calculations" based on electron theory have recently been remarkably successful in deriving transition temperatures of BaTiO₃[1], although their agreement with measured values is not adequate. In order to use the experimental information of phase transitions in understanding or developing the electron theory, the transient process of phase transitions occurring for a quasi-static temperature change must be observed with extremely precise temperature resolution for an infinitesimally small temperature change. Simultaneous measurements of various physical properties with a heat anomaly are also needed to examine the exact coincidence of occurrence in the same sample over a small temperature range. In addition, such measurements on cooling are necessary, because features of the cooling process should be clarified experimentally for development and understanding of theories.

For such purposes, we have developed a versatile "mK-stabilized cell" of a small size having a high temperature resolution with a very small temperature fluctuation of less than 1 mK [2].

2. "mK-STABILIZED CELL"

Diagrams of the cell, including a cross section of a prototype of the "cell," are shown in Figs. 1 and 2. It is based on the heat flux DSC with a temperature stability within ± 0.2 mK as seen in Fig. 3. It is possible to

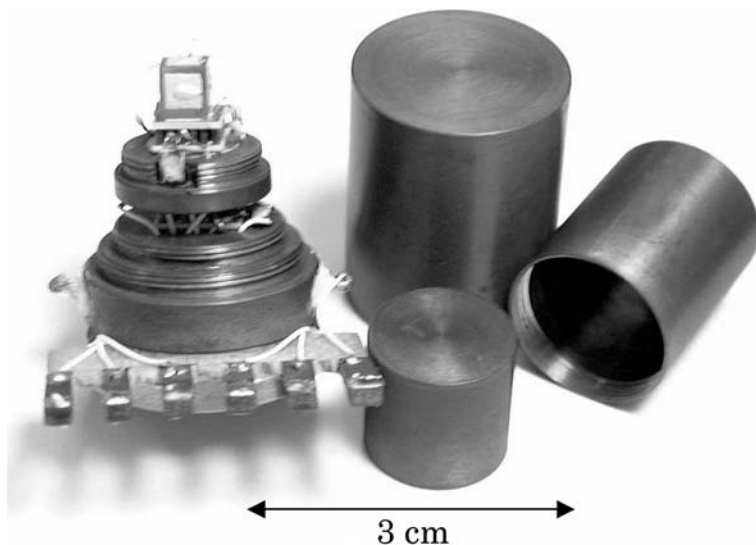


Fig. 1. Photograph of the “mK-stabilized cell” with the shells disassembled. BaTiO₃ sample cube is seen on the plate of the heat flux sensor. Electrode is glued on each sample face.

change the temperature of the cell at nearly quasi-static condition while passing through the transition points. This enables simultaneous measurements of the endothermic heat and exothermic heat along with dielectric constants, displacement currents, etc. with a high degree of temperature resolution [3, 4]. The displacement currents caused by the slight displacement of atoms due to the phase transitions are measured along three crystallographic axes. X-ray diffraction measurements for sensing thermal anomalies are also possible by a minor modification, i.e., by providing windows on the shells of the “cell” for the incident and reflected X-rays [5].

3. RESULTS FOR THE 403 K PHASE TRANSITION IN BaTiO₃

The method was applied to the uppermost temperature (403 K) phase transition in BaTiO₃ single crystal made by the top-seeded solution growth (TSSG) method, the transition mechanism of which has been under study for a long time due to the differences of understanding depending on the experimental methods or conditions. The single crystals used were obtained from three different sources. All of them are as-grown and as-cut samples, showing the same behavior essentially except for minor differences.

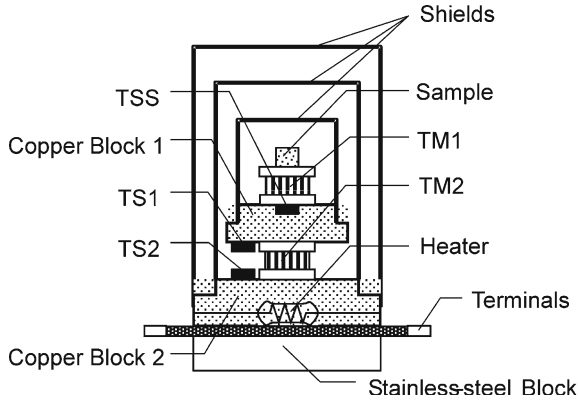


Fig. 2. Cross section of the “cell” for precise heat flux measurements. Two coaxial copper blocks and a stainless-steel block are used as the framework. Three coaxial copper shields for thermal radiation are tightly fixed to the copper blocks by screws. The copper blocks and thermoelectric modules are mutually stacked and glued. Two coated metal resistors connected in parallel serve as the main heater. For fine temperature regulation, the thermoelectric module TM2 using the Peltier effect is set between the two copper blocks as the heat pump. Another thermoelectric module TM1 is for the heat flux sensor using the Seebeck effect. TS1, TS2, and TSS are temperature sensors. TS2 is near the heater, and TSS is near the sample.

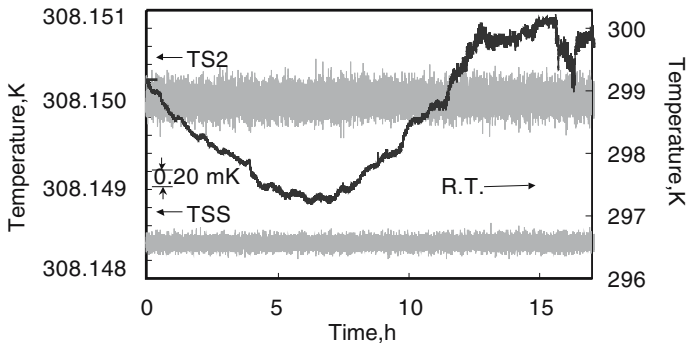


Fig. 3. Diagram showing the performance of the “cell.” The temperature fluctuation measured by TSS near the sample is within ± 0.20 mK for a room temperature change of 3 K. Allowable error of the temperature is within $\pm 0.2\%$.

For the study of ferroelectrics, an ac electric field is usually applied to a sample to obtain hysteresis curves, but we did not apply it here in order to clarify how the transition occurs in BaTiO₃ by a perturbation of temperature. Heat flux measurements were carried out for both heating and cooling, using the “cell.” The endothermic heat at the transition is shown in Fig. 4, and the exothermic heat is seen in Fig. 5. Compared to the heating mode, the transition behavior on cooling is not represented by a single step but by multi-steps. The change of the dielectric constant along the crystallographic [100] direction on cooling shows correspondence with the thermal anomalies as seen in Fig. 6. It is noted that the value of the dielectric constant is almost constant between T_1 and T_2 . The displacement currents along the crystallographic (100) directions flow correspondingly on cooling as shown in Fig. 7.

We made resonant ultrasonic measurements along the [100] direction using the “cell,” after developing a new excitation method for resonances [6]. The results very near the transition point on heating and on cooling are shown in Figs. 8 and 9, respectively. The sample does not show a simple softening on cooling but changes its elastic modulus between the two thermal anomalies at T_1 and T_2 .

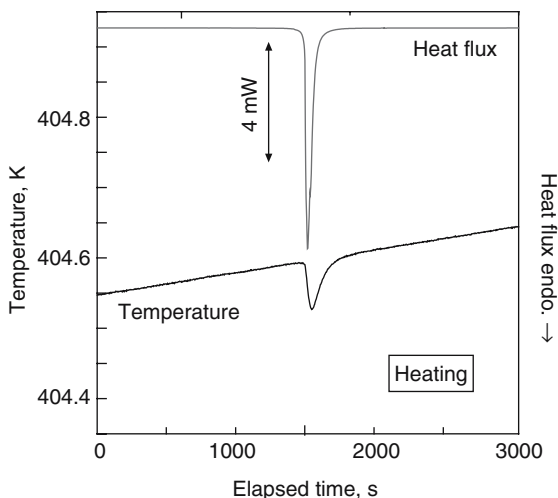


Fig. 4. Endothermic heat and the temperature on heating at the 403 K cubic-tetragonal phase transition in BaTiO₃ as a function of the elapsed time. Noise of the heat flux is 25 μ W. The rate of temperature change is 33 μ K \cdot s⁻¹. A decrease of temperature in the sample is seen at the transition point due to the latent heat.

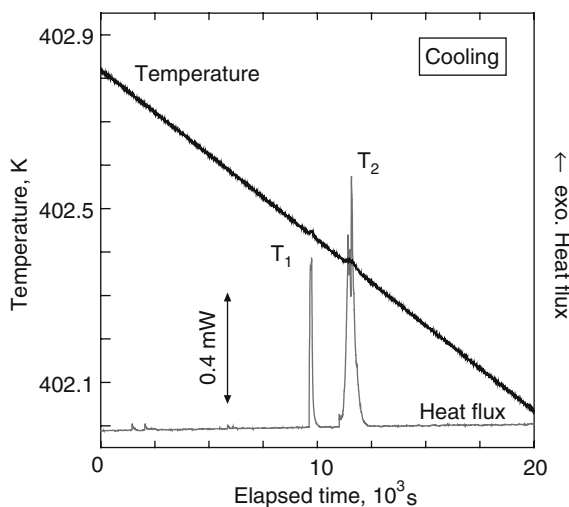


Fig. 5. Exothermic heat and the temperature on cooling at the 403 K cubic-tetragonal phase transition in BaTiO_3 as a function of the elapsed time. The rate of temperature change is $33 \mu\text{K} \cdot \text{s}^{-1}$. The transition temperature on cooling differs from that on heating. Two thermal anomalies are observed at T_1 and T_2 on cooling. A slight increase of the temperature in the sample is seen at T_1 and T_2 due to the latent heat.

Figure 10 shows an X-ray precession pattern at room temperature, where weak extra spots are observed in addition to the main Bragg spots. The crystal system in the room temperature phase below the transition point has been determined from the analysis; two types of structures (tetragonal and monoclinic coordinating with each other [7]) are revealed.

4. DISCUSSION

It must be emphasized that the results of the exothermic heat experiment on cooling with a very slow temperature change shown here are significantly different from the results derived by a treatment of a simple expansion of the horizontal temperature axis of the exothermic heat with a simple shape, which is observed by the ordinary fast temperature change method. We have shown that BaTiO_3 reveals an inevitable transient process with a nearly quasi-static temperature change. It is thought that the cooling process with an infinitesimally small temperature change shows more complicated features than the simple heating process for crystals of three components such as BaTiO_3 and CsPbCl_3 [8, 9].

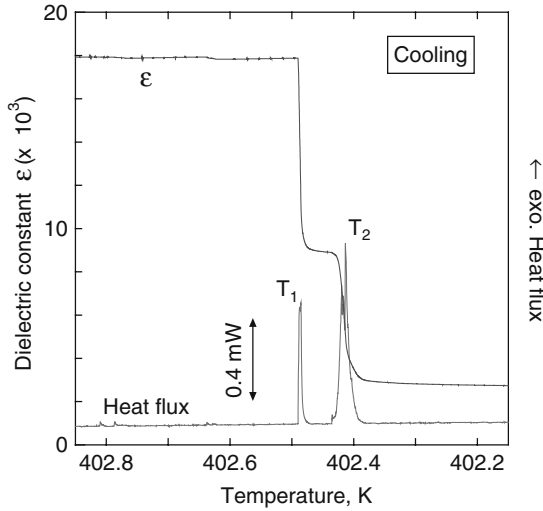


Fig. 6. Dielectric constant of BaTiO₃ along the crystallographic [100] direction at the cubic-tetragonal phase transition on cooling at a frequency of 1 MHz and an oscillator level of 0.1 V. The uncertainty of the dielectric constant is 0.15%. The rate of temperature change is 33 μK·s⁻¹. Heat flux curve is also shown for reference.

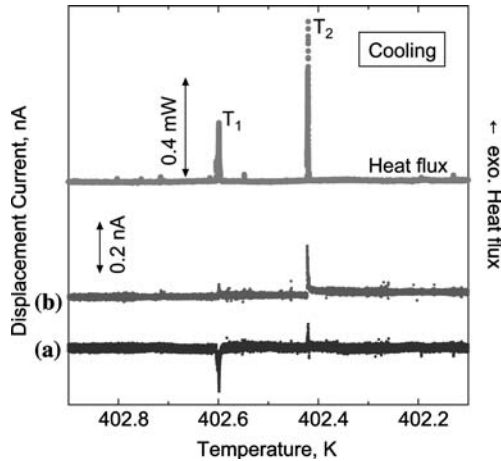


Fig. 7. Displacement currents in BaTiO₃ along two crystallographic (100) directions at the cubic-tetragonal phase transition on cooling. Allowable error of the displacement current is within 1%. Heat flux curve is also shown for reference.

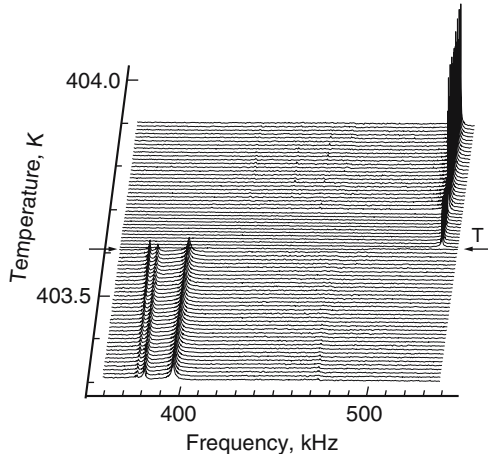


Fig. 8. Shift of the ultrasonic resonance frequency on heating at the transition temperature T , where endothermic heat is observed. Resolution of frequency is of the order of 1 ppm. Resonance peaks are shown stereographically.

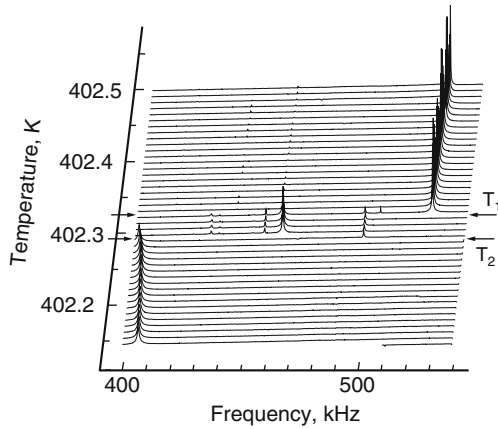


Fig. 9. Shift of the ultrasonic resonance frequency across the transition temperature on cooling. Resonance peaks are shown stereographically. Exothermic heat is observed at T_1 and T_2 , where we can see the abrupt change of the resonance frequency. The existence of an intermediate state is strongly suggested from the results.

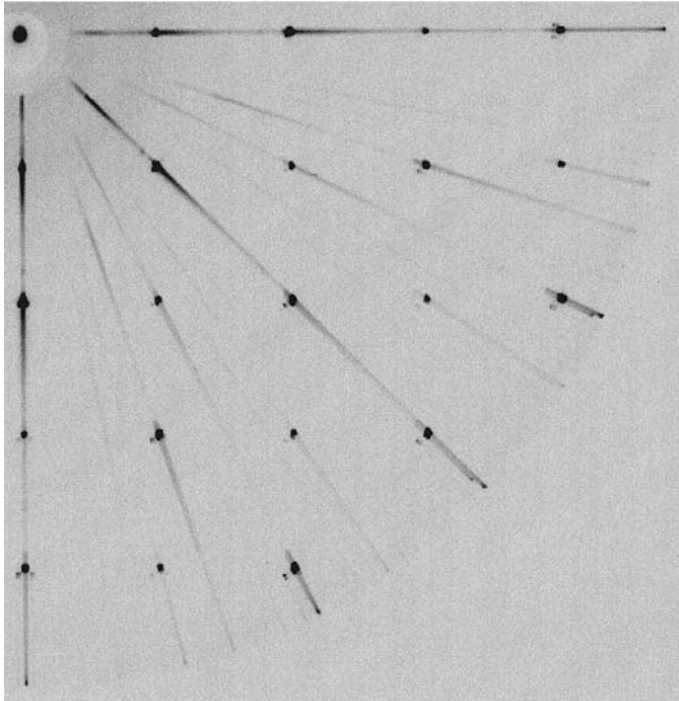


Fig. 10. X-ray precession patterns at room temperature. Weak extra spots are observed in addition to the main Bragg spots.

A new feature of the 403 K transition in BaTiO₃ has been determined by the present measurements. The transition process on cooling is not so simple as has been understood until today but is of a multi-step nature as revealed by the methods used here. Samples have inevitable surface strain caused by cutting. The sample etched by phosphoric acid has also revealed two separated thermal anomalies similarly but the temperature width of each thermal anomaly and the temperature interval of the two thermal anomalies have been extremely narrowed [10].

Using X-ray diffraction it has been observed that BaTiO₃ on cooling does not have a simple structure change from cubic to tetragonal with the polarization along the [100] direction due to the displacement of the body-centered ion, but changes to two types of structures coordinating with each other in the phase below the transition temperature. It is also observed that there exists some intermediate state on cooling in the very narrow temperature range between the two thermal anomalies at T_1 and T_2 based on the results of dielectric constant and resonant frequency measurements.

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