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High temperature single-crystal X-ray diffraction study of tetragonal and cubic perovskite-type $BaTiO_3$

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1 Introduction

The BaTiO3 perovskite has been intensively studied for its excellent ferroelectric properties at ambient conditions. The ferroelectric transition of BaTiO3 is considered to be of the displacement type and its ferroelectricity has mainly been discussed based only on the displacement of Ti ion from the central position in the TiO_6 octahedron. However, the recent XAFS studies have proposed that it includes both characters of the order-disorder type and displacement type. In order to examine the relationship between the structural changes in the tetragonal and cubic phases of $BaTiO_3$ and its ferroelectric phase transition mechanism, we have carried out the single crystal X-ray structure analyses in the wide temperature range 298 K to 778 K. In this study [1], we have determined the temperature dependence of mean square displacements for each atom and of the distortion in the ferroelectric phase. The possibility of the Ti displacement from central position of the TiO6 octahedron in the cubic phase is assessed together with the mechanism of ferroelectricity.

2 Experiment

A single crystal used for X-ray measurements was carefully ground to a sphere 140(1)μm in diameter and put into a silica-glass capillary. Temperature fluctuation during the data collections was kept within ±0.2 K. Single-crystal X-ray diffraction measurements were carried out with a four-circle diffractometer at the BL-10A beam line of the Photon Factory, Tsukuba, Japan, using monochromatized synchrotron X-ray (λ = 0.70006 Å) radiation. The unit-cell parameters at each temperature were determined by the least-squares method from a set of 25 reflections within the range of $45° \le 2\theta \le 50°$. Intensity data were collected within $2° \le 2\theta \le 120°$ for each temperature by continuousω–2θ scan mode, and consequently reflections between 1124 and 605 were measured for each phase. After the corrections for Lorentz-polarization factors and absorption effects, the intensity data were averaged in Laue symmetry *4mm* and *m3m* to give independent reflections between 618 and 132 for the tetragonal and cubic phases, respectively. All the measured reflections and all the independent reflections after averaging were observed with accuracies of $|F_o| \ge 3\sigma(|F_o|)$, and the latter sets of reflections were employed for the structure refinements. Internal residuals of the equivalent reflections (R_{int}) varied between 0.0085 and 0.0130 for each temperature. The structure refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$ using a full matrix least-squares program RADY. The alternative of the indexing *hkl* or *hk-l* are possible because of the acentric structure for the tetragonal phase.

3 Results and Discussion

The temperature factors U_{eq} will follow straight lines and pass through the origin by classical statistical dynamics if the effect of configurational disorder is negligible. When the static distribution is present, the 0 K intercept has a positive value. All lines can be extrapolated to the zero value at 0 K, except for the straight line for Ueq of Ti in the cubic phase (Fig. 1). In the tetragonal crystals, there is no experimental observation on configurational disorder. The straight line for Ueq of Ti in cubic phase deviates significantly from the origin. This suggests strongly that Ti includes the clear configurational disorder (statistical distribution) effect only in the cubic phase [1].

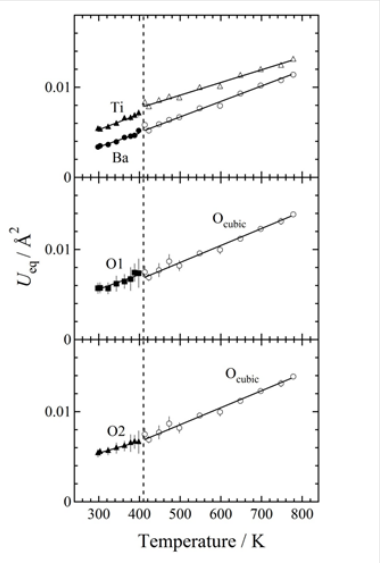

Fig. 1: Temperature dependence of U_{eq} for each atom in $BaTiO_3$.

References

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