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# Single-crystal X-ray diffraction study of tetragonal and cubic perovskite-type $PbTiO_3$

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## 1 Introduction

Perovskite-type PbTiO3 has been intensively studied for a long time because of their useful functional properties such as ferroelectric properties at ambient conditions. PbTiO3 shows a ferroelectric-paraelectric phase transition at around 763 K. The low temperature tetragonal phase is polar and ferroelectric with the acentric space group *P4mm* and crystal system of high temperature form is cubic (*Pm3m*). In order to examine the relationship between the structural changes in the tetragonal and cubic phases of $PbTiO_3$ 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 928 K. In this study [1], we have determined the temperature dependence of the distortion in the ferroelectric phase and of mean square displacements for each atom. The possibility of the Ti displacement from central position of the $TiO_6$ 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 ($\lambda = 0.70006$ 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 $45° \leq 2\theta \leq 50°$. Intensity data were collected within $2° \leq 2\theta \leq 120°$ for each temperature by continuous$\omega$–$2\theta$ scan mode, and consequently reflections between 1105 and 590 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 620 and 129 for the tetragonal and cubic phases, respectively. All the measured reflections and all the independent reflections after averaging were observed with accuracies of $|F_o| \geq 3\sigma(|F_o|)$, and the latter sets of reflections were employed for the structure refinements. The structure refinements were carried out by minimizing the function $\Sigma w(|F_o|-|F_c|)^2$ 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

Figures 1 and 2 show the temperature dependence of Ti-O1 and Pb-O2 bond distances. The differences between the longer and shorter distances show that Ti and Pb occupy off-center positions in $TiO_6$ and $PbO_{12}$ polyhedra, respectively. The differences between the longer and shorter bond distances obviously decrease with increasing temperature. This shows that the distortion in each polyhedron decreases and cation moves from off-center position to center position in each polyhedron with increasing temperature toward the phase transition point. [1].

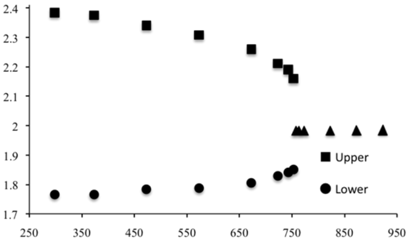

Fig. 1: Temperature dependence of the longer and shorter Ti-O1 distances in $TiO_6$ octahedron.

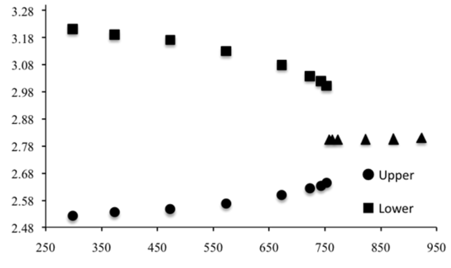

Fig. 2: Temperature dependence of the lomger and shorter Pb-O2 distances in $PbO_{12}$ polyhedron.

## References

[1] A.Yoshiasa, T.Nakatani, A.Nakatsuka, M.Okube, K.Sugiyama and T. Mashimo, *Acta Cryst.,* **B72**, 381-368 (2016).

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