Charge Density distribution during phase transition of simple perovskite oxides by single crystal X-ray diffraction.

T. Nishioka1, M. Hayashi1, T. Galica1, H. Kasai1, E. Nishibori1

Department of physics, University of Tsukuba and Tsukuba Research Center for Energy Materials Science, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8571 Japan.
s2220170@u.tsukuba.ac.jp

Keywords: Charge Density Study, Phase transition, SrTiO3 and LaAlO3

Perovskite oxides have attracted much attention in the wide field of materials science such as physics, chemistry, and geoscience. SrTiO3 is a typical perovskite material and shows a phase transition at 105 K. The structure and phase transition of SrTiO3 were investigated by many researchers [1-3]. The charge density and anharmonic thermal vibration studies of the high temperature phase of SrTiO3 were also reported by a single crystal X-ray diffraction [3], a convergent beam electron diffraction [1], and ray diffraction [2]. The charge density distribution and anharmonic thermal vibration of the low temperature phase of SrTiO3 provide us crucial information for deep understanding of mechanism for a transition. However, the high-quality single crystal diffraction data of the low temperature phase of SrTiO3 available for charge density study have never been measured due to several experimental difficulties, such as twinning etc. In the present study, we performed the temperature dependence of charge density studies for SrTiO3 including both high and low temperature phases from synchrotron radiation single crystal X-ray diffraction (SRXRD). The temperature dependence of charge density study of LaAlO3 perovskite was also carried out for the reference.

The high-quality small sized with less than 50 mm single crystals of SrTiO3 and LaAlO3 were prepared for SRXRD. Multi-temperature single crystal X-ray diffraction experiments through a phase transition for SrTiO3 were successfully carried out at SPring-8 BL02B1 beamline. High energy X-ray with 50 keV wavelength was used as an incident X-ray. Almost no peak splitting due to twinning was observed up to d=0.3 Å reciprocal resolution. A CdTe PILATUS detector was used for the data collection. A serious counting loss was observed in the F bunch mode operation at SPring-8. We used an X-ray in the C bunch mode operation for measurements of the data for charge density study. The data were processed by CrysAlisPro. The initial structures were solved and refined by SHELX suite implemented in the Olex2. The theoretical charge density and structure factors were prepared by WIEN2k.

The structures of SrTiO3 and LaAlO3 were further analysed by XD2016. Charge density distributions and anharmonic thermal vibrations were determined in the processes. The charge density distribution of SrTiO3 high temperature cubic phase was almost consistent with those of the previous convergent electron diffraction [1] and theoretical study by WIEN2k. The polarized distribution of valence electron of oxygen was clearly recognized in the determined charge density. The anharmonicity was also determined from the data with reciprocal resolution data up to 0.3 Å. The determined anharmonicity was consistent with the previous study [3].


This work was supported by JSPS KAKENHI (Grants No. JP19KK0132, JP20H04656 and JP21H05235). The synchrotron experiments were performed at SPring-8 BL02B1 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2021B0183, 2022A1744 and 2022B1595).