

## Particle-size dependence of resonant X-ray emission spectroscopy in BaTiO<sub>3</sub>

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### Introduction

Since the historical discovery of large ferroelectricity during World War II, BaTiO<sub>3</sub> (BTO) has been a key material for electrolytic condensers and a most important perovskite oxide up to the present day. Due to the strong demands on memory devices for downsizing, a critical size of electrolytic substrate itself has been decreased down to several hundreds of nanometer. In that trend, intensive researches on BTO nanoparticles have been made. An abnormal enhancement of the dielectric constant at a certain particle size ( $d$ ) is reported by Wada *et al.* [1], whereas a monotonic decrease of tetragonality is also reported by several groups [2]. Recently, we have performed Ti 2p soft X-ray emission (SXE) study and found that displacement of Ti atoms in oxygen-octahedrons remain even at  $d = 50$  nm, which was concluded from  $d$ - $d$  excitation peaks observed in SXE spectra [3].

In the BTO, however, Ti has nominally  $3d^0$  configuration. Therefore, the hybridization of Ti  $3d$  states and O  $2p$  states is of great importance for the appearance of  $d$ - $d$  excitation peaks. The resonant X-ray emission (RXE) spectroscopy is suitable for getting information on the local electronic properties of oxides via charge-transfer excitation peaks. In this report, Ti  $1s$  RXE spectra on BTO nanoparticles are presented.

### Experimental

Ti  $1s$  RXE measurement were performed on the bending magnet beamline BL-7C. The RXE spectra were obtained using a curved Ge(111) crystal monochromator installed in the vacuum chamber, "Escargot". The overall energy resolution was about 1 eV.

BTO nanoparticles with  $d = 50, 85, 120$  and  $200$  nm were prepared. Each powder sample packed in a dip was mounted on the sample holder. All the experiments were carried out under room temperature and vacuum of the order of  $10^{-5}$  Torr.

### Results and Discussion

Figure 1 shows the Ti  $1s$  RXE spectra of BTO nanoparticles only within the neighborhood of elastic peaks. The excitation photon energy was 4983.6 eV, which is located just below the white line in the absorption spectra. Between the elastic peaks and  $K\beta_5$  peaks, two weak energy-loss peaks caused by charge-transfers from occupied O  $2p$  bands to unoccupied Ti  $3d$  bands are observed (CT1 and CT2). The loss-energy of CT1 is  $\sim 13.5$  eV which is com-

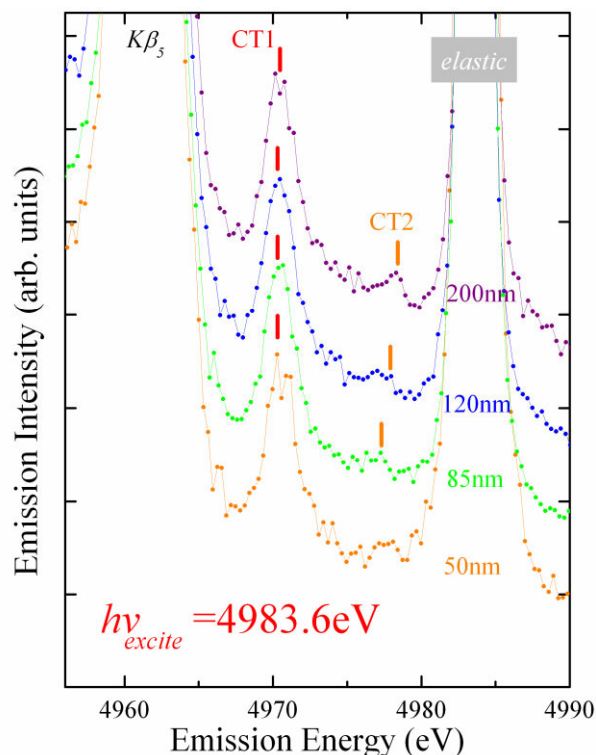


Figure 1. Ti  $1s$  resonant inelastic x-ray scattering spectra of BaTiO<sub>3</sub> nanoparticles for  $d = 50, 85, 120$  and  $200$  nm. The excitation photon energy (4983.6 eV) is located just below the white line in the absorption spectra. Each spectra is normalized at a peak labelled CT1.

mon to other titanates, whereas that of CT2 seem to shift slightly from 5.3 to 6.3 eV with decreasing  $d$  together with a decrease of intensity. For  $d = 50$  nm, CT2 completely disappears. These results are consistent with the change in crystal structures observed by X-ray diffraction: BTO is almost cubic-like at  $d = 50$  nm. It should be mentioned that a  $d$ - $d$  excitation peak is clearly observed for  $d = 50$  nm [3] even in a cubic phase. The giant ferroelectricity may appear by the relative enhancement of Ti displacement in oxygen-octahedrons.

### References

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