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Soft X-ray emission study of $BaTiO_3$ nanoparticles

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Introduction

$BaTiO_3$ (BTO) is one of the most promising candidates for the host materials of next-generation high-density memory devices, because of its well-known strong ferroelectricity. BTO has a perovskite structure with Ti displacement from a body-center in tetragonal symmetry at room temperature. Recently, nano-sized BTO powders have been studied intensively. It has been reported that the dielectric constant of nano-BTO has a maximum at a certain diameter, several tens of nm, and rapidly reduces to zero with decreasing the size [1].

Ti in bulk BTO has nominally $3d^0$ configuration, but actually it is strongly mixed with a charge transferred $3d^1L^{-1}$ configuration by the covalency hybridization. In the case of nano-BTO, the crystal symmetry becomes higher (T_d•O_h) with decreasing the size, which was confirmed by X-ray diffraction. Then, what is the origin of enhanced ferroelectricity in nano-BTO? Does $3d^1L^{-1}$ configuration still remain in nano-BTO? We therefore measured soft X-ray emission (SXE) spectra in order to obtain the information of valence-band configuration.

Experimental

SXE spectra were obtained at beamline BL-2C. A soft X-ray monochromator consisting of a Rowland type grazing-incidence monochromator with a 5m spherical grating (1200 lines/mm) [2] was used. X-ray absorption spectra were obtained by the total electron yield (TEY) method. Energy resolutions of both TEY and SXE spectra at 450 eV were ~0.1 eV and ~0.4 eV, respectively.

BTO nano particles with averaged diameters (*D* nm) of *D*=30, 50, 85, 120 were prepared. All the experiments were carried out under room temperature and ultrahigh vacuum of the order of 10^{-9} Torr.

Results and Discussion

Figure 1 shows the Ti 2*p* TEY spectra of BTO(50nm). The assignments of main peaks are labeled in the figure. A vertical bar indicates excitation energy in the SXE spectra shown in Fig. 2, in which the spectra are plotted against the energy shift from elastic peaks (a dotted line). A dashed line indicates the Ti $L_{\beta1}$ fluorescence peaks. Vertical bars indicate *d*-*d* excitations. Statistical accuracy is rather low, however, a slight enhance of *d*-*d* excitations in *D*=85 and 50 were observed, which means that Ti displacement from the body center remains at *D*=50 even though crystal symmetry approaches to cubic. Therefore, displacement of Ti is a key role for the advent of strong ferroelectricity in nano-BTO.

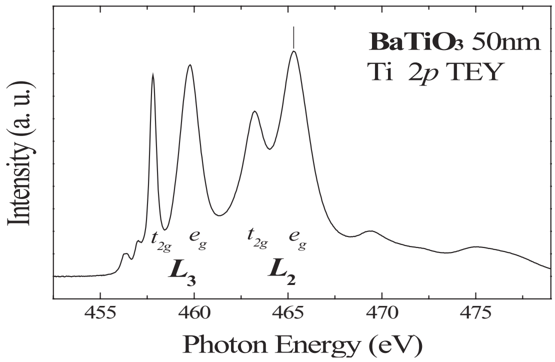

Fig. 1 TEY spectra of $BaTiO_3$(50nm) at Ti 2*p*-edge. The L_2-e_g edge is chosen for the excitation energy of SXE measurements shown in Fig. 2

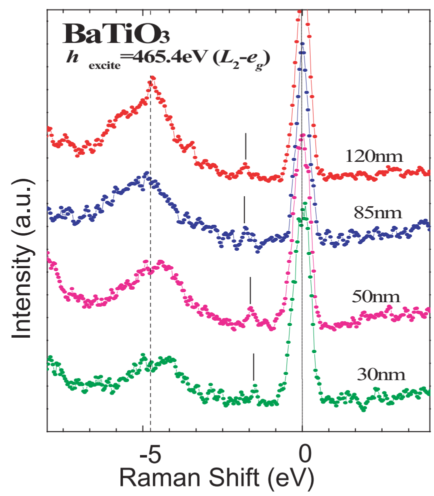

Fig. 2 SXE spectra of BTO(*D* nm) for *D*=120, 85, 50 and 30. The excitation energy is 465.4eV. A dotted and a dashed line indicate the elastic peaks and Ti $L_{\beta1}$ fluorescence peaks, respectively. Vertical bars indicate the *d*-*d* excitation peaks

References

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