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Characterization of local phases of BaTiO₃ ceramics by high-resolution electron energy loss spectroscopy

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The electrical features of BaTiO₃ ceramics have been known to be crucially determined by the crystal system of their grains. Therefore, it is important to identify the relation of the tetragonal-cubic phase transition with local structural and chemical conditions. The variation in the electron energy structure of BaTiO₃ in terms of phase transition has been reported by some theoretical research groups [1,2]. Nevertheless, little electron-beam-related experimental researches have been carried out to identify the energy band structure of BaTiO₃, which can be related with the tetragonal-cubic phase transition.

The BaTiO₃ ceramics used in this study was prepared by a routine-sintering method. The purity of BaTiO₃ powder was 99.8%. BaTiO₃ powders were die-pressed under 200 MPa. The powder compact was heat-treated at 1360°C in air for 4 h and then air-quenched to room temperature. To investigate the phase distribution within a nanoscale BaTiO₃ powder, ~50 nm-sized BaTiO₃ powders were prepared by the hydro-thermal method. In-situ X-ray diffraction examination was carried out to obtain structural information of the tetragonal and cubic phases of the ceramics. In-situ EELS measurements were also performed from a particular region in the sintered BaTiO₃ ceramic specimen; the tetragonal and cubic phase transition was induced by keeping the TEM specimen at particular temperatures in a heating stage. EELS spectra were acquired at room temperature and 150°C, respectively.

Conventional TEM investigation was carried out using an electron microscope operated at 300 keV (TITAN TM 80-300, FEI company). The electron probe diameter was below 1 nm. For the evaluation of the electronic structure of the BaTiO₃ ceramics, the energy-loss near-edge structure (ELNES) of Ti L_{2,3} were measured; the EELS measurement was carried out with the Gatan GIF 2002 system (parallel EELS).

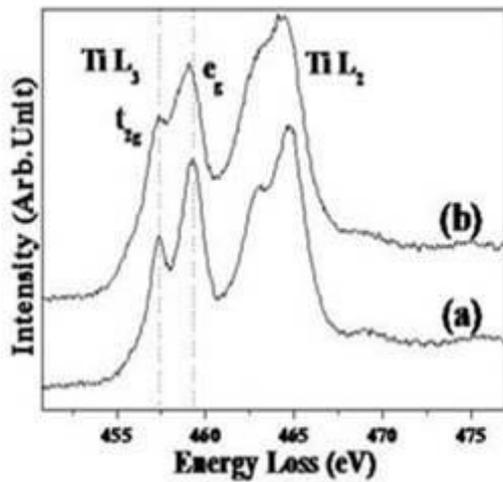
The crystal structure and lattice parameters of the BaTiO₃ ceramics were confirmed in terms of temperature; the calculated results are summarized in Table 1. In the XRD data, the cubic phase appears to have lattice parameters (a, b and c axis) larger than those for the tetragonal phase condition. It is expected that in BaTiO₃, crystal field effect is stronger in a tetragonal phase than in a cubic phase. It was found that the fine structure of the titanium L_{2,3} edge and their satellite peaks are sensitively varied with the tetragonal-cubic phase transition. Figure 1 shows the spectra taken from the tetragonal and cubic phases of BaTiO₃ ceramic; spectra (a) and (b) were obtained from the same region of BaTiO₃ ceramic specimen at room temperature and 150°C, respectively. The peak splitting of Ti L₃ edge of tetragonal-phased BaTiO₃ ceramics was widened due to the increased crystal field effect compared to that of cubic-phased BaTiO₃. The satellite peaks were also shifted to higher energies by about 0.8 eV for tetragonal-phased BaTiO₃ with respect to the cubic-phased BaTiO₃ ceramics.

The phase distribution within nanoscale BaTiO₃ powders, in other words, the presence of tetragonal (or cubic) phases in terms of the distance from the surface was investigated by EELS techniques. Figure 2 shows the spectra recorded at positions 1, 4, 7 and 20 nm, away from the surface, respectively, in the BaTiO₃ powders. All the spectra are aligned such that the maximum of the first peak (Ti L₃ t_{2g} peak) is located at the same value in the spectra and these are denoted by vertical dotted lines. The L₃ edge splitting of the core region was found to be little smaller than that of shell region. In particular, the energy gap between the two peaks t_{2g} and e_g varied significantly with changing the distance between the probed position and the surface from 1 to 20 nm. These results suggest that EELS technique can be used to identify the local phase of sintered BaTiO₃ ceramic.

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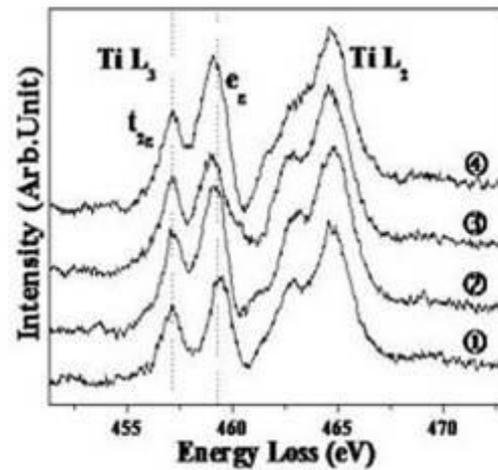
	25 °C	150 °C
a (Å)	3.9924	4.0459
b (Å)	3.9924	4.0459
c (Å)	4.0309	4.0459
c/a	1.009	1
Space group	P4mm	Pm3m

Table 1. Lattice parameters of BaTiO₃ ceramics. These values were obtained when the ceramics were at room temperature and 150°C, respectively.



(Figure 1)

Figure 1. EELS spectra of Ti L_{2,3} edge of BaTiO₃ ceramics. The ceramics were at room temperature (a) and 150°C (b), respectively.



(Figure 2)

Figure 2. EELS spectra of Ti L_{2,3} edge of nanoscale BaTiO₃ powders. (a) The EELS measurements were carried out at positions 1(①), 4(②), 7(③) and 20 nm(④) away from the surface, respectively.