Identification of Local Phase of Nanoscale BaTiO₃ Powders by High-Resolution Electron Energy Loss Spectroscopy

Sun-Min Moon,¹ Xiaohui Wang,² and Nam-Hee Cho^{1,*}

¹Department of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

²Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Abstract: The electron energy loss spectroscopy (EELS) technique was applied to investigate the local variation in the phase of barium titanate (BaTiO₃) ceramics. It was found that the fine structure of the titanium L_{2,3} edge and their satellite peaks were sensitively varied with the tetragonal–cubic phase transition. The peak splitting of Ti-L₃ edge of tetragonal-phased BaTiO₃ ceramics was widened because of the increased crystal field effect compared with that of cubic-phased BaTiO₃. In case of nanoscale BaTiO₃ powders, the L₃ edge splitting of the core region was found to be smaller than that of the shell region. The energy gap between peaks t_{2g} and e_g varied from 2.36 to 1.94 eV with changing the probe position from 1 to 20 nm from the surface. These results suggest that the EELS technique can be used to identify the local phase of sintered BaTiO₃ ceramics.

Key words: BaTiO₃, phase, EELS, nanopowder, tetragonal, cubic

INTRODUCTION

Barium titanate (BaTiO₃) ceramics are one of the most popular ferroelectric materials with the perovskite structure. It has been widely used in various electronic devices such as multilayer capacitors, infrared detectors, fuel evaporators, varistors, and electro-optic devices for their unique and useful electrical characteristics (Cao & Brinker, 2008).

It has been known that BaTiO₃ has four different kinds of crystal structures such as rhombohedral, orthorhombic, tetragonal, and cubic phases depending on temperature. In particular, its unit cell is of the cubic phase above Curie temperature (~120°C); this condition has nonpolar characteristics. Below the Curie temperature, the unit cell is slightly distorted to have the tetragonal phase; its dipole is parallel to its <001> direction (Smolenskii et al., 1984). In case of nanoscale BaTiO₃ ceramics, some researchers have suggested that a single crystalline particle consists of both tetragonal and cubic phases (Wada et al., 2007).

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 conditions. The variation in the energy band structure of BaTiO₃ in terms of phase transition has been reported by some theoretical research groups (Bagayoko et al., 1998). There has also been considerable progress in achieving better understanding of the lattice dynamics and the origin of the ferroelectricity from first principle total-energy calculations. It has been reported that Ti–O hybridization is essential to understand the ferroelectric instability in BaTiO₃ ceramics (Cohen & Hrakauer, 1990, 1992; Yu & Krakauer, 1994). 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.

In this study, we have examined the variation in the energy band structure associated with the tetragonal–cubic phase transition in BaTiO₃ by using the electron energy loss spectroscopy (EELS) technique. The electron energy structure of BaTiO₃ ceramics includes the fine details of titanium L_{2,3} edge and their satellite peaks, and these were examined by EELS and/or scanning transmission electron microscopy (STEM) methods. The crystal structure and ferroelectric transition-related information were also obtained by *in situ* X-ray diffraction, and these were related with the EELS results.

EXPERIMENTAL PROCEDURE

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 1,360°C in air for 4 h and then air-quenched to room temperature.

We carried out an *in situ* X-ray diffraction examination 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 transmission electron microscopy (TEM) specimen at particular temperatures in a heating stage. EELS spectra were acquired at room temperature and 150°C, respectively.

To investigate the phase distribution within a nanoscale BaTiO₃ powder, 50-nm-sized BaTiO₃ powders were prepared by the hydrothermal method. Ba(OH)₂·8H₂O and Ti(OH)₄·xH₂O were used as source materials, and the synthesis was carried out at 180°C for 6 h. The details of the synthesis process were reported previously (Moon & Cho, 2009).

Table 1. Lattice Parameters of BaTiO₃ Ceramics.*

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

*Values were obtained when the ceramics were at room temperature and 150°C, respectively.

TEM specimens were prepared by ion milling with 6-keV-Ar⁺ ions; the incident angle was kept at 6°. Conventional TEM investigation was carried out using an electron microscope operated at 300 keV (Titan TM 80-300, FEI company). The EELS measurement was carried out with the Gatan GIF 2002 system (parallel EELS). The electron probe diameter was below 1 nm. The energy resolution at the zero-loss peak was ~0.6 eV. For the evaluation of the electronic structure of the BaTiO₃ ceramics, the energy-loss near-edge structure of Ti-L_{2,3} were measured. The spectra were acquired by the STEM mode; the aperture size and energy dispersion were 2 nm and 0.1 eV/channel, respectively.

RESULTS AND DISCUSSION

We confirmed the crystal structure and lattice parameters of the BaTiO₃ ceramics in terms of temperature by using the X-ray diffraction (XRD) method. The calculated results are summarized in Table 1. In the XRD data, the cubic phase appears to have lattice parameters (*a*, *b*, and *c* axes) 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.

A TEM bright-field image of BaTiO₃ ceramic is shown in Figure 1a. Figure 1b gives the selected area diffraction pattern taken from the BaTiO₃ ceramic (Fig. 1a) with the

incident electron beam parallel to the [001] direction. The sharp reflections confirm that the BaTiO₃ ceramic is a high-quality single crystal.

In order to estimate the thickness (*T*) of the specimen, we used the following log-ratio method (Moon & Cho, 2009)

$$T = \lambda \ln(I_t/I_0),$$

where *I*₀ is the sum of zero-loss peak counts, *I*_t is the sum of total spectrum counts (zero-loss peak plus extrapolated loss part), and *λ* is the inelastic mean free path. The calculation provides the specimen thickness of about 5.8 nm; the specimen was thin enough to be used for characterizing the BaTiO₃ ceramic by EELS experiment (Egerton, 1986).

The ferroelectric properties of BaTiO₃ ceramics are closely related to the distortion of the octahedron consisting of oxygen atoms (Cohen & Hrakauer, 1990, 1992; Yu & Krakauer, 1994). The density distribution of unoccupied electronic states of the Ti atoms is sensitively affected by the short-range coordination with oxygen atoms. The four well-split peaks in the Ti-L_{2,3} edges are attributed to the excitation of electrons in 2*P*_{3/2} and 2*P*_{1/2} subshells to unoccupied *t*_{2g} and *e*_g states (Leapman & Grunes, 1980). As a consequence, the position, full-width at half-maximum, and shapes of the Ti-L_{2,3} peaks are dependent on the variation of the short-range coordination, in other words the phase types of the lattice (Thole & Laan, 1988).

Figure 2 shows the spectra taken from the tetragonal and cubic phases of BaTiO₃ ceramic; spectra (a) and (b) were obtained from the same region in Figure 1a at room temperature and 150°C, respectively. Both spectra are aligned so that the maximum position of the first peak (Ti-L₃ *t*_{2g} peak) is located at 457.5 eV; the maximum of the peaks are denoted by vertical dotted lines. The crystal-field splitting of the cubic-phased BaTiO₃ ceramic is a little smaller with respect to that of tetragonal-phased BaTiO₃ ceramic. This energy gap of ~0.4 eV can be attributed to the difference in the lattice type and parameters; the variation in the octa-

Figure 1. **a:** Bright-field transmission electron microscopy image of the BaTiO₃ ceramics. **b:** Selected area diffraction pattern of the BaTiO₃ ceramic. The pattern was recorded with the electron beam parallel to [001].

Figure 2. Electron energy loss spectroscopy spectra of Ti- $L_{2,3}$ edge of BaTiO₃ ceramics. The ceramics were at room temperature (a) and 150°C (b), respectively.

hedron with the phase transition results in the change in the Ti–O bond length. It has been reported that the shorter Ti–O bond length leads to a stronger crystal field, which finally results in the larger crystal-field splitting (Zhang et al., 2005). Consequently, in Figure 2 we noticed the variation of electron energy structure in the BaTiO₃ ceramic samples with tetragonal–cubic phase transitions.

Two satellite peaks are present above the near-edge peaks; these were confirmed by multipeak Lorentzian fitting (Fig. 3). The coefficient of determination (R^2) of the fitting is >0.98 in this work; this indicates that the Lorentzian function is a reasonable model for the separation of satellite peaks. These satellite peaks are attributed to the transfer of electrons from the O 2*p* valence band to the unoccupied Ti 3*d* orbital in the intermediate state of EELS processes. The satellites are shifted to lower energies by about 0.8 eV for the cubic-phased BaTiO₃ with respect to the tetragonal-phased BaTiO₃ ceramics. This implies that the longer inter-atomic distance leads to a less interaction between O 2*p* and Ti 3*d* states. In other words, cubic phase with the longer neighbor atoms (Ti–O) bond length leads to the weaker crystal field; as shown in Figure 3, the cubic phase has the satellite positions of 468.09 and 475.51 eV. These are lower than the positions for the satellites at 468.85 and 475.68 eV shown in Figure 3a.

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 4a shows the size and shape of the nanoscale BaTiO₃ powders prepared by hydrothermal synthesis methods. Most of the powders were confirmed to be of a single crystallite as illustrated in Figure 4b. The average size of the powders was about 46 nm, and appeared to have high crystallinity. Figure 4c shows the spectra taken at positions 1, 4, 7, and 20 nm away from the surface, respectively, in 50-nm-sized BaTiO₃ powders. All the spectra are aligned such that the maximum of the first peak (Ti- L_3 t_{2g} peak) is located at the same value in the spectra and these are denoted by vertical dotted lines. The energy gap between the two peaks of L_3 t_{2g} and e_g were 2.36,

Figure 3. Satellites peaks of Ti- L_2 edge of BaTiO₃ ceramics. The ceramics were at room temperature (a) and 150°C (b), respectively.

2.01, 1.96, and 1.94 eV for the positions at 1, 4, 7, and 20 nm away from the surface, respectively (Fig. 4d).

In other words, the crystal-field splitting gradually decreased from a shell region to a core region in the nanoscale BaTiO₃ particle. This result indicates that nanoscale BaTiO₃ particles consist of a tetragonal phase in the surface region and a cubic phase in the core region, respectively. These results appear to agree well with the fact that the shell is dominantly composed of the tetragonal phases, whereas the inner region of cubic phases, which were previously verified high-resolution transmission electron microscopy techniques (Moon & Cho, 2007).

CONCLUSION

The EELS technique was applied to investigate the local variation in the electronic structure associated with the tetragonal–cubic transition of BaTiO₃ ceramics. 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. The peak splitting of Ti- L_3 edge of tetragonal-phased BaTiO₃ ceramics was widened because of the increased crystal field effect compared with that of

Figure 4. Electron energy loss spectroscopy (EELS) spectra of Ti- $L_{2,3}$ edge of nanoscale BaTiO_3 powders. **a:** Bright-field transmission electron microscopy images of the as-prepared nanoscale BaTiO_3 powders. **b:** Microelectron diffraction pattern of the nanoscale powders. **c:** The EELS measurements were carried out at positions 1(①), 4(②), 7(③), and 20 nm(④) away from the surface, respectively. **d:** The energy gap between the two peaks t_{2g} and e_g varies from 2.35 to 1.95 eV as the distance between the probed position and the surface varies from 1 to 20 nm.

cubic-phased BaTiO_3 . In addition, the satellites were shifted to higher energies by about 0.8 eV for tetragonal-phased BaTiO_3 with respect to the cubic-phased BaTiO_3 ceramics.

In case of nanoscale BaTiO_3 powders, the L_3 edge splitting of the core region was found to be a little smaller than that of the shell region. In particular, the energy gap between the two peaks t_{2g} and e_g varied from 2.36 to 1.94 eV with changing the distance between the probed position and the surface from 1 to 20 nm. It is highly likely that the shell region of the nanoscale BaTiO_3 powders is of a tetragonal phase, whereas a cubic phase in the core region. These results also suggest that the EELS technique can be used to identify the local phase of sintered BaTiO_3 ceramic.

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REFERENCES

- BAGAYOKO, D., ZHAO, G.L., FAN, J.D. & WANG, J.T. (1998). *Ab initio* calculations of the electronic structure and optical properties of ferroelectric tetragonal BaTiO_3 . *J Phys: Condens Matter* **10**, 5645–5655.
- CAO, G. & BRINKER, C.J. (2008). *Annual Review of Nano Research*. Singapore, London: World Scientific Publishing Co.
- COHEN, R. & HRAKAUER, H. (1990). Lattice dynamics and origin of ferroelectricity in barium titanate (BaTiO_3): Linearized-augmented-plane-wave total-energy calculations. *Phys Rev* **B42**, 6416–6423.
- COHEN, R. & HRAKAUER, H. (1992). Electronic structure studies of the differences in ferroelectric behavior of barium titanate and lead titanate (PbTiO_3). *Ferroelectrics* **136**, 65–83.
- EGERTON, R.F. (1986). *Electron Energy-Loss Spectroscopy in the Electron Microscope*. New York, London: Plenum Press.
- LEAPMAN, R.D. & GRUNES, L.A. (1980). Anomalous L_3/L_2 white-line ratios in the 3d transition metals. *Phys Rev Lett* **45**, 397–401.
- MOON, S.-M. & CHO, N.-H. (2007). Size effects on the crystal structure of nanoscale BaTiO_3 powders prepared by hydrothermal synthesis. *Met Mat Int* **13**, 329–333.
- MOON, S.-M. & CHO, N.-H. (2009). Investigation of phase distribution in nanoscale BaTiO_3 powders prepared by hydro-thermal synthesis. *J Electroceram* **23**, 121–126.
- SMOLENSKII, G.A., BOKOV, V.A., ISUPOV, V.A., KRAINIK, N.N., PASYNKOV, R.E. & SOKOLOV, A.I. (1984). *Ferroelectrics and Related Materials*. New York, London, Paris, Montreux, Tokyo: Gordon and Breach Science Publishers.
- THOLE, B.T. & LAAN, G. (1988). Branching ratio in X-ray absorption spectroscopy. *Phys Rev* **B38**, 3158–3171.
- WADA, S., HOSHINA, T., TAKIZAWA, K., OHISHI, M., YASUNO, H., KAKEMOTO, H. & TSURUMI, T. (2007). Origin of ultrahigh dielectric constants for barium titanate nanoparticles. *J Kor Phys Soc* **51**, 878–881.
- YU, R. & KRAKAUER, H. (1994). Linear-response calculations within the linearized augmented plane-wave method. *Phys Rev* **B49**, 4467–4477.
- ZHANG, Z., VISINIOU, A., HEYROTH, F., SYROWATKA, F., ALEXE, M., HESSE, D. & LEIPNER, H.S. (2005). High-resolution electron energy-loss spectroscopy of $\text{BaTiO}_3/\text{SrTiO}_3$ multilayers. *Phys Rev* **B71**, 064108-1–064108-7.