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Insights into Degradation Mechanisms and Vacancy Ordering in $BaTiO_3$

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$BaTiO_3$ is widely used in commercial ceramic capacitors. As one of the most interesting structural defects in perovskite oxides, oxygen vacancies in $BaTiO_3$ have long been known to be responsible for many experimentally observed electrical behaviors [1]. The extent of oxygen deficiency can be controlled by processing the oxide in a reducing atmosphere or/and by doping. The ABO_3 perovskites, in general, show a strong ability to tolerate a large number of oxygen vacancies while maintaining their basic structure even at high defect concentrations. The potential impact of oxygen nonstoichiometry in capacitor degradation has stimulated us to research the defect structure of base metal electrode (BME) multilayer ceramic capacitors (MLCCs) after the devices were degraded under an applied DC voltage. Here we present a first report of modulated and long-range ordered structures of $BaTiO_3$ that are associated with oxygen deficiency in the perovskite. These studies provide unprecedented microstructural insight into the electrical degradation mechanisms in $BaTiO_3$ capacitors.

Commercial BME ($BaTiO_3$/Ni) capacitors were electrically degraded under applied voltage of 1-5 V at 325 °C in N_2. The microstructure was investigated using a 200 kV transmission electron microscope equipped with a field emission gun (JEOL 2010F) and a parallel electron energy-loss spectrometer (Gatan Enfina PEELS).

Electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) revealed three states of $BaTiO_3$ defect structures: traditional tetragonal perovskite structure, modulated and long-range ordered structures. Figure 1 shows HRTEM images of the modulated and long-range ordered structure, which were found only in the electrically degraded samples. The inserts are the corresponding electron diffraction patterns, which were indexed as the $[1\bar{1}0]$zone axis of the tetragonal perovskite. The appearance of satellite spots in the electron diffraction pattern in fig. 1(a) is associated with the modulation in structure and/or microchemistry of the $BaTiO_3$. Since the satellites are in the <111> directions, the structural modulation occurred in the {111} planes of the $BaTiO_3$ grain, which is clearly evidenced by the periodic-like variations in contrast of the HRTEM image. The periodicity is 8-10 d_{111}. In figure 1 (b), a long-range ordered structure with a periodicity of $3d_{111}$ was revealed by the presence of the superlattice reflections in the inserted electron diffraction pattern. The long range ordering is clearly shown in the HRTEM image.

Figure 2 shows the differences in the EELS obtained from the $BaTiO_3$ regions of traditional tetragonal perovskite, modulated and ordered structures. All the spectra are normalized to the continuum interval 25 eV before the onset of the oxygen K edge (532 eV) and offset for clarity. Evidence for the excess oxygen vacancies in the regions with modulated and ordered structures come from a shift in the Ti $L_{2,3}$ edge of about 1 eV down in energy and an increase in the integrated Ti:O intensity ratios. Noticeable changes in the oxygen k-edge fine structure are also apparent, which are currently being analyzed.

These experimental results show that the modulated and long-range ordered structures were formed from severe oxygen deficiencies, which were electrochemically induced in the $BaTiO_3$ with applied external fields. The oxygen vacancies are compensated by a decrease in the Ti valence, implying that electrical degradation is accelerated by the Ti reduction in BME multilayer ceramic capacitors. These HRTEM and EELS results will be discussed in relation to AC electrical property measurements of the pristine and electrically degraded capacitors.

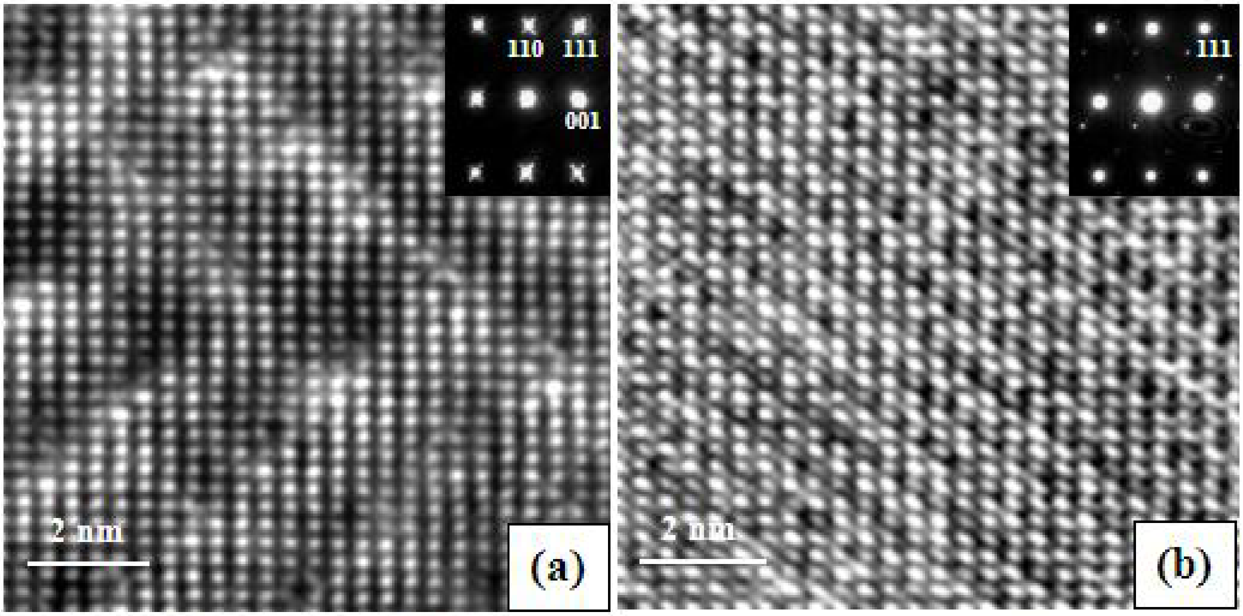

Figure 1. High resolution TEM images of modulated (a) and long range ordered (b) structure of $BaTiO_3$ processed in reducing atmosphere

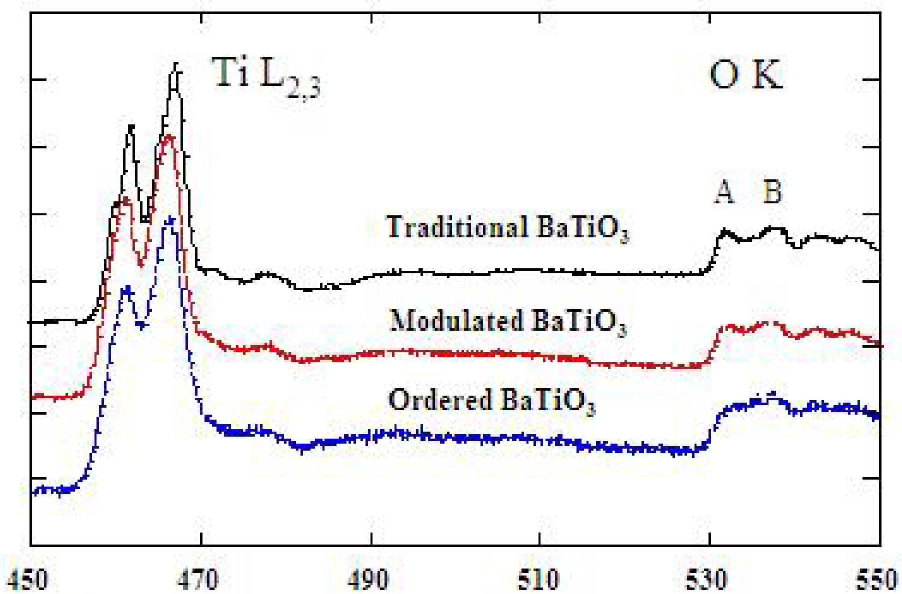

Figure 2. EELS from the $BaTiO_3$ of tetragonal perovskite, modulated and ordered structure showing the shift in Ti L edges, relative lower count rate under peak A for O K edge.

Reference:
1. H. Chazono and H. Kishi, Jpn. J. Appl. Phys, 40, 5624 (2001).

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