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HRTEM Study of a New Non-Stoichiometric $BaTiO_{3-\delta}$ Structure

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$BaTiO_3$-based multilayer ceramic capacitors (MLCCs) with Ni internal electrodes are co-fired in reducing atmospheres to avoid oxidation of the electrode. Although dielectric materials are doped by acceptor, donor and amphoteric dopants to minimize the oxygen vacancy content, there is still a large concentration of oxygen vacancies that are accommodated in the $BaTiO_3$ active layers. In general, ABO_3 perovskites demonstrates a strong ability to accommodate the oxygen vacancies and maintain a regular pseudo-cubic structure. Oxygen deficient barium titanate can be transformed to a hexagonal polymorph (h-BT) at high temperatures[1,2]. In this paper, we report the new modulated and long range ordered structures of non-stoichiometric $BaTiO_{3-\delta}$ that are observed in the electrically degraded Ni-$BaTiO_3$ MLCCs at low temperature.

The Ni-$BaTiO_3$ MLCCs are produced by co-firing $BaTiO_3$ dielectric layers with Ni internal electrodes at ~ 1300 °C in a PO_2 of ~ 10^{-10} atm followed by an reoxidation process at ~ 800 °C in a PO_2 of ~ 10^{-8} atm. The capacitors are intentionally electrically degraded during the highly-accelerated life test (HALT) at 140C under a 400 V d.c. field stress. TEM observations are performed using a JEOL 2010F transmission electron microscope equipped with a field-emission gun operated at 200 kV. The preliminary modelling is carried using Carine Crystallography 3.1 software. High resolution image and electron diffraction are simulated using MAC Tempas software.

Figure 1(a) is a HRTEM image of $BaTiO_{3-\delta}$ where δ is about 0.33 and figure 1 (b) is the EEL spectra obtained from the regions with and without the modulated defects. The δ value is determined using electron energy-loss spectroscopy (EELS)[3]. The insert is the corresponding electron diffraction pattern that is indexed as the $[10\bar{1}]$ zone axis. There are satellites in addition to the basic reflections of pseudo-cubic $BaTiO_3$. The satellites are associated with the network-like changes in image intensity due to the modulation in microstructure and/or microchemistry in the $BaTiO_3$ lattice. These modulations are regularly spaced with the intervals from 8 to 10 inter-planar distances of {111} planes. Furthermore, the superlattice reflections are observed in the electron diffraction patterns taken from some adjacent areas, indicating superstructure reflections at $\pm\frac{1}{3}(hkl)$ positions and the associated HRTEM images indicate contrast consistent with a tripling of the unit cell in a <111> direction, as shown in figure 2 (a) and (b). These modulated structures and long range ordering in {111} planes of $BaTiO_{3-\delta}$ are thought to be associated with the distribution of O vacancies. The simplest charge compensation for the oxygen vacancies results in a 2:1 Ti^{3+}:Ti^{4+} ratio and a formula, $Ba(Ti^{4+}_{\frac{1}{3}}Ti^{3+}_{\frac{2}{3}})O_{2.67}$, is proposed which assumes that the oxygen vacancies are ordered on every 3rd {111} plane. The structure of the $Ba(Ti^{4+}_{\frac{1}{3}}Ti^{3+}_{\frac{2}{3}})O_{2.67}$ is inserted in figure 2 (a). Simulations of the <110> zone axis diffraction pattern (Figure 2 c) and HRTEM image match well with experimental observations. The reduction in the valence state of the Ti cations plays an important role in the degradation of insulation resistance of the dielectrics in degraded Ni-$BaTiO_3$ MLCCs.

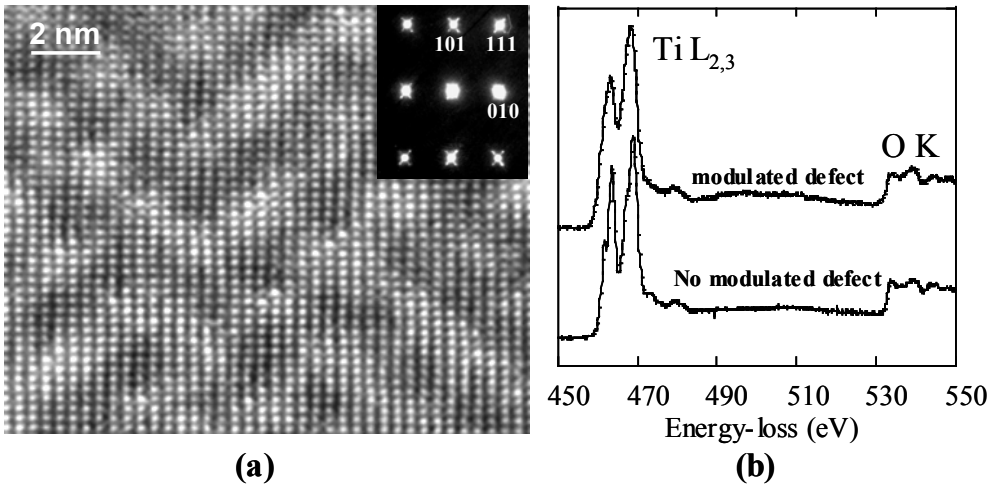

Figure 1. HRTEM image of modulated structure in non-stoichiometric $BaTiO_{3-\delta}$. The satellites appearing around the basic reflection of regular $BaTiO_3$ in the inserted electron diffraction pattern.

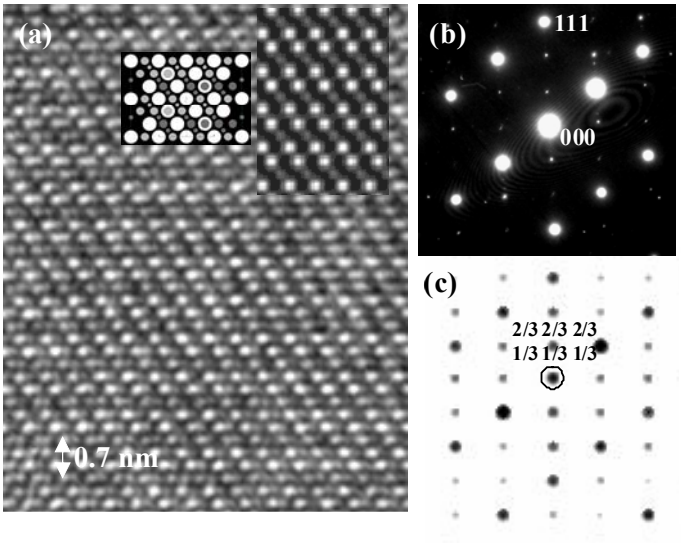

Figure 2. (a) HRTEM image with inset simulation and structure model of $Ba(Ti^{4+}_{1/3}Ti^{3+}_{2/3})O_{2.67.}$ (b) Electron diffraction pattern obtained along the <110> zone axis. **(c)** The simulation of the diffraction pattern showing tripling of the unit cell along the [111] direction**.**

Acknowledgments

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