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HRTEM Study of a New Non-Stoichiometric BaTiO_{3-δ} Structure

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BaTiO₃-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 BaTiO₃ active layers. In general, ABO₃ 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-δ} that are observed in the electrically degraded Ni-BaTiO₃ MLCCs at low temperature.

The Ni-BaTiO₃ MLCCs are produced by co-firing BaTiO₃ dielectric layers with Ni internal electrodes at ~ 1300 °C in a PO₂ of ~ 10⁻¹⁰ atm followed by an reoxidation process at ~ 800 °C in a PO₂ 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-δ} 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 BaTiO₃. The satellites are associated with the network-like changes in image intensity due to the modulation in microstructure and/or microchemistry in the BaTiO₃ 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-δ} are thought to be associated with the distribution of O vacancies. The simplest charge compensation for the oxygen vacancies results in a 2:1 Ti³⁺:Ti⁴⁺ ratio and a formula, Ba(Ti⁴⁺_{1/3}Ti³⁺_{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(Ti⁴⁺_{1/3}Ti³⁺_{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-BaTiO₃ MLCCs.

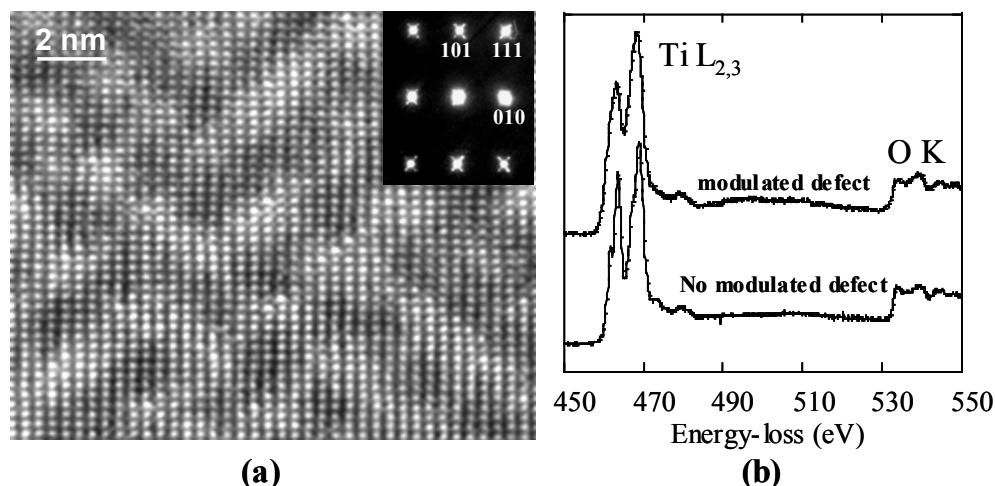


Figure 1. HRTEM image of modulated structure in non-stoichiometric $\text{BaTiO}_{3-\delta}$. The satellites appearing around the basic reflection of regular BaTiO_3 in the inserted electron diffraction pattern.

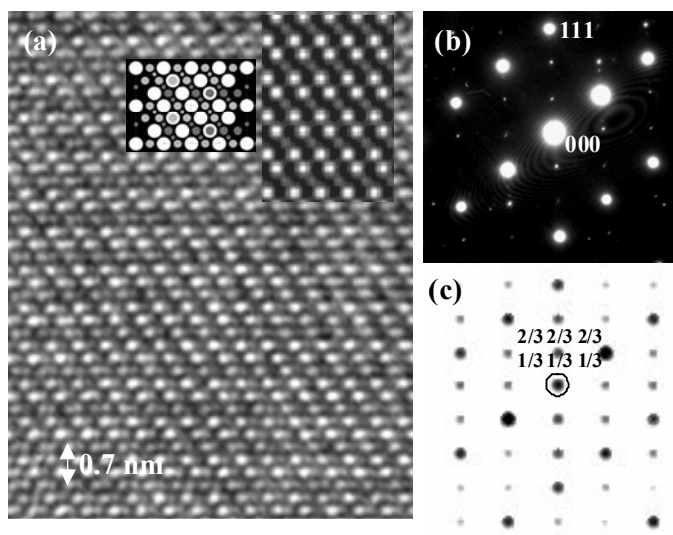


Figure 2. (a) HRTEM image with inset simulation and structure model of $\text{Ba}(\text{Ti}^{4+}_{1/3}\text{Ti}^{3+}_{2/3})\text{O}_{2.67}$. (b) Electron diffraction pattern obtained along the $\langle 110 \rangle$ zone axis. (c) The simulation of the diffraction pattern showing tripling of the unit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

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