

B-site Cation Ordering in Ba₃MnNb₂O₉ by Atomic Resolution HAADF-STEM and Their Valence State by EELS

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Perovskite-related transition metal oxides are among the most intriguing material systems in the field of solid state chemistry and physics. Their physical properties are significantly affected by the changes in chemistry and crystal structure, which is brought about by B-site cation ordering or disordering. The cation ordering of these perovskites affects their dielectric properties and magnetic ground states. It has been shown that dielectric properties strongly depend on B-site ordering [1]. Ba₃MnNb₂O₉ is one of the magnetically and geometrically frustrated materials, which has attracted intense research interests in recent years since the inherent spin structure of these materials exhibits new and unusual magnetic phases [2]. Accurate knowledge of the microstructures and atomic ordering of this material lead to clear understanding of its physical properties, such as its magnetic properties or magnetic ground state.

In this paper, we use atomic resolution high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) imaging technique to study the order/disorder of Mn and Nb in Ba₃MnNb₂O₉ samples, a polycrystalline sample synthesized by solid state reaction, and a single crystal samples grown by optical floating zone (OFZ) method. We use electron-energy-loss spectroscopy (EELS) core-loss spectrum to investigate the electronic structure and B-site cation valence [3]. In this paper, we study two types of samples, STEM study was carried out on a probe-aberration-corrected, cold-field-emission JEM JEOL-ARM200cF at 200 kV, equipped with a JEOL HAADF-STEM detector and a Gatan GIF Quantam963 with DualEELS capability. The STEM resolution is 0.078 nm, and energy resolution is 0.5 eV at full emission.

The best orientation to check the B-site ordering is to view along $\langle 110 \rangle_c$ of the cubic perovskite unit cell, where the *c* means the indexing from a cubic cell. In this projection, the B-site atoms, Mn and Nb, are sandwiched between the Ba atomic planes. The HAADF-STEM Z-contrast image of ordered crystal shows distinctly alternating low-high-high intensity, where Mn is the lowest intensity columns, and Nb columns have higher intensity (Fig. 1a). An intensity profile of this atomic plane (insets) confirms very clearly the ...-Mn-Nb-Nb-... ordering. A new type of B-site ordering is shown in Fig. 1c, where the intensity profile of Mn-Nb plane has a low and a high alternating intensity variation. This new ordering also reflected in the FFT diffraction pattern with one superlattice spot at $\frac{1}{2}\{111\}_c$ (Fig. 1d). This new type of b-site cation has 1Mn:1Nb ordering, ...-Mn-Nb-Mn-Nb-...

Mn valence in oxides has been extensively studied using its white-lines, L₂ and L₃ [4]. In addition to the effect of background window width and position on the L_{2,3} relative peak height, sample thickness also influences the relative L_{2,3} peak heights, as shown in Fig. 2a. Even after exactly the same background subtraction and plural scattering removal, as shown in Fig. 2b, two Mn L_{2,3} core-loss spectra taken from the same crystal shows peak height difference when normalized to L₂ peak. Their relative peak height difference should not be used as evidence for valence change if the difference of their intensity ratio is

within statistical error. As shown in Fig. 2c, the $L_{2,3}$ white line ratio of Mn in these oxides has larger value than that of typical MnO due to the contributed Nb^{5+} electrons [5].

References:

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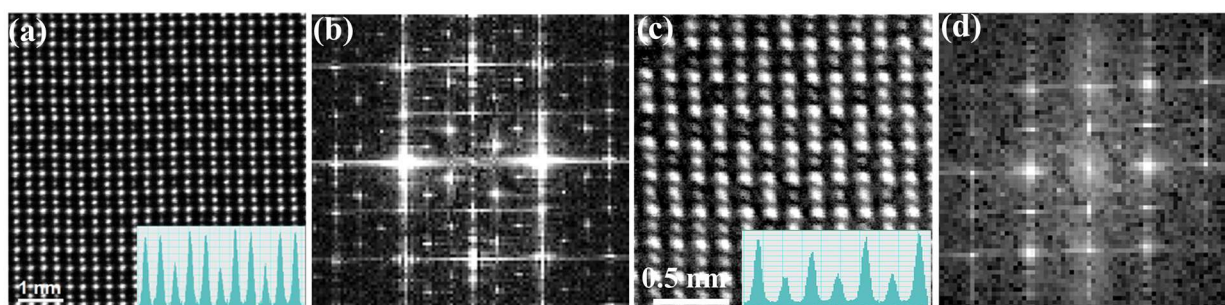


Figure 1. (a) HAAD-STEM image of a 1Mn:2Nb ordered phase in $Ba_3MnNb_2O_9$; (b) FFT of (a); (c) HAADF-STEM image of a 1Mn:1Nb ordered phase; (d) FFT of (c)

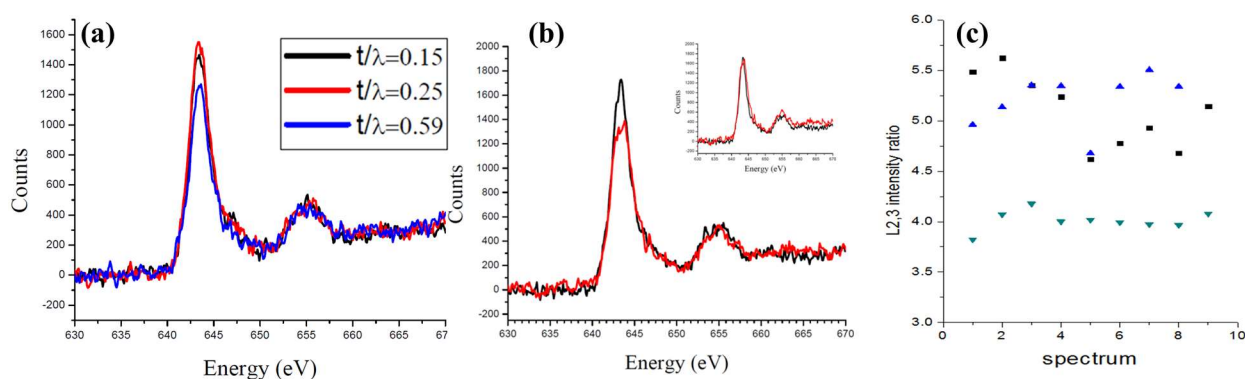


Figure 2. (a) Mn $L_{2,3}$ core-loss spectrum from different sample thickness; (b) two normalized Mn $L_{2,3}$ spectra from the same crystal region; inset: the same spectra normalized to L_2 ; (c) Mn $L_{2,3}$ white line intensity ratio of 9 spectra taken from the same crystal for both phases compared to that of MnO(green).