

## High Resolution EELS Investigation Of Hexagonal Transition Metal Perovskites

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It is well established that the substitution of Ti in BaTiO<sub>3</sub> to give Ba<sub>3</sub>Ti<sub>2</sub>MO<sub>9</sub>, where M= Ti<sup>3+</sup>, V, Cr, Mn, Fe, Co, Ru, Rh, Ir, Pt, can stabilise the high temperature 6H hexagonal structure at room temperature [1]. The work presented here is a comparative study of the structure and bonding in two of these compounds, Ba<sub>3</sub>Ti<sub>2</sub>RuO<sub>9</sub> and Ba<sub>3</sub>Ti<sub>2</sub>MnO<sub>9</sub>, with a view to understanding their structure-property relationships and the mechanism by which the 6H structure is stabilized at room temperature. Using convergent beam electron diffraction (CBED) we have shown that the space group of both compounds is the non-centrosymmetric P6<sub>3</sub>mc [2]. In this paper, we report the results so far of our investigation into the bonding of these and related compounds using high resolution electron energy loss spectroscopy (HREELS).

Experiments were performed on the world's first commercial monochromated field emission gun transmission electron microscope [3] with a high-resolution electron energy loss spectrometer [4]. The nominal energy resolution of 0.1eV combined with an electron probe diameter of less than 2nm, permits the detection of fine features in the near edge structure of the EEL spectrum from small volumes of specimen. This enables us to probe electronic structure effects from nanoscale specimen volumes.

Using this instrument, we have observed the different electronic configurations of the Ru and Mn ions in Ba<sub>3</sub>Ti<sub>2</sub>RuO<sub>9</sub> and Ba<sub>3</sub>Ti<sub>2</sub>MnO<sub>9</sub> by examining the O-K edge (FIG. 1) in their EEL spectra. A striking difference is evident in the intensity of the band covering the transition metal t<sub>2g</sub>-O2p hybrid states in these otherwise very similar spectra. The hybrid Mn t<sub>2g</sub>-O2p is present as a small shoulder on the O-K edge onset in Ba<sub>3</sub>Ti<sub>2</sub>MnO<sub>9</sub> but the Ru t<sub>2g</sub>-O2p hybrid appears to be in the same energy range as the Ti t<sub>2g</sub>-O2p energy level in the Ba<sub>3</sub>Ti<sub>2</sub>RuO<sub>9</sub> compound. Mn is expected to be in 4+ oxidation state with a high spin configuration with 3 d electrons in the t<sub>2g</sub> sublevel and Ru<sup>4+</sup> is low spin with 4 d electrons in the t<sub>2g</sub> sublevel. The different occupancies in the t<sub>2g</sub> lead to a greater transition probability into the Mn t<sub>2g</sub>-O2p band. These results are consistent with a crystal field theory interpretation of Ru and Mn ions in a perfect oxygen octahedral field.

We have also observed that the distortion of the oxygen octahedra surrounding the Ti ions in Ba<sub>3</sub>Ti<sub>2</sub>MnO<sub>9</sub>, Ba<sub>3</sub>Ti<sub>2</sub>RuO<sub>9</sub> and tetragonal BaTiO<sub>3</sub> is highly comparable. This is indicated by the consistency of the relative heights and widths of the t<sub>2g</sub> and e<sub>g</sub> peaks between all three spectra on the Ti L<sub>2,3</sub> edges (FIG. 2). The octahedral configuration of the oxygen atoms around the Ti atoms breaks the Ti d orbital degeneracy into two sublevels, t<sub>2g</sub> and e<sub>g</sub> through hybridisation. The width of the e<sub>g</sub> peak on the Ti L<sub>2,3</sub> edge thus reflects the octahedral distortion around the Ti ion. This observation supports the suggestion that the 6H structure is stabilised at room temperature due to the distortion of the octahedral symmetry of the face sharing octahedra.

Density functional theory calculations, using the Wien 2k code, of the O-K edges will also be presented here.

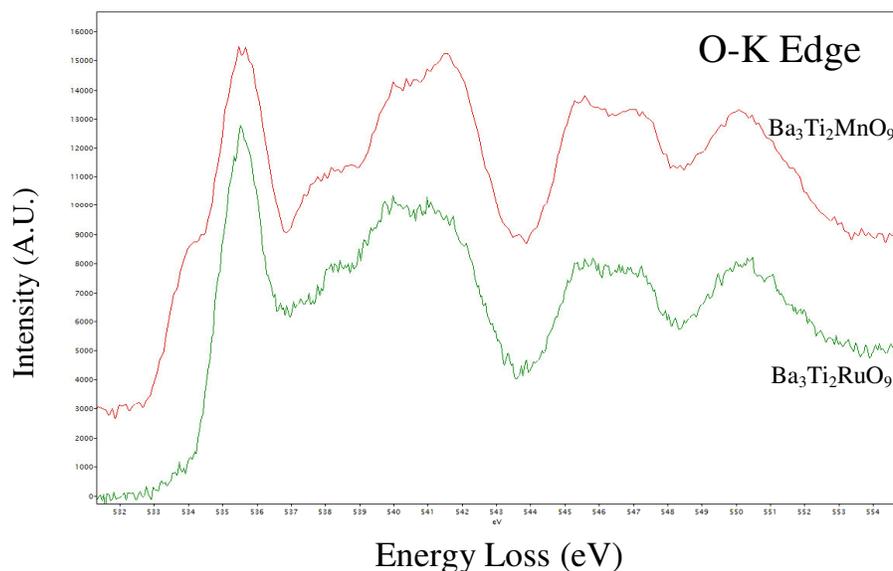


FIG. 1. Comparison between O-K edges in  $\text{Ba}_3\text{Ti}_2\text{MnO}_9$  and  $\text{Ba}_3\text{Ti}_2\text{RuO}_9$ .

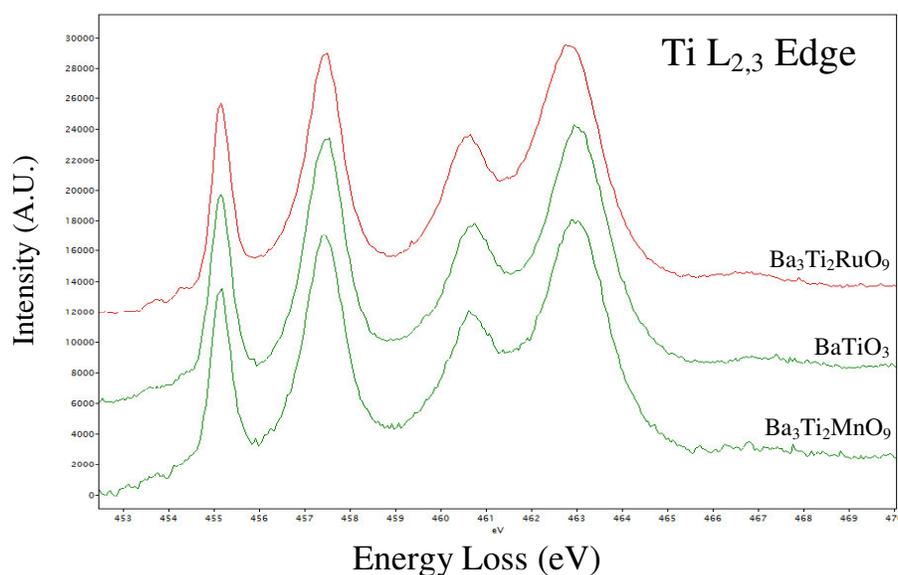


FIG. 2. Comparison between Ti  $L_{2,3}$  edges in  $\text{Ba}_3\text{Ti}_2\text{MnO}_9$  and  $\text{Ba}_3\text{Ti}_2\text{RuO}_9$  and tetragonal  $\text{BaTiO}_3$ .

#### References

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