

Cation ordering and octahedral tilting in the new A-site deficient $\text{La}_2\text{CaMg}_2\text{W}_2\text{O}_{12}$ perovskite

D. D. Khalyavin

Institute of Materials & Engineering Science, ANSTO, Menai, Australia

The crystal structure of a new A-site deficient $\text{La}_2\text{CaMg}_2\text{W}_2\text{O}_{12}$ perovskite oxide has been solved in the space group $I2/a$ from X-ray powder diffraction data in combination with group theoretical analysis (Fig.1).

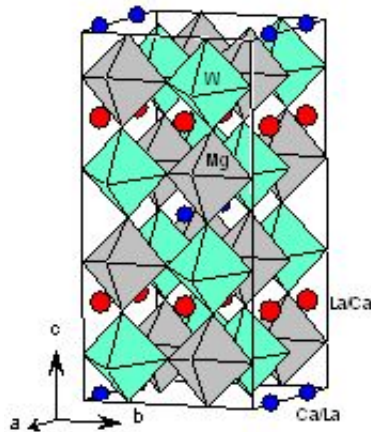


Fig.1 The crystal structure of $\text{La}_2\text{CaMg}_2\text{W}_2\text{O}_{12}$

The highest symmetry structural motif which does not involve octahedral tilting is characterized by $Ibam$ space group and represents a sequence of $[(\text{La}/\text{Ca})\text{O}]-[\text{Mg}_{1/2}\text{W}_{1/2}\text{O}_2]-[(\text{Ca}/\text{La})_{1/2}\text{O}]'-[\text{Mg}_{1/2}\text{W}_{1/2}\text{O}_2]-[(\text{La}/\text{Ca})\text{O}]-[\text{Mg}_{1/2}\text{W}_{1/2}\text{O}_2]-[(\text{Ca}/\text{La})_{1/2}\text{O}]''-[\text{Mg}_{1/2}\text{W}_{1/2}\text{O}_2]$ layers stacked along the b axis. The cation deficient layers, $[(\text{Ca}/\text{La})_{1/2}\text{O}]'$ and $[(\text{Ca}/\text{La})_{1/2}\text{O}]''$, are predominantly populated by Ca^{2+} ions ordered in rows along the c direction. A half-period shift along the a direction between these layers leads to a quadrupling of the pseudocubic perovskite unit cell, a_p , in the b direction. The interchange of the cation poor layers with the cation rich ones, along with the rock salt type cation ordering between Mg^{2+} and W^{6+} , results in $2a_p * 4a_p * 2a_p$ type superstructure. An antiphase octahedral tilting around the a axis reduces the symmetry from the orthorhombic $Ibam$ to monoclinic $I2/a$.