

# Structural and Functional Evolution of MnRMnSbO<sub>6</sub>

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It is well known that ABO<sub>3</sub> oxides present a broad polymorphism depending on their chemical composition and the used pressure and temperature synthesis conditions. Among this set of polymorphs perovskite structures are of special interest, as their structural features originate a widespread variety of functional properties. During the last decades, double perovskites (DPv) have been targeted as potential candidates for chemical substitution either in A or B sites, thus multiplying the possible magnetic and electric behaviors<sup>1</sup>.

The most common DPv in the literature are A<sub>2</sub>BB'O<sub>6</sub> with B-site rock-salted motifs and AA'B<sub>2</sub>O<sub>6</sub> with A-site layered arrangements. There are some examples of columnar order among A-site cations<sup>2,3</sup> and very few oxides combining orders within both A and B sites. All of these double double perovskites (DDPv) up to date, stabilize the mentioned layered and rock-salt orders among A/A' and B/B' cations respectively<sup>4</sup>. However, the large size and charge mismatches in the high pressure - high temperature MnRMnSbO<sub>6</sub> series have recently been found to stabilize a new type of DDPv structure<sup>5</sup>.

The evolution of the structural features upon substituting R for progressively smaller rare earths is studied in this work. The extreme size and charge mismatch in both A (Mn<sup>2+</sup>/R<sup>3+</sup>) and B (Mn<sup>2+</sup>/Sb<sup>5+</sup>) sites induces a surprising stabilizing effect on these DDPv for the largest rare earths. As R is changed by a smaller cation, this structure gets gradually distorted and the columnar arrangement of A-site cations cannot be achieved for R smaller than Eu<sup>3+</sup>. Then a conventional rock-salt A<sub>2</sub>BB'O<sub>6</sub> DPv structure is obtained instead.

The magnetic properties of both polymorphs are studied from magnetic susceptibility and magnetization measurements and the magnetic structures of the new DDPv derivatives are determined from neutron powder diffraction. As expected, not only the structural modifications but also the magnetic anisotropy of the different rare earths is involved in the magnetic behavior of these compounds.

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