

*Polar and magnetic structures of NaLnCoWO<sub>6</sub> doubly ordered perovskites*

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In the growing field of research on magneto-electric materials, attention has been drawn to a recently discovered class of AA'BB'O<sub>6</sub> perovskites that exhibit ordering on both cation sublattices [1-3]. These compounds are interesting from a structural perspective in that they exhibit rock-salt ordering of the B-site cations and layered ordering of the A-site cations. The latter type of ordering was, until recently, very rare in stoichiometric perovskites and in fact, A-site layering and B-site rock-salt ordering are synergistic and the removal of one leads to the disappearance of the other. The combination of layered ordering of A-site cations, rock-salt ordering of B-site cations and octahedral tilting results in space group symmetries that differ from other perovskites and most of the reported AA'BB'O<sub>6</sub> compounds crystallize in polar space groups. Furthermore, the availability of four distinct cation sites opens the door to the design of magnetic materials. In particular, compounds with this structure type show potential for multiferroic behavior by virtue of a relatively subtle coupling between two different magnetic sublattices and their tendency to crystallize in polar space groups.

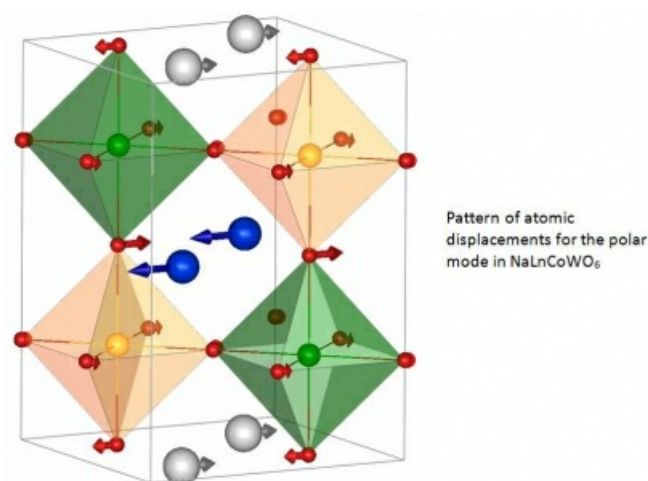
We recently extended the series of NaLnCoWO<sub>6</sub> compounds already known for Ln= La[2], Nd[1] to Ln= Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Y by high temperature solid state reaction at ambient and high pressures. The refinement of room temperature X-ray powder diffraction data shows that in all cases the B-site order is complete, as would be expected when the oxidation states of the B and B' cations differ by four (Co<sup>2+</sup> vs W<sup>6+</sup>). The A-site order is complete or nearly complete in all samples as well. The structure is highly distorted with a complex rotation pattern of the oxygen octahedra. High-resolution synchrotron and neutron diffraction data allow us to determine unambiguously that most of these compounds are monoclinic with a polar P2<sub>1</sub> space group, as confirmed by the observation of second harmonic generation. In addition all compounds order antiferromagnetically at low temperature (typically TN below 20K).

Comparing the structure with the parent paraelectric phase of P4/nmm symmetry by applying symmetry-adapted analysis, we found that the two predominant distortion modes are tilting modes of the octahedron framework. The third distortion mode is polar and results from a secondary induced instability (cf figure). Our findings therefore suggest that most NaLnCoWO<sub>6</sub> compounds can be considered improper ferroelectrics. We evaluate relatively high electrical polarization values ( $P \sim 15 \mu\text{C}/\text{cm}^2$ ) by the point charge model calculated from the observed atomic displacement with nominal charges. The evolution of the polar mode amplitude as a function of the rare-earth cation will be discussed.

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**Keywords:** [doubly ordered perovskite](#), [polar distortion](#), [improper ferroelectric](#)