Experimental report

15/11/2017

Proposal: 5-23-693 **Council:** 10/2016

Title: Crystal structure investigation ofdouble ordered perovskite NaLnCoWO6 (Ln=La, Pr, Nd, Tb, Ho)

Research area: Materials

This proposal is a new proposal

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Samples: NaLnCoWO6 (Ln=La, Pr, Nd, Tb, Ho)

Instrument	Requested days	Allocated days	From	To
D2B	2	2	19/12/2016	21/12/2016

Abstract:

This proposal concerns the NaLnCoWO6 compounds, a new family of AA'BB'O6 double layer perovskites. These compounds show potential for multiferroic behavior by their tendency to crystallize in polar space groups. They exhibit rock salt ordering of the B-site cations and layered ordering of the A-site cations. Their structures are highly distorted with a complex rotation pattern of oxygen octahedra and the presence of various superstructures is observed in TEM. To correctly determine the symmetry, the oxygen positions have to be determined precisely. The high resolution NPD will be combined with high-resolution synchrotron measurement (done in September 2016 at Cristal, Soleil) to fully resolve this complex structural problem.

Experimental Report

Abstract
This experiment investigated the crystal structures of the new doubly ordered perovskite family $NaLnCoWO_6$ (Ln= Y, La, Pr, Nd, Tb, Ho), which exhibit the rather rare layered A/A' ordering and the rock-salt B/B' ordering simultaneously. Their structures are highly distorted with a complex rotation pattern of oxygen octahedra. Combining the high resolution neutron powder diffraction (NPD) data with the high resolution synchrotron X-ray powder diffraction (SXRPD) data, we unambiguously demonstrated that the three new compounds $NaLnCoWO_6$ (Ln=Y, Tb, and Ho) synthesized under high pressure possess the polar space group $P2_1$. The polarizations are estimated from NPD refinement as large as ~14 to ~20 μC/cm^2. In the other three compounds $NaLnCoWO_6$ (Ln= La, Pr, and Nd) synthesized at ambient pressure, more complex superstructures were observed, which make proper refinement impossible. Furthermore, the phase transition of $NaLaCoWO_6$ was studied, the low temperature phase was also unambiguously determined as the symmetry of $P2_1$, while the superstructure is only present in the high temperature phase.

Report
Recently, attention has turned to a rather less explored material class, the doubly ordered perovskite $AA'BB'O_6$, which exhibit simultaneous ordering on both cation sublattices. [1-2] These compounds are interesting from a structural perspective in that rather rare layered A/A' ordering is established together with the rock-salt ordering of the B/B' sites. The possibility of substituting four distinct cation sites opens the door to new magnetic materials design with novel topologies. Furthermore, 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 have undertaken within the PhD thesis of Peng Zuo, a search for new compounds in this class of doubly ordered perovskites.

The high resolution NPD data collected helped to solve the peak overlapping issue and show neutrons' advantage of probing the light oxygen in the presence of heavy elements such as W. With the high resolution NPD data collected on the beamline D2B, and combining these data with the high resolution SXRPD data collected at Synchrotron SOLEIL, we performed joint Rietveld refinements for $NaLnCoWO_6$ (Ln= Y, Tb, Ho) and unambiguously determined that they possess the polar space group $P2_1$. The high angular resolution of the NPD patterns allowed to reveal details of the structures. The joint refinement patterns of $NaYCowO_6$ are taken as an example here, as illustrated in Figure 1. The refined crystal structure is also shown here in Figure 2. Moreover, with these NPD data, the subtle oxygen rotations are more precisely understood and the polarizations are estimated to be as large as ~20 μC/cm^2 for $NaYCoWO_6$. The polar structures were analyzed in terms of symmetry modes, and the group-subgroup relationship has been built to understand the symmetry reduction. (see Figure 3) All these results have been published in [3].

The room temperature NPD measurements of $NaLnCoWO_6$ (Ln=La, Pr, Nd) show that more complicated superstructures exist in these compounds synthesized at ambient pressure. Because of the satellites arising from the superstructures, proper Rietveld refinement cannot be performed on the NPD patterns. However, the superstructure satellites are hardly observed in the corresponding SXRPD patterns, indicating the superstructures are closely related to oxygen octahedra. The superstructure of $NaLaCoWO_6$ is supposed due to an oxygen octahedral tilt twinning, in a pattern of stripes with a new periodicity of $12a_p$ deduced from electron microscopy. Tilt twinning models based on $C2/m$ and $P2_1/m$ symmetries were built to simulate the NPD patterns, it found that the local symmetry is $P2_1/m$. (see Figure 4) Further investigations on the superstructures of $NaPrCoWO_6$ and $NaNdCoWO_6$ are still under way.

Another issue this proposal aimed to solve is to understand the phase transition of the $NaLaCoWO_6$ compound. Even though the NPD pattern measured at room temperature is not suitable for refinement, satellites are absent in the low temperature phase. The low temperature

phase can also be unambiguously determined as the polar symmetry $P2_1$, from the joint refinement shown in Figure 5.

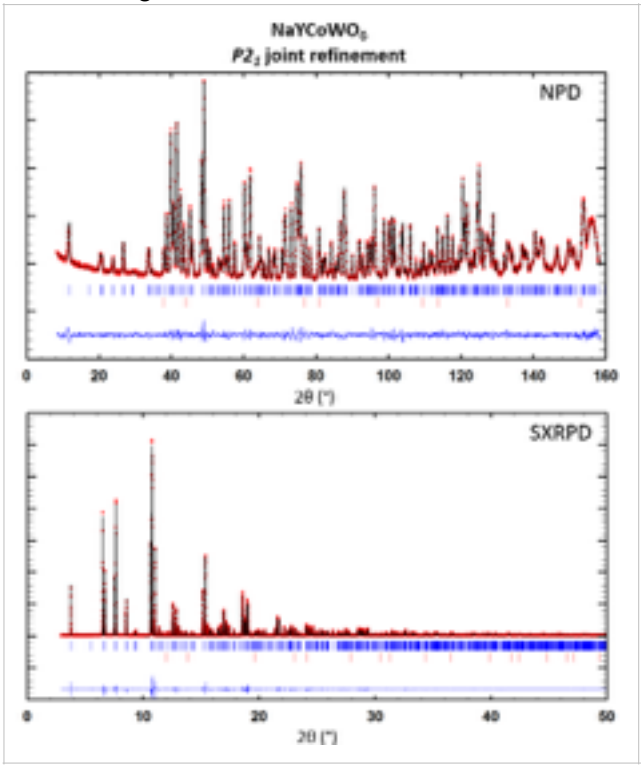

Figure 1. The $P2_1$ joint refinement patterns of $NaYCoWO_6$, the good refinement quality confirms the space group.

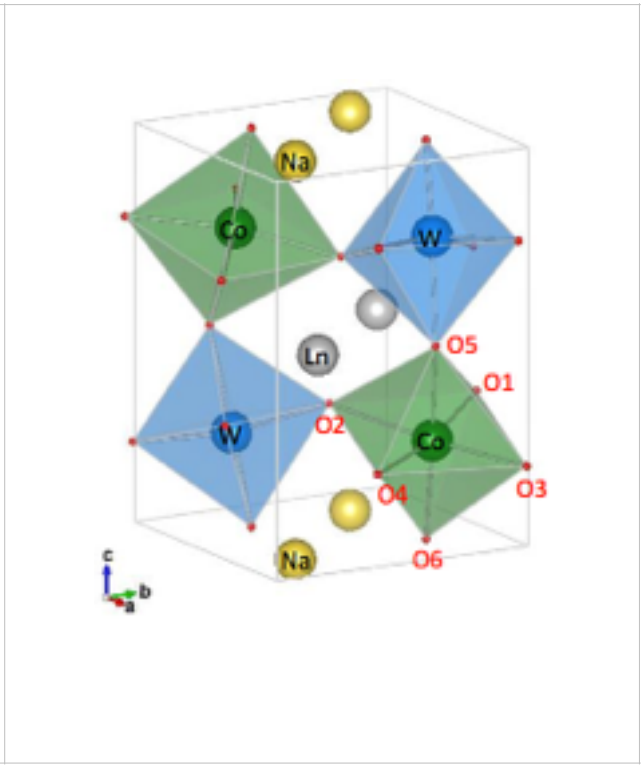

Figure 2. The refined crystal structure of $NaYCoWO_6$.

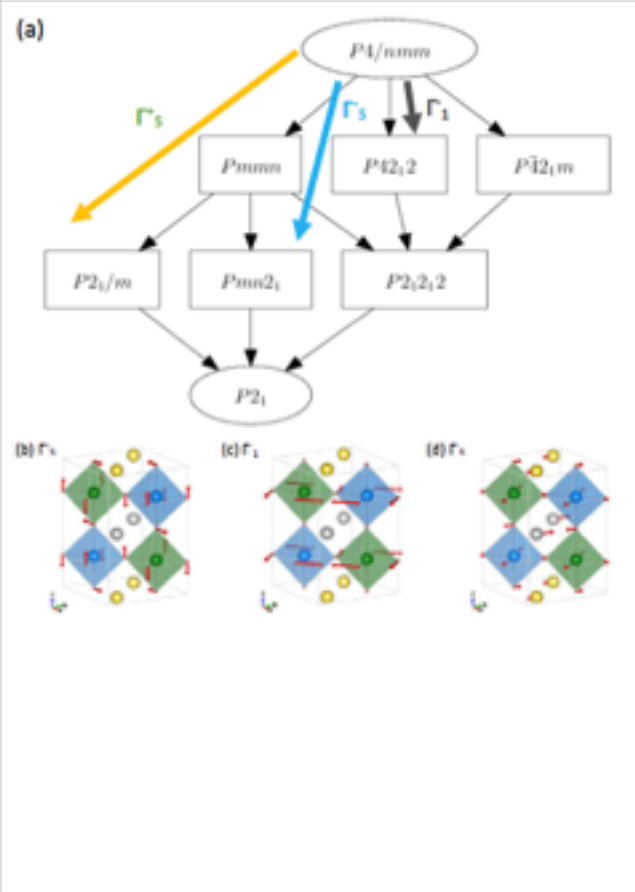

Figure 3. (a) Group-subgroup tree from the parent *P4/nmm* symmetry to $P2_1$, and the corresponding symmetry modes (b)-(d).

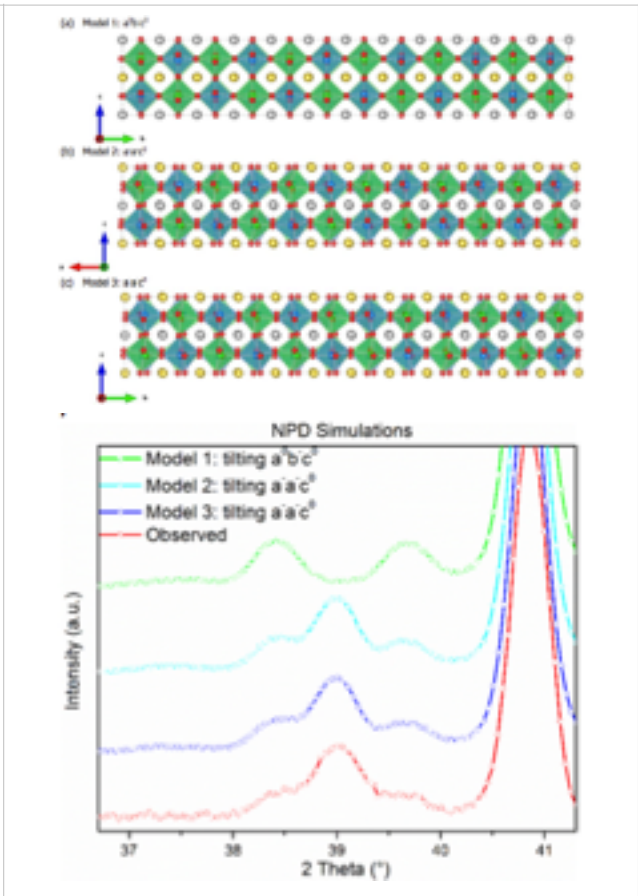

Figure 4. Tilt twinning models based on (a) *C2/m* and (b)-(c) $P2_1/m$, and the corresponding simulated NPD patterns.

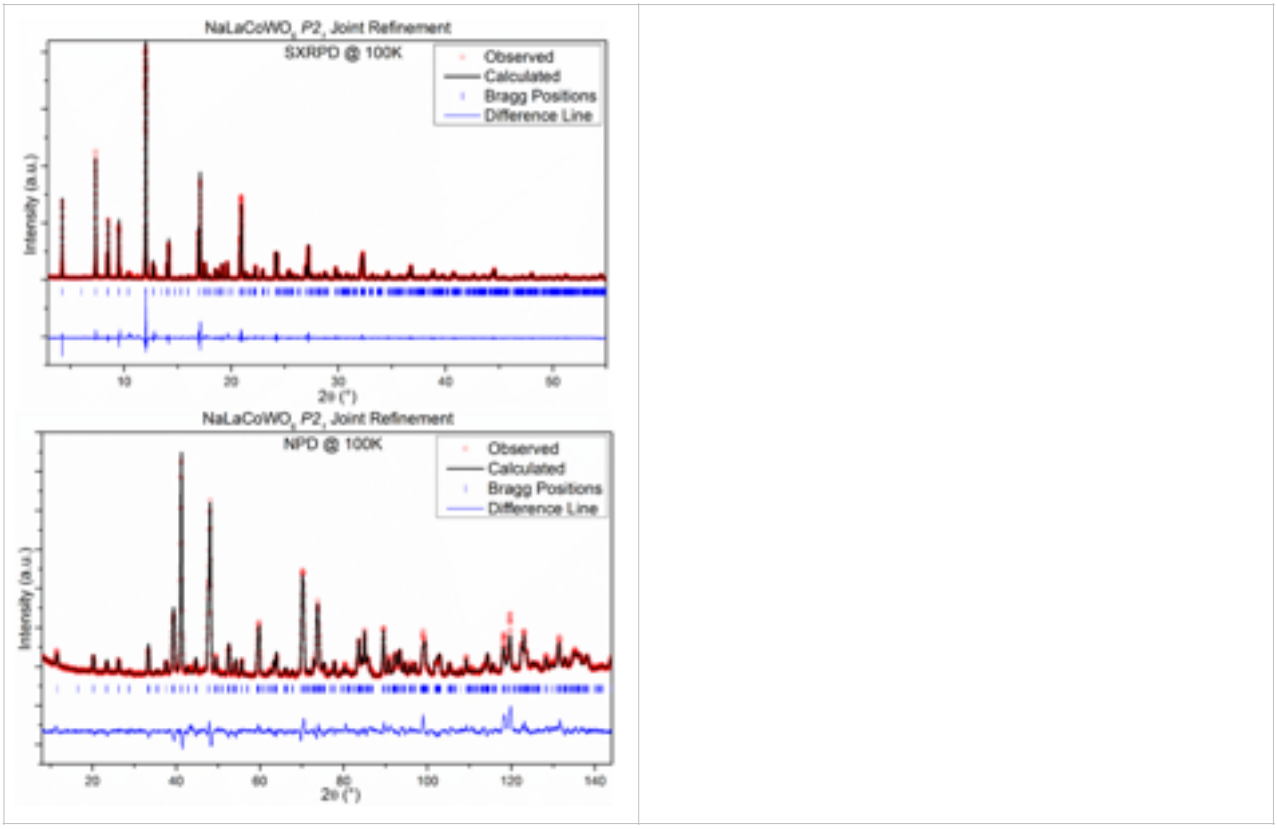

Figure 5. The $P2_1$ joint refinement patterns of the low temperature $NaLaCoWO_6$ phase.

References

[1] *Knapp, M. C. & Woodward, P. M., J. Solid State Chem.* ***179****, 1076-1085 (2006).*
[2] *King, G., Thimmaiah, S., Dwivedi, A. & Woodward, P. M. Chem. Mater. 19, 6451-6458 (2007).*
[3] *Zuo, P., Colin, C. V., Klein, H., Bordet, P., Suard, E., Elkaim, E., & Darie, C., Inorganic Chemistry,* ***56(14)****, 8478-8489 (2017).*