Experimental report

10/10/2025

Proposal: 5-23-790 **Council:** 10/2022

Title: Anion order in new K2NiF4-type layered perovskite oxynitrides

Research area: Chemistry

This proposal is a new proposal

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Samples: Nd2AlO3N
Nd2TaO1.5N2.5

Instrument	Requested days	Allocated days	From	To
D20	2	2	16/04/2023	18/04/2023

Abstract:

Transition metal perovskite oxynitrides ABO3-xNx, formed by rare earth or alkaline earth cations at the A sites show colossal magnetoresistance, thermoelectricity, spontaneous polarization and visible light photocatalytic properties among other properties. Anion order in perovskite oxynitrides affects their physical properties and is directed by the differences in charge and electronegativity between the two anions. Layered perovskite oxynitrides of Ruddlesden-Popper type structure An+1BnO3n+1-xNx are known for few examples, but we have recently prepared the new n=1 compound Nd2TaO1.5N2.5 and Nd2AlO3N using a new synthetic route. The determination of N/O distribution in these layered compounds is important to understand the general principles of anion order in perovskite oxynitrides and to interpret their physical properties. We request 2 days on D20 to determine accurately the anion coordinates and to investigate the N/O order in Nd2TaO1.5N2.5 and Nd2AlO3N between 1.6-300 K. This will allow to determine possible symmetry lowering at low temperature and to settle the issues of structural symmetry and anion ordering in Ruddlesden-Popper oxynitrides.

Anion order in new K_2NiF_4-type layered perovskite oxynitrides

Introduction

Layered perovskite oxynitrides with Ruddlesden-Popper type structure $A_{n+1}B_nO_{3n+1-x}N_x$ are known for few examples, restricted to aluminum, tantalum and niobium at the B sites.[1] Existing n=1 (K_2NiF_4 type) members with alkaline earth cations at the A sites are Sr_2TaO_3N, Ba_2TaO_3N and Sr_2NbO_3N. Lanthanide derivatives were initially reported by Marchand et al for R_2AlO_3N (R= La, Sm, Nd), and we have recently discovered the tantalum compounds $R_2Ta(O,N)_4$ (R= La, Nd, Sm, Eu).[2]

Anion order has been investigated in Sr_2TaO_3N, Sr_2NbO_3N, $Ce_2TaO_{1.19}N_{2.81}$ and Nd_2AlO_3N using neutron diffraction. [2, 3, 4] The two first compounds show the untilted symmetry *I4/mmm* of the K_2NiF_4 aristotype, with a preferred occupancy of oxide anion in the apical sites of the octahedra and a disordered distribution of O and N at the equatorial sites,[3] whereas $Ce_2TaO_{1.19}N_{2.81}$ shows a tilted *Pccn* superstructure with nitrides occupying the equatorial sites of the octahedra and N/O disordered in the axial sites. [2] Nd_2AlO_3N has been reported to show the non-centrosymmetric space group *I4mm* with total order of N atoms at one of the apical sites of the octahedra,[4] which would lead to the existence of long-range ordered dipoles and spontaneous polarization.

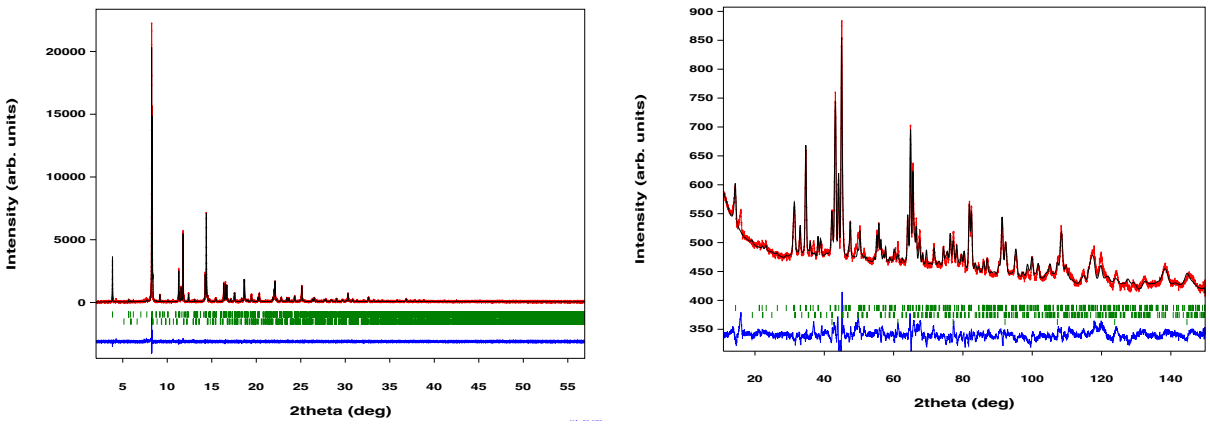
The compounds $R_2TaO_{4-x}N_x$ with R= La, Nd, Sm and Eu were prepared by solid state reaction between nitrides and oxides under N_2(g) at temperatures between 1200 and 1700 ºC. [2] By using the same synthetic approach we have also prepared Nd_2AlO_3N and Sm_2AlO_3N at 1500 ºC, a different method compared with that reported by Marchand and coworkers that was performed in a vacuum sealed tube at 1300 ºC. [4] The different conditions of synthesis that we have used for Nd_2AlO_3N and Sm_2AlO_3N may affect the anion order, as observed in other perovskite oxynitrides, as well as the polar character of the structure. Electron diffraction patterns along several zone axes indicate the untilted symmetry (*I4/mmm* or *I4mm*) for the Al compounds, but in the Ta samples we observed additional reflections compatible with a supercell of parameters a, b $=\sqrt{2}\ a_0$, $c=c_0$ that were indexed in the orthorhombic *Pccn* space group (where a_0 and c_0 are the parameters of the *I4/mmm* aristotype for K_2NiF_4 structure).[2]

In this experiment we have investigated the anion ordering in $Nd_2TaO_{1.46}N_{2.54}$ and Nd_2AlO_3N. The neutron powder diffraction data were complementary of synchrotron X-ray powder diffraction data acquired in the MSPD beamline of Alba synchrotron.

Results of the experiment

Neutron powder diffraction data for $Nd_2TaO_{1.46}N_{2.54}$ and Nd_2AlO_3N were collected on the D20 diffractometer using 80 mg of sample placed in a vanadium can. The neutron wavelengths were 1.54 Å for $Nd_2TaO_{1.46}N_{2.54}$ and 1.36 Å for Nd_2AlO_3N, and the data were taken at 6 K and 100 K for the tantalum compound and at 1.6 K, 100 K and 300 K for the aluminum oxynitride.

A combined Rietveld refinement of synchrotron X-ray and neutron diffraction data at room temperature of $Nd_2TaO_{1.46}N_{2.54}$ (Figures 1a and 1b) was performed in the *Pccn* space group and led the cell parameters: a=5.70468(5), b=5.70456(7), c=12.32399(8) Å. As starting model we used a random distribution of nitrogen and oxygen in the three anion positions of the *Pccn* model, considering full occupancy in all sites. The refined N/O population for the two equatorial sites were 78/22 for X2 site and 100 % of N in X3, whereas the obtained occupancies of the axial site X1 were 37 % of N and 63 % of O % for each anion (Figure 1). This anion distribution shows a preferred order of the nitride anions at the equatorial sites of the tantalum octahedra, as observed for $Ce_2TaO_{1.19}N_{2.81}$ and in agreement with Pauling's second crystal rule.[2] The refined anion stoichiometry, 2.52 N and 1.48 O per formula is in excellent agreement with chemical analysis results. The bond distances for the equatorial positions were significantly shorter (d(Ta-X2)= 2.0507(16), d(Ta-X3)= 2.0190(8) Å) than for the axial site (d(Ta-X1)= 2.1903(6) Å). Refinements from neutron diffraction data at low temperature data did not lead to significant differences in the structural model compared with the refinements performed at room temperature.



(a) (b)

Figure 1. Rietveld fits resulting from the combined refinement of (a) synchrotron X-ray powder diffraction data (λ= 0.41385 Å) and (b) neutron powder diffraction data (λ= 1.54 Å) of $Nd_2TaO_{1.46}N_{2.54}$ at room temperature. Upper and lower reflection markers correspond to $Nd_2TaO_{1.46}N_{2.54}$ (95 % w/w) and $NdTaO_2N$ (5 % w/w). In (b) the third row of reflections correspond to vanadium from the sample holder.

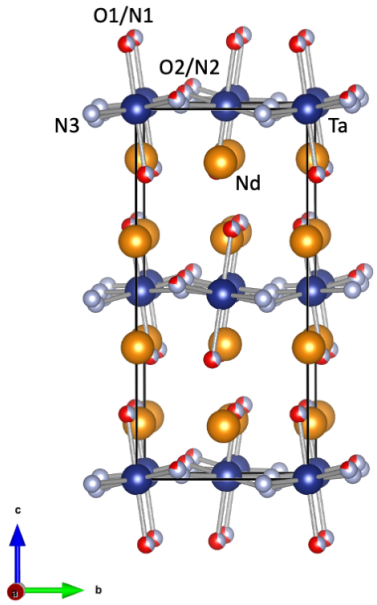
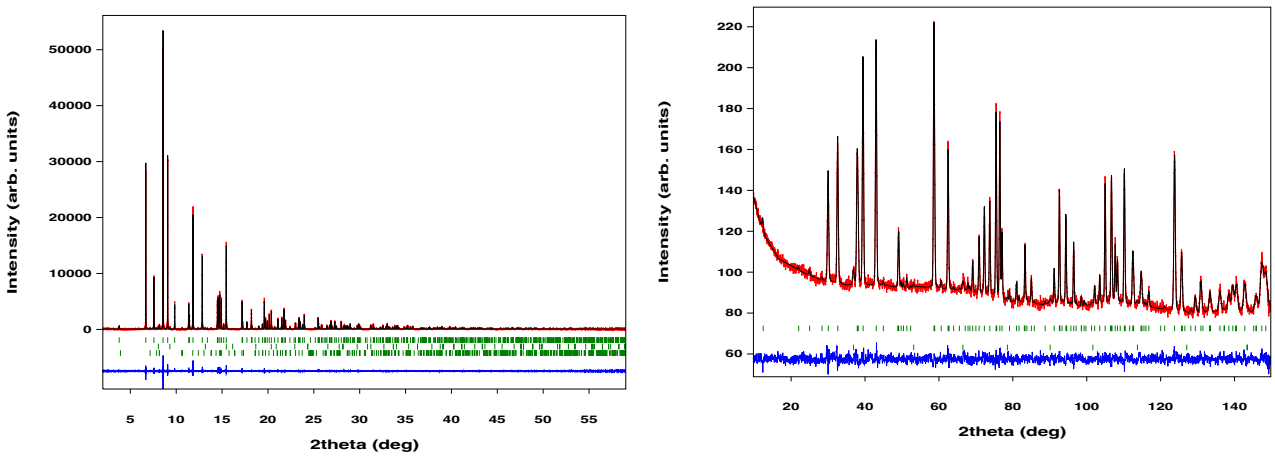


Figure 2. Structural model of $Nd_2TaO_{1.46}N_{2.54}$ from the combined refinement of synchrotron X-ray and neutron powder diffraction data. O and N atoms are represented as red and gray spheres respectively.

A combined Rietveld refinement of synchrotron X-ray and neutron diffraction data at room temperature of the Nd_2AlO_3N sample (Figures 3a and 3b) was performed in the *I4/mmm* and *I4mm* space groups and led the cell parameters a=3.703314(3), c= 12.545382(14) Å. An improvement in the agreement factors was observed for the non centrosymmetric *I4mm* model compared to *I4/mmm*, and showed a different anion distribution compared to that found by Marchand et al (Figure 4a). [4] The refinement was performed starting with a random distribution of nitrogen and oxygen in the anion positions considering full occupancy in all sites, with the N/O contents restricted to the analyzed stoichiometry 1/3. As in the previous report, our results showed that the oxygen atoms order in the equatorial sites of the octahedra, but the two anions are only partially ordered in both axial positions X2 and X3, with populations O/N 68/32 for X2 site and 32/68 in the X3 site (Figure 4b). The partial N/O order resulted into two distinct Al-X2 (2.182(15) Å) and Al-X3 (2.034(15) Å) bond distances. Refinements from neutron diffraction data at low temperature data did not lead to significant differences in the structural model compared with the refinements performed at room temperature.



(a) (b)

Figure 3. Rietveld fits resulting from the combined refinement of (a) synchrotron X-ray powder diffraction data (λ= 0.414171 Å) and (b) neutron powder diffraction data (λ= 1.36 Å) of Nd_2AlO_3N at room temperature. Lower reflection markers in (a) correspond to NdN (0.72 % w/w) and Nd_2O_3 (1.50 % w/w).

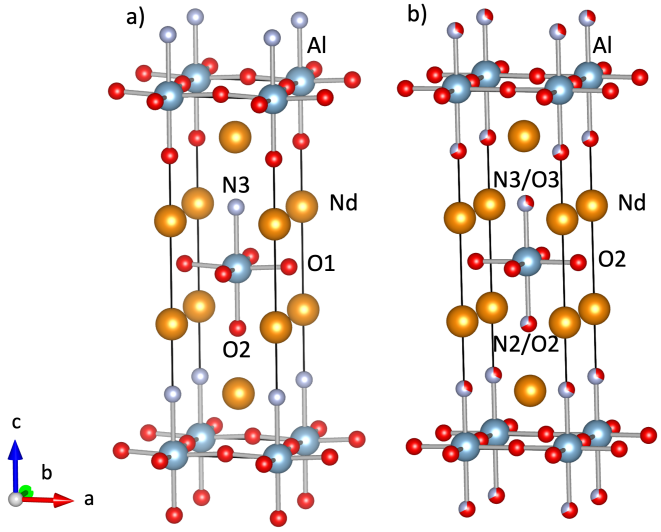


Figure 4. Structural model of Nd_2AlO_3N (a) reported by Marchand et al for a sample prepared at 1300 ºC, and (b) obtained from the combined refinement of synchrotron X-ray diffraction and neutron diffraction data of this experiment.

References

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3. a) G. Tobías, J. Oró-Solé, D. Beltrán-Porter, A. Fuertes. *Inorg. Chem.*, **40**, 6867 (2001). b) G.Tobías, D.Beltrán-Porter, O.Lebedev, G.Van Tendeloo, J.Oró-Solé, J. Rodríguez-Carvajal and A. Fuertes. *Inorg. Chem.*, **43**, 8010 (2004).

4. R.Marchand, R.Pastuszak and Y.Laurent. *Rev. Chim. Min.* **19**, 684 (1982).