Experimental report

04/09/2022

Proposal: **5-23-769**

Council: 4/2021

Title: Solving the structure of new Ruddlesden-Popper Oxyfluorides with unique structural distortions by high resolution neutron powder diffraction

Research area: Chemistry

This proposal is a new proposal

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Samples: $La_2CuO_3F_2$
$La_2Ni_{0.3}Cu_{0.7}O_{2.5}F_3$
La_2CuO_4:F70%
$La_4Co_3O_9F_2$
$La_4Ni_3O_{9.5}F$
$La_2Ni_{0.7}Cu_{0.3}O_{2.5}F_3$
$La_2CuO_3F_{1.5}$
La_2CuO_4:F20%
La_2CuO_4:F10%
La_2CuO_4:F30%
$La_4Ni_3O_{8.5}F_3$

Instrument	Requested days	Allocated days	From	To
D2B	3	2	03/09/2021	05/09/2021

Abstract:

Ruddlesden-Popper oxyfluorides are promising candidates for intercalation electrodes in fluoride ion batteries. Finding ways to synthesize new oxyfluorides containing high amounts of F¿ is therefore of high interest. By low-temperature topochemical fluorination with PVDF we synthesized several hitherto unknown oxyfluorides including the first n = 3 Ruddlesden-Popper oxyfluoride $La_4Co_3O_9F_2$. By neutron diffraction we plan to solve the structure of seven new Ruddlesden-Popper oxyfluorides as well as four hitherto unknown intermediates occurring during their formation. Understanding the structural relationships between these intermediates and final products (with the support of DFT calculations) can help to develop new fluoride battery materials.

Solving the structure of new n = 1 and n = 3 Ruddlesden-Popper Oxyfluorides with unique structural distortions by high resolution neutron powder diffraction

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Ruddlesden-Popper (RP) oxyfluorides obtained by topochemical fluorination of La_2BO_4 (B = Ni, Cu, Co) exhibit a variety of unusual distorted versions of the K_2NiF_4 archetype structure, which differ from other n = 1 RP-oxyfluorides. In previous studies two oxyfluorides were found, namely $La_2NiO_3F_2$ and $La_2NiO_{2.5}F_3$ (denoted as 2F-oxyfluoride and 3F-oxyfluoride in the following) each with different NiO_4F_2 octahedral tilting schemes. In the case of the 2F-oxyfluoride the formation of channels with alternating small and wide diameter was found with the later hosting interstitial oxygen atoms.[1] In the 3F-oxyfluoride we found a totally different ordering scenario for the first time.[2] Here, layer wise rotations of the NiO_4F_2 octahedra along one Ni-O-Ni axis result in three rather large and one small interstitial site. As a result a 50% occupation of the interlayer with F^- and a 25% occupation with O^{2-} were derived from joint Rietveld refinements of XRD and NPD data. This finding was additionally confirmed by DFT and BVS calculations.

Recently, we for the first time prepared the corresponding cuprates ($La_2CuO_3F_2$ and $La_2CuO_{2.5}F_3$) and their formation reaction was studied by *in situ* XRD revealing the presence of three reaction intermediates (interCu#1-3) with different structural distortions. To solve the structures of these intermediates as well as the one of $La_2CuO_{2.5}F_3$ was one aim of this proposal. The structure of the 3F cuprate $La_2CuO_{2.5}F_3$ was solved by refining joint XRD and NPD data and a triclinic distorted (P-1) version of the nickel 3F structure was found (see Figure 1) with a = 5.7088(1) Å, b = 5.7088(1) Å, c = 13.0839(2) Å, α = 89.65(2)°, β = 90.42(1)° and γ = 90.08(1)°. In case of the reaction intermediates, a first intermediate was obtained from the reaction with 10 % PVDF and an orthorhombic structure (*Bmab,* a = 5.3570(4) Å, b = 5.4314(2) Å, and c = 13.1828(2) Å) similar to La_2CuO_4 but with increased orthorhombic splitting and partial interlayer occupation was found. Refinements for the second and third intermediate (obtained with 40% and 70% PVDF) are still in progress. Preliminary Pawley refinements point to a primitive orthorhombic space group for InterCu#2 (a = 5.3562(1) Å, b = 5.5564(1) Å, and c = 13.1598(3) Å). For InterCu#3 also a primitive cell was found but with tetragonal metric (a = 5.4886(1) Å, and c = 13.1167 Å). The final refinements are hampered by the fact that the diffraction pattern of all three intermediates exhibit residual reflections of the preceding as well as the succeeding intermediate. Therefore, efforts are in progress to isolate the intermediates with higher purities

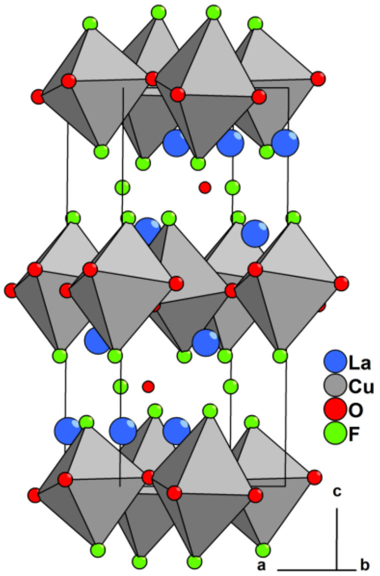

Figure 1: Crystal structure of $La_2CuO_{2.5}F_3$ (SG: P-1).

as the structures of all intermediates are needed for a quantitative phase analysis of *in situ* data, with the aim to gain a deeper understanding of the fluorination reaction mechanism.

Measurements of members of the $La_2(Ni_{1-x}Cu_x)O_{2.5}F_3$ substitution series were performed to investigate the impact of the expected Jahn-Teller distortion of the $Cu(O,F)_6$ octahedra on the crystal structure. The entire substitution series was found to be accessible in preliminary studies and NPD measurements were performed for three different substitution levels ($x = 0.3$, 0.7, and 0.9). In the case of $x \geq 0.7$ the formation of two well defined phases was observed so that measurements were performed for two different $x = 0.7$ samples. As a result of the joined XRD and NPD refinements the same structural distortion as in the case of $La_2NiO_{2.5}F_3$ (SG: *P*4$_2$*/nnm*) was confirmed for all three compounds. With the NPD data allowing for a more precise determination of the anionic sub lattice we were able to detect a splitting of the apical octahedral position (X_{ap}) in one Jahn-Teller-elongated (i.e. a longer Ni/Cu-X_{ap} bond of 2.4 Å) and a significantly less elongated (Ni/Cu-X_{ap} = 2.2 Å) position. The refined occupation factors closely resembled the Ni/Cu content of the samples.

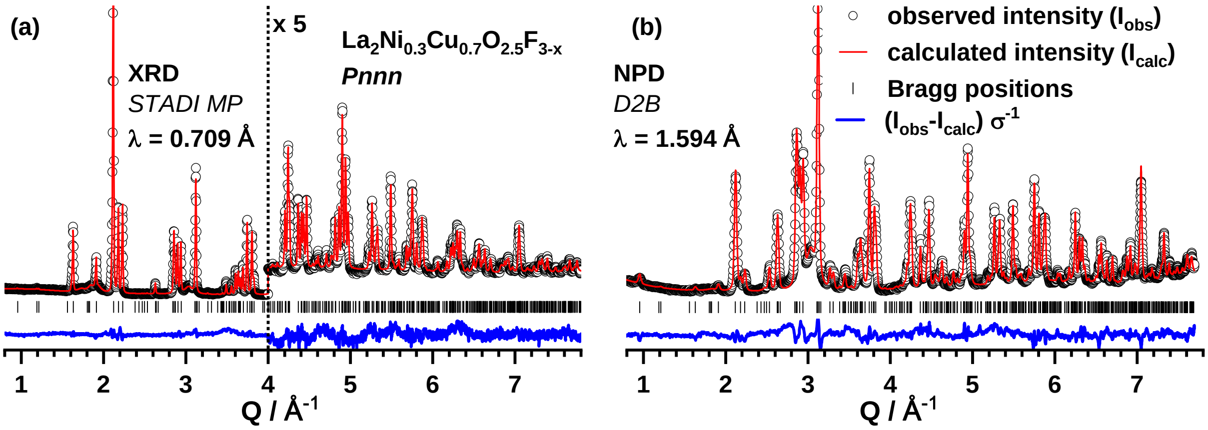

Figure 2: X-ray (a) and neutron diffraction (b) patterns of $La_2Ni_{0.3}Cu_{0.7}O_{2.5}F_{3-x}$ and Rietveld refinements in pace group *Pnnn*.

For the second $x = 0.7$ compound, which was identified as a first decomposition intermediate by *in situ* XRD studies, an orthorhombic unit cell with space group *Pnnn* (a = 5.6212(1) Å, b = 5.7529(1) Å, and c = 13.1239(2) Å) was obtained from the Rietveld refinements shown in Figure 2. This compound was found to consist of octahedra with split apical positions with significantly different atomic coordinates and a 50/50 occupation in contrast to the 30/70 occupation found in the tetragonal version. This finding can be interpreted as an intergrowth of two locally different structures. One local structure resembles the distortion of $La_2NiO_{2.5}F_3$ with layer wise octahedral rotations and a ¾ interlayer occupation while the other local structure exhibits the tilting scheme observed for $La_2NiO_3F_2$ with a ½ occupation of the interlayer channels. Here HRTEM investigations are needed for a confirmation.

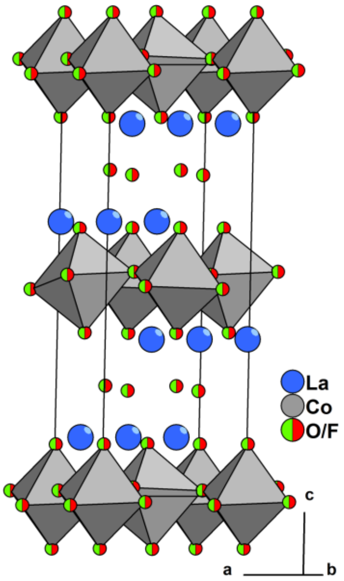

Figure 3: Crystal structure of $La_2CoO_3F_3$ (SG: $P2_1/c$).

The structure of $La_2CoO_3F_3$ was also solved based on the data obtained within this proposal. Here, joined XRD/NPD refinements revealed a monoclinic distortion of the K_2NiF_4 structure with a strongly elongated c-axis of $c_{oxyfluoride} = 15.11$ Å ($c_{oxide} \approx 12.6$ Å) resulting from fully occupied NaCl-interlayers. The structure of an analogous compound $La_2CoO_4F_2$ with similar unit cell parameters crystallizing in *C2/m* was published before (but solely based on XRD data). With the aid of NPD we were able to precisely refine the anionic sublattice and based on the presence of super structure reflections like (121), (023) and (122) a P-centered lattice and the space group $P2_1/c$ (a = 5.3057(1) Å, b = 5.3740(1) Å, c = 15.1115(2) Å, and β = 91.26(1)°) were derived. It seems very likely that the already published structure also crystalizes in $P2_1/c$ as the reflections of the anionic sub lattice are very weak in the XRD data. The structure of $La_2CoO_3F_3$ is shown in Figure 3; a mixed anion site occupation was derived from BVS calculations.

The third system investigated in this proposal are compounds of the n = 3 Ruddlesden-Popper series ($A_4B_3O_{10}$). Here, we addressed the structure of of the three first n = 3 Ruddlesden-Popper oxyfluorides namely $La_4Ni_3O_{10-y}F_{y+d}$, $La_4Co_3O_9F_2$, and $La_{0.5}Sr_{3.5}Fe_3(OF)_{10.5}$. Pawley refinements revealed a monoclinic P-centered space group for the Ni- as well as the Co-compound. Structure refinements are still going on as these are hampered by strongly anisotropic broadened reflections with (00l) component, which is most probably the result of a high degree of disorder in the rock salt interlayers. For the n = 3 oxyfluoride $La_{0.5}Sr_{3.5}Fe_3(OF)_{10.5}$, on the other hand, diffraction patterns with sharp reflections were obtained. Here, measurements were performed at 1.594 Å as well as 2.398 Å as additional reflections were observed at low diffraction angles. By combined refinement of X-ray and neutron powder diffraction datasets the crystal structure was solved in space group *Pbca* (a = 5.5381(2) Å, b = 5.5453(1) Å, and c = 29.2556 Å). It is depicted in Figure 4. The additional reflections were best fitted by a magnetic structure model with G-type AFM ordering in the space group *Pbc'a'*. The presence of AFM ordering above room temperature is currently studied by Mößbauer spectroscopy.

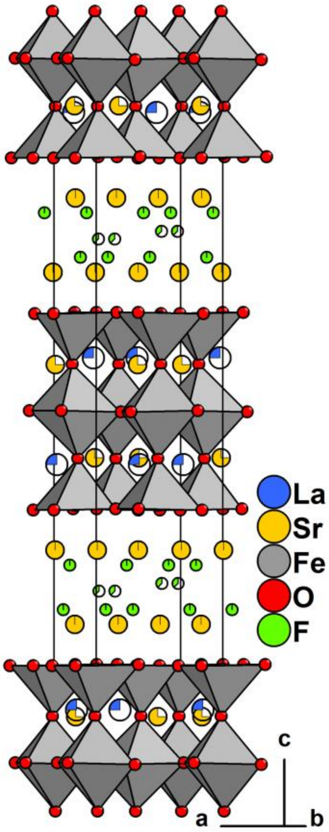

Figure 4: Crystal structure of $La_{0.5}Sr_{3.5}Fe_3(O,F)_{10,5}$ (SG: *Pbca*).

References

(1) Wissel, K. et al. *Inorg. Chem.* **2018**, *57* (11), 6549–6560.

(2) Jacobs, J. et al. *Inorg. Chem.* **2021**, *60* (17), 13646–13657.