Experimental report

25/07/2022

Proposal: **5-23-732** **Council:** 4/2019

Title: Charge and Magnetic Orders in the Complex A-Site-Layer-Ordered Perovskite Y0.4Ba0.9Ca0.7Fe2O6 with Unusually High Valence Fe3.8+

Research area: Materials

This proposal is a new proposal

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Samples: Y0.4Ca0.9Ba0.7Fe2O6

Instrument	Requested days	Allocated days	From	To
D2B	2	1	18/09/2019	19/09/2019
D20	1	1	17/09/2019	18/09/2019

Abstract:

Topochemical oxidation of the complex A site ordered perovskite compound with general formula Y0.4Ca0.9Ba0.7Fe2O5.20 results in the unusual high valence state Fe3.8+. The instability of this Fe 3.8+ at room temperature leads to a novel charge ordering in a layered-manner derived from the A-site ordering.

At low temperature, a charge disproportionation takes place accompanied with an antiferromagnetic ordering. Neutron Diffraction experiments would provide essential information for detecting possible charge orderings as a result of the charge disproportionation as well as the magnetic structure derived from the magnetic transition.

Charge and Magnetic Orders in the Complex A-Site-Layer-Ordered Perovskite $Y_{0.4}Ba_{0.9}Ca_{0.7}Fe_2O_6$ with Unusually High Valence $Fe^{3.8+}$

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The proposal 5-23-732 aimed at determining fine structural details of $Y_{0.4}Ca_{0.9}Ba_{0.7}Fe_2O_{5.20}$ and of its derivative obtained by topotactical oxidation with ozone. In the parent compound electron microscopy shows a complex perovskite-type superstructure (ap ~ 3.8 Å is referred to the lattice parameter of the ideal cubic perovskite structure) related to the five-fold A cation ordering in a stacking sequence Y(Ca)-Ba-Ca(Y)-Ca(Y)-Ba-Y(Ca) in combination with the ordering of the different oxygen polyhedra surrounding the Fe cations in P-O-T-O-P-P sequence. The alternation of the Fe-Fe distances along the stacking axis in the tetrahedral chains originates a 10ap superstructure. Mössbauer spectra and magnetic measurements suggest different oxidation states of the Fe cations within the structure, which seems to be ordered, the charge is distributed in a layered manner with two Fe^{4+} layers (Fe1 and Fe3) separated by one $Fe^{3.5+}$ layer (Fe2) in the sequence Fe^{4+}-$Fe^{3.5+}$-Fe^{4+}-Fe^{4+}-$Fe^{3.5+}$.

This charge order (CO) must be confirmed by direct evidence such as Bond Valence Sums (BVS) calculation, to this end NPD is a powerful technique since provides details on the oxygen substructure and reliable metal-oxygen distances. Besides, NPD provides information about the magnetic order in the structure.

The topotactically oxidised compound presents interesting magnetic and structural features worth to be studied.

Our preliminary results show that the precursor $Y_{0.4}Ba_{0.9}Ca_{0.7}Fe_2O_{5.2}$ with dark brown color crystallizes in a perovskite-related structure with space group *Ibmm* and unit cell $\sqrt{2}a_p\ x\ \sqrt{2}a_p\ \ x\ 10a_p$ (a_p denotes the cubic perovskite axis). Low-temperature ozone oxidation leads to a shiny black powder of composition $Y_{0.4}Ba_{0.9}Ca_{0.7}Fe_5O_{5.9}$ (Figure 1). The intercalation of extra oxygen induces a reduction of symmetry to S.G. $P2_1/n$. A complete structural model has been developed and refined, allowing a satisfactory fitting of experimental data (Fig. 2). BVS calculations in this oxidized material confirms previously proposed scenario where Fe ions with the highest-oxidation state for Fe placed between the mainly Ca layers is observed (this Fe layer is the most distorted within the structure, green layer in the figure below).

We are currently working on the magnetic structures, which are somewhat complex because of a complex distribution of magnetic sub-lattices in the materials.

Figure 1.

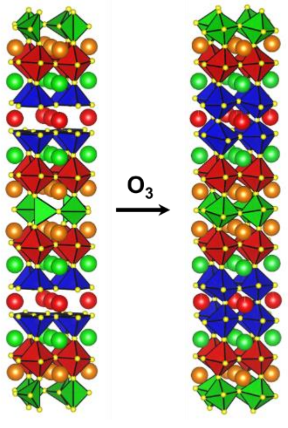

Figure 2.