Experimental Report

03/04/2014

Proposal: **5-24-537** **Council:** 10/2012

Title: Oxyhalides in the Ba-Fe-O-X system(X=Cl, F)

This proposal is a new proposal

Researh Area: Materials

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Samples: BaFeClxOy

Instrument	Req. Days	All. Days	From	To
D2B	1	1	13/05/2013	14/05/2013

Abstract:

we have explored the stability of oxy-halides in the Ba-Fe-O-X system (X=F, Cl). In this sense, we have prepared four samples in the BaFeClxOy system. Depending on the halogen content two polypypes (hchc)-4H and (chchh)2 -10H has been stabilized.

In the atomically-resolved HAADF images obtained in an aberration corrected TEM microscope the anion substructure was initially observed. In this image, the halogen distribution through the anionic sublattice is visualized. From this, it is evidenced that halogen are not coordinated to the Fe atom but only to the larger barium ones.

Our aim is to obtain a detailed structural characterization of the four BaFeClxOy samples with high resolution powder diffractometer D2B in order to establish how the oxygen rearrangement is modified by the incorporation of halides in the anionic sublattice as well as to accurately locate the halogen atom in the structure.

The perovskite structure of ideal formula ABO_3 can be built from two extreme close packing types of AO_3 layers (hexagonal and cubic) with the B cations in the octahedral holes. Between these two extreme forms a wide variety of perovskite-based structures form by a combination of various cubic (c) and hexagonal (h) stacking layer sequences can be stabilized. As a result, many perovskite-type structures contain both corner and face-sharing octahedral $[BO_6]$. Such materials are generally termed hexagonal polytypes.

The main interest of this family of compounds is that they represent a wide variety of interesting physical properties: electrical, magnetic, dielectrical and catalytic properties. Research in these materials has undergone a huge development due to their potential applications in the field of solid oxide fuel cells (SOFCs). In particular, the commercial development of SOFCs remains delayed due to one crucial factor, the working temperature (800 – 1000 ºC). If the working temperature could be reduced, lower manufacturing costs, improved materials compatibility and long-term durability can all realized. Lower temperatures require highly mobile anionic species, and recently it has been considered the possibility of modifying the anionic sublattice by the partial substitution of O-for F-. In this sense, recent works seems to indicate that partially fluoridated-hexagonal perovskites open efficient 2D oxide conduction paths because of their particular structures. These results stimulated the search in the lackluster field of hexagonal perovskites.

Fe cations can adopt several oxidation states (III and IV) in perovskite related oxides and is stable in both octahedral and tetrahedral oxygen environments. For that we have explored the stability of oxy-halides in the Ba-Fe-O-X system (X=F, Cl). In this sense, we have prepared four samples in the BaFeClxOy system. Depending on the halogen content two polypypes (hchc)-4H and $(chchh)_2$ -10H has been stabilized.

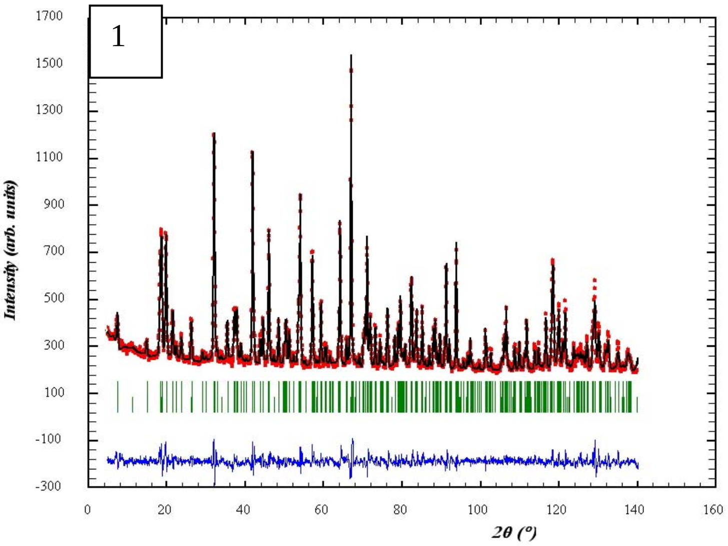
A detailed structural and magnetic characterization of the BaFeClxOy system have been carried out on high resolution powder diffractometer D2B.

Neutron diffraction data for the 10H-polytype were fitted with space group P63/mmc at 300 K, figure 1. The structure consists of trimers of face-sharing octahedra connected through their terminal corners to two tetrahedral (figure 2). Three distinct sites for Fe are found in this structure; Fe1 and Fe2 are the octahedral sites associated with the outer and central octahedra of the trimers, respectively, and Fe3 is the tetrahedral site. Cl anions are incorporated into anionic-deficient h'-[BaClO] layers in which Cl and O3 occupy distinct crystallographic positions, yielding Fe_2O_7 pairs of corner-sharing tetrahedra and $ClBa_5$ trigonal bipyramid.

We refined the occupancy factor of all the oxygen atoms. The obtained occupation numbers reveal oxygen vacancies in the all BaO_{3-y} layers of the 10H polytype. This result gives rise to an oxygen content corresponding to 2.5 per formula unit, $BaFeCl_{0.13}O_{2.5}$ refined composition.

Even at room temperature, the PND data show heavy magnetic contributions, which correspond to the 3D-AFM ordering. We refined from data collected at room temperature using the propagation vector k = (0,0,0) for the magnetic structure. This model results in a magnetic structure consisting of ferromagnetic sheets with the magnetic moments stacked antiferromagnetically perpendicular to the c-axis (Figure2).

The study of the others samples of this system is in progress.



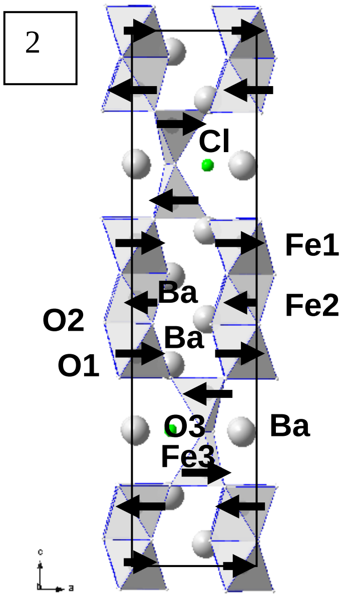


Figure 1. *Calculated and observed ND-profiles of the Rietveld refinement for 10H-*BaFeCl$_{0.13}$O$_{2.5}$ oxide.. *The second phase corresponds to the antiferromagnetic magnetic structure which exists at room-temperature.*

*Figure 2. Schematic representation of the structure and the magnetic model of 10H-*BaFeCl$_{0.13}$O$_{2.5}$ oxide.