Experimental report

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Proposal:	**5-31-2366**	**Council:**	10/2014

Title: The evolution of magnetic structure in CaBaCo4-xMxO7 (x ≤ 2; M=Fe, Zn) compounds.

Research area: Materials

This proposal is a new proposal

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Samples: CaBaCo2-xFexO7
CaBaCo3ZnO7

Instrument	Requested days	Allocated days	From	To
D2B	2	3	31/07/2015	03/08/2015

Abstract:

Recently, a new mixed oxide of Co was found with a noncentrosymmetric structure and showing strong magnetoelectric coupling: The new multiferroic CaBaCo4O7. The Co has a tetrahedral coordination and it is located in four non-equivalent crystallographic sites. Two of them are ascribed to Co3+ and the other two to Co2+. This material has been doped using different transition metals. Magnetic properties of the parent compound are strongly modified by doping but the most striking point was the finding of a new magnetic structure for CaBaCo3FeO7. The main objective of this proposal is to precisely determine this new magnetic structure and to find the relationship between the magnetic ground state and the type of substitution in the Co sublattice. In this way, we are going to study the effect of a substitution with both trivalent (Fe3+) and divalent (Zn2+) cations. Moreover, as the differences in the magnetic structure between CaBaCo4O7 and CaBaCo3FeO7 compounds are significant,we will follow the evolution of the magnetic ground state upon increasing the Fe content in the chemical composition.

The evolution of magnetic structure in $CaBaCo_{4-x}M_xO_7$ ($x \leq 2$; M=Fe, Zn) compounds.

Neutron patterns of $CaBaCo_{4-x}Fe_xO_7$ (x=0.5, 1, 1.5, 2) and $CaBaCo_3ZnO_7$ were measured at D2B. The samples were prepared in air at 1100ºC followed by a quench into air. Some Fe-doped samples were prepared in argon current flow in order to test its effect on the oxygen stoichiometry but no significant effects were found in the neutron patterns. In the same way, a sample of $CaBaCo_3ZnO_7$ was prepared in oxygen atmosphere with the same result. Therefore, the report is focused on the samples prepared in air.

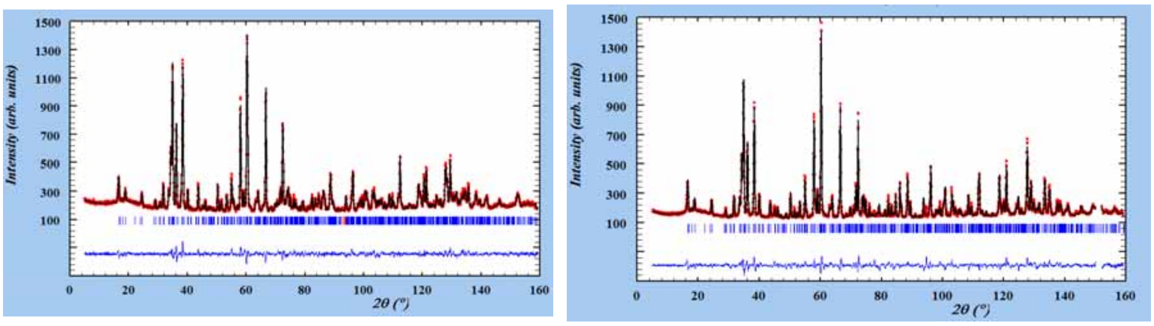

Fig. 1. Examples of neutron refinements at room temperature for $CaBaCo_3FeO_7$ (left) and $CaBaCo_{2.5}Fe_{1.5}O_7$ (right).

The neutron patterns of $CaBaCo_{4-x}Fe_xO_7$ samples at room temperature can be refined using the orthorhombic cell of $CaBaCo_4O_7$ compound (space group *Pbn2₁*) as can be seen in Fig. 1. Superstructure peaks arising from the orthorhombic distortion are clearly noticeable for x=0.5 and x=0.1 samples. Such peaks are hardly noticeable for x≥1.5 samples but the refinement with the orthorhombic model works better than using the hexagonal lattice (*P6₃mc* space group). Cryofurnace was employed to collect patterns between 500 and 2 K. Unfortunately, spurious contribution from the cryofurnace was observed in some patterns so that regions were removed before performing the refinements. No magnetic contribution was noticeable at room temperature so the patterns collected at 300 and 500 K were alike. The lattice parameters at 300 K are summarized in table I.

Sample	$CaBaCo_{3.5}Fe_{0.5}O_7$	$CaBaCo_3FeO_7$	$CaBaCo_{2.5}Fe_{1.5}O_7$	$CaBaCo_2Fe_2O_7$
a (Å)	6.31635(4)	6.33243(5)	6.35721 (15)	6.36466(15)
b (Å)	11.02198 (8)	11.02195(10)	11.00866 (24)	11.02164(22)
c (Å)	10.22810 (7)	10.25234(8)	10.27468 (9)	10.30152(10)
Vol. (Å^3)	712.067(9)	715.570(10)	719.066(24)	722.641(23)

Table I. Refined lattice parameters from neutron diffraction patterns collected at 300 K.

There are four non-equivalent sites in the unit cell for Co/Fe atoms. The refinements clearly reveal that the atom distribution is not random. The Fe atom preferably occupy the site at x~0, y~0 and z~0.895, whereas the Co atoms are more abundant in the other three sites. In Fig. 2, there are two projections of the unit cell emphasizing the 4 crystallographic sites for Co/Fe atoms. These atoms have a tetrahedral coordination sharing vertices but two layers are distinguished in the bc plane. Tetrahedra at the site 1 (yellow and Fe-rich) share corners with tetrahedra above and below them but not among them. Tetrahedra corresponding to sites 2, 3 and 4 (other colors and Co-rich) form a Kagome-like lattice (frustrated) and also share corners between them.

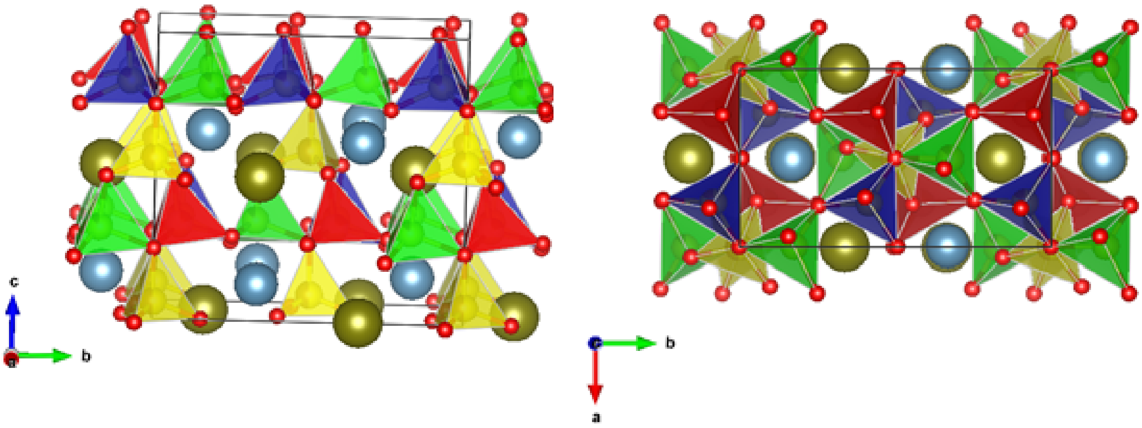

Fig. 2. Two projections of the orthorhombic cell for $CaBaCo_{4-x}Fe_xO_7$ samples. Brown, blue and red circles stand for Ba, Ca and O atoms whereas transition metals are in the center of the tetrahedra.

At low temperatures, magnetic contribution is clear as can be seen in Fig. 3. The stronger magnetic peaks can be indexed as (1/3,1,0), (2/3,0,2), (4/3,2,0) + (1/3,3,1) and (1/3,3,1). This confirms that the magnetic order follows the propagation vector **k** = (1/3,0,0) for all $CaBaCo_{4-x}Fe_xO_7$ samples here studied.

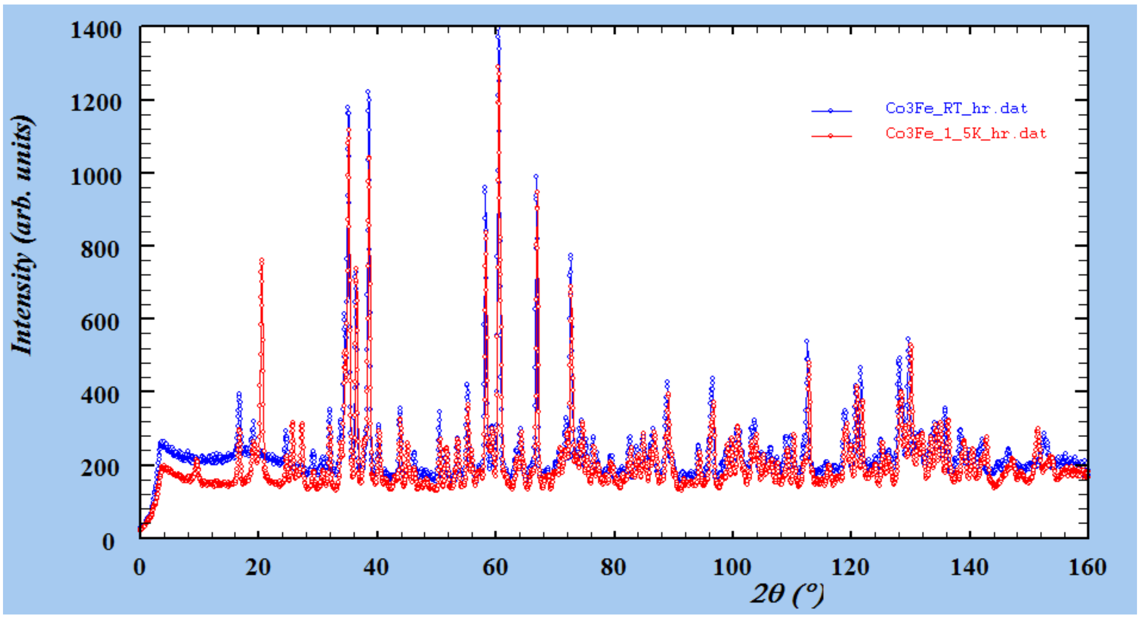

Fig. 3. Comparison of the neutron patterns for $CaBaCo_3FeO_7$ at 300 (blue line) and at 1.5 K (red line).

There are six possible magnetic arrangements following the irreducible representation Δ with k-point (1/3, 0, 0). The best fit is obtained with a constrained model belonging to the Shubnikov Pb'n'2_1 magnetic space group. The model suggests that magnetic moments are aligned along the ac-plane and the main magnetic interaction is an antiferromagnetic coupling between the Co/Fe atoms located at the site 1 (see Fig. 2) and the ones at the other three sites. Figure 4 shows an example of the refinements obtained at low temperature.

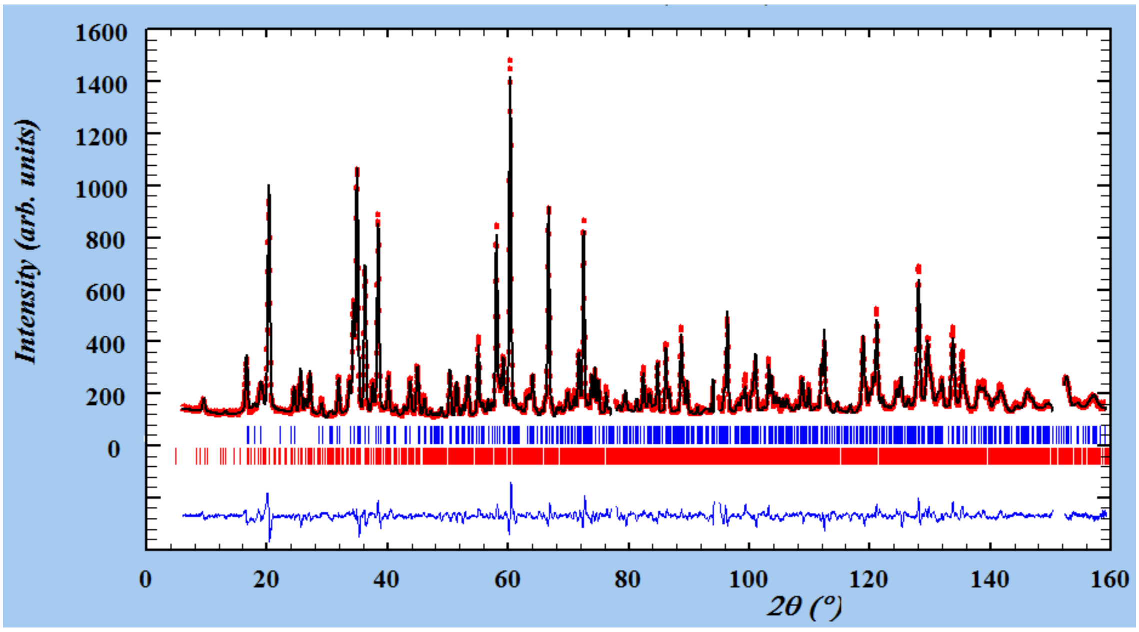

Fig. 4. Refinement of the neutron patterns for $CaBaCo_3FeO_7$ at 1.5 K using the magnetic model indicated in the report. Contribution from the cryofurnace has been removed.

Regarding the Zn-doped sample, our refinements reveal the same orthorhombic lattice at room temperature but the atomic occupation follows the opposite trend to the Fe-based samples. In this case, Zn preferably occupies the sites 2-4 while the site 1 is rich in Co. At low temperature, we do not detect any sign of long range magnetic ordering (see Fig. 5). Only diffuse scattering around 20º seems to indicate the presence of a short range magnetic order contribution.

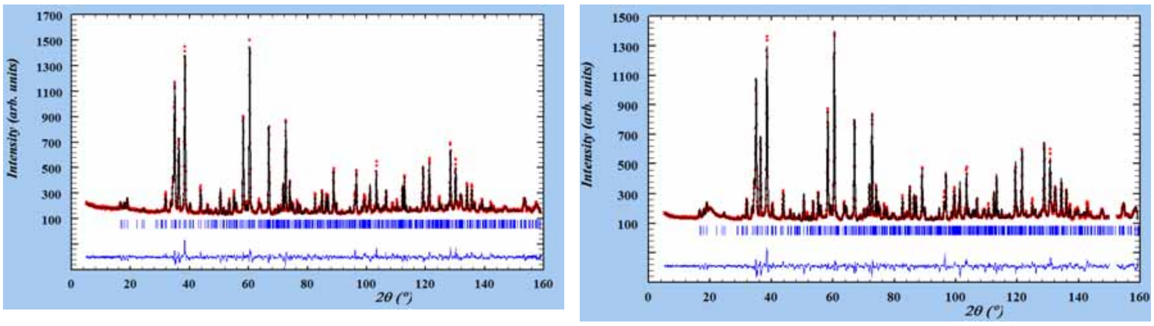

Fig. 5. Examples of neutron refinements for $CaBaCo_3ZnO_7$ at room temperature (left) and at 1.5 K (right).