Experimental report

25/07/2022

Proposal: **5-21-1116**

Council: 4/2018

Title: Magnetic ordering of Fe with different oxygen environments in the layered-ordered perovskite system Tb0.8-yBa0.8Ca0.4+yFe2O5+d(y=0,0.2,0.4)

Research area: Materials

This proposal is a new proposal

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Experimental team: Xabier MARTINEZ DE IRUJO LABALDE

Local contacts: Clemens RITTER

Samples: Tb0.8-yBa0.8Ca0.4+yFe2O5+d (y = 0, 0.2, 0.4)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	29/09/2018	02/10/2018
D20	1	1	22/10/2018	23/10/2018

Abstract:

The modification of the Tb/Ca ratio in the Tb0.8-yBa0.8Ca0.4+yFe2O5+d; (y = 0, 0.2 and 0.4) has resulted in the formation of different superstructures due to the ability of Fe to adopt different oxygen-environments and the various types of stacking sequence for the A cations. In addition, Fe is magnetically ordered within the different local environments in the structure above room temperature (~ 850 K).

Neutron Diffraction technique would provide us essential information about the oxygen sublattice within the crystal structure in order to determine the different environments for the Fe cations. As a second objective, this technique would allow us to study the magnetic structures associated with the Fe cations in the present system.

Magnetic ordering of Fe with different oxygen environments in the layered-ordered perovskite system Tb0.8-yBa0.8Ca0.4+yFe2O5+d (y=0,0.2,0.4)

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The aim of the proposal 5-21-116 was to determine the details (concentration and vacancies order) of the oxygen sub-structure and to study of the magnetic structures associated with the Fe cations in three members of the series $Tb_{0.8-y}Ba_{0.8}Ca_{0.4+y}Fe_2O_{5+\delta}$ (y = 0, 0.2, 0.4). In these three oxides, Fe is long-range magnetically ordered above room temperature due to the major presence of Fe^{3+}. Fe^{3+} (d^5, S = 5/2 in high spin state) located in the B-sites of perovskite and brownmillerite related structures tend to adopt a G-type antiferromagnetic ordering above room temperature. However, our experiments of thermal evolution of the magnetic susceptibility do not show an antiferromagnetic-like transition in these compounds. On the contrary, ferri-/ferro-magnetic contributions seem to appear associated with a different behaviour of the Fe^{3+} moments placed in different oxygen environments. Besides, Mössbauer spectroscopy shows different local environments for the iron magnetically ordered within the structure.

The NPD data collected in the framework of the present experiment allowed to fully understand the structure and properties of these materials, including multiferroism observed in some of them. The results have been published in two papers: Chem. Mater. 2019, 31, 15, 5993–6000 (DOI:10.1021/acs.chemmater.9b02716) and Inorg. Chem. 2021, 60, 8027−8034 (DOI: 10.1021/acs.inorgchem.1c00529).

Figure 1, taken from Chem. Mater. 2019, 31, 15, 5993–6000, explains the origin of multiferroism in $Gd_{1.2}Ba_{1.2}Ca_{0.6}Fe_3O_8$ (isostructural with $Tb_{0.8}Ba_{0.8}Ca_{0.4}Fe_2O_{5.33}$, y=0).

Figure 2 (from Inorg. Chem. 2021, 60, 8027−8034) describes the superexchange interactions responsible for the magnetic structures of materials of the homologous series $A_{3m+5n}Fe_{3m+5n}O_{8m+13n}$, where A = RE, Ba, and Ca, including some of the compounds studied in the present experiment.

Figure 1

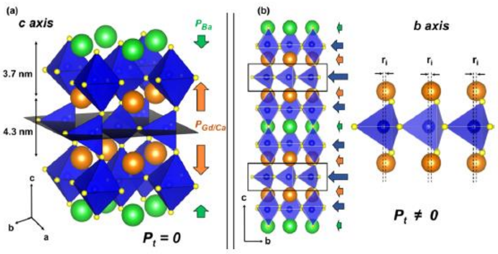

Figure 5. Graphic representation of the polar unit cell of $Gd_{1.2}Ba_{1.2}Ca_{0.6}Fe_3O_8$. (a) Arrows indicate polarization due to Ba atoms (green) and Gd/Ca atoms (orange) displacements along the *c*-axis. The length of the arrows is proportional to *P*. The *m* plane perpendicular to the *c*-axis (represented in gray) cancels out P_t. (b) Arrows indicate polarization in the different layers (Ba−O layers in green, Gd/Ca−O in orange, Fe−O in octahedral layers, and Fe−O in tetrahedral layers), including the anionic and cationic contributions along the *b*-axis. r_i is the shift distance of the Fe atoms with respect to the A-cations along the *b*-axis.

Figure 2

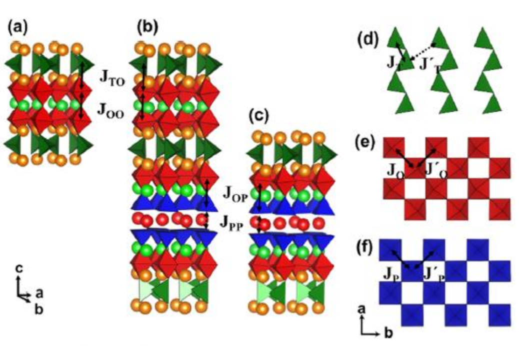

Figure 7. Superexchange interactions of Fe-O-Fe within the structures of $RE_{1.2}Ba_{1.2}Ca_{0.6}Fe_3O_8$, $RE_{2.2}Ba_{3.2}Ca_{2.6}Fe_8O_{21}$, and $REBa_2Ca_2Fe_5O_{13}$ (a−c) interlayer paths and (d−f) intralayer paths.