Experimental report

06/01/2021

Proposal: **5-31-2680** **Council:** 4/2019

Title: INVESTIGATING HIGH-TC SPIRAL ORDERS IN YBa(Cu1-xCox)FeO5 MULTIFERROICS WITH ENHANCED ANISOTROPY AND SPIN-ORBIT COUPLING

Research area: Materials

This proposal is a new proposal

Main proposer: **Jose Luis GARCIA MUNOZ**

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Samples: YBa(Cu1-xCox)FeO5 x=0.02; 0.05; 0.075; 0.10; 0.125; 0.15; 0.20; 0.25

Instrument	Requested days	Allocated days	From	To
D2B	2	2	27/01/2020	29/01/2020
D20	3	3	17/01/2020	20/01/2020

Abstract:

The low-magnetic ordering temperatures (typically <100 K) critically restrict the potential uses of magnetoelectric multiferroics for spintronics and low-power magnetoelectric devices. YBaCuFeO5 (YBCFO) displays magnetism-driven ferroelectricity at unexpectedly high temperatures (above RT), being one of the best candidates to switchable, magnetism-driven ferroelectricity at zero field. The stability range of its spiral phase can be extended far beyond room temperature by manipulating the Cu/Fe chemical disorder in the bipyramids and some structural parameters or distances. As an alternative strategy to upgrade its multiferroic properties, the substitution of Cu2+ by Co2+ is proving to be one of the most interesting. In addition to promoting B-site cation disorder, this substitution increases the magnetic anisotropy in the system and the spin-lattice coupling thanks to the significant orbital moment contribution from Co2+ ions, with direct incidence on the stability of the spiral and the magnetoelectric coupling.

Experimental report

Proposal number: 5-31-2680
Schedule: (D1b) 17th- 20th Jan 2020 and (D2b) 27th-29th Jan 2020
Experiment title: Investigating high-Tc spiral orders in $YBa(Cu_{1-x}Co_x)FeO_5$ multiferroics with enhanced anisotropy and spin-orbit coupling
Participants: Arnau Romaguera Camps, Xiaodong Zhang, Jose Luis Garcia Muñoz and Oscar Ramon Fabelo (LC)

Abstract

The low-magnetic ordering temperatures (typically <100 K) critically restrict the potential uses of magnetoelectric multiferroics for spintronics and low-power magnetoelectric devices. $YBaCuFeO_5$ (YBCFO) displays magnetism-driven ferroelectricity at unexpectedly high temperatures (above RT), being one of the best candidates to switchable, magnetism-driven ferroelectricity at zero field. The stability range of its spiral phase can be extended far beyond room temperature by manipulating the Cu/Fe chemical disorder in the bipyramids and some structural parameters or distances. As an alternative strategy to upgrade its multiferroic properties, the substitution of Cu^{2+} by Co^{2+} is proving to be one of the most interesting. In addition to promoting B-site cation disorder, this substitution increases the magnetic anisotropy in the system and the spin-lattice coupling thanks to the significant orbital moment contribution from Co^{2+} ions, with direct incidence on the stability of the spiral and the magnetoelectric coupling.

Experimental part

There were no problems with the beam, cryofurnace or d20 and d2b diffractometers during the measurements, and quality neutron patterns could be collected within the desired temperature range, between 10 and 500K.

In this experiment, we focused on the compositions $YBaCu_{1-x}Co_xFeO_5$ with x=0, 0.01, 0.02, 0.03, 0.05, 0.075, 0.10, 0.15 and 0.25. The samples have been prepared using the conventional solid-state reaction method although we also measured several powder specimens obtained by crushing single crystals. Most of the samples were prepared following the same cooling rate of 300K/h to room temperature after the last annealing. Additionally, for selected compositions (e.g. x=0.10) we studied the influence of the cooling rate after the last annealing on the magnetic transitions, the Fe/Cu cationic disorder and the stability of the incommensurate spiral magnetic phase. So, samples prepared under different cooling rates were also studied, including fast quenching processes in liquid nitrogen.

In general, D2b measurements were carried out at room temperature with a neutron beam wavelength λ = 1.594 Å. Neutron patterns with good statistics were collected in order to discern chemical disorder at the B-site and fine structural details. A number of compositions (very few) were also measured at 10k. The data recorded by the 2dim detector were integrated using both the high flux and high resolution modes.

In D20 the samples were measured in dynamic mode by means of temperature ramps with heating rates 2K/min, in the temperature interval 10-500K using wavelength $\lambda = 2.41$ Å. Moreover, most of the samples were also measured with longer counting times at fixed selected temperatures (generally at T=10K and 500K). The last temperature T=500K corresponds to the paramagnetic state.

Figure 1(a), as an example, displays the refined D2B diffraction pattern for $YBaCu_{1-x}Co_xFeO_5$ x=0.02 sample at 300 K. Patterns are similar for all compositions: they are well described using the *P4mm* symmetry, which gives the best agreement factors and accounts for different spatial disorder of the transition metals. The partial cationic disorder at the B-site (key for generating magnetic frustration and the magnetic spiral) was determined, as well as the incommensurability q [$\mathbf{k_2}$=(1/2 1/2 1/2 ± q)] of the spiral phase. We found that the overall cation disorder at the B-sites increases by doping without changing the sample preparation process.

Figure 1(b) shows the refined cell parameters of each sample at RT. The figure reveals that there is a systematic tendency of the cell to increase *a* and decrease *c* by cobalt doping. The volume is expanding as a function of Co content (the effective ionic radii of Co^{2+} is higher than Cu^{2+}). A full description of the evolution of the cationic disorder and the fine structural details with doping will be conveniently published.

Based on d20 measurements, de evolution of the successive magnetic transitions in $YBaCu_{1-x}Co_xFeO_5$ was determined (Fig. 2), as well as the changes in the stability of the different competing commensurate and incommensurate phases. The temperature evolution of the neutron patterns for each composition has been fully analyzed by Rietveld refinements and the evolution of the main magnetic parameters has been extracted. Full descriptions of the different magnetic structures between 10 and 500K have been obtained along the series. The T-x phase diagram has been constructed in the range 10K-500K. A comprehensive description of these results will be published.

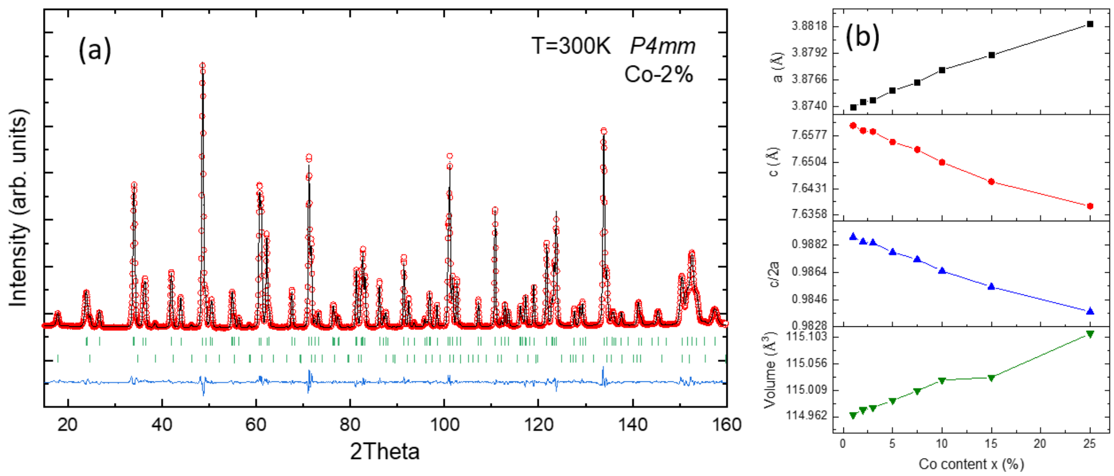

Figure 1. (a) Rietveld refinement (black curve) of the D2B neutron diffraction intensities (red circles) at T=300K. Bottom blue line is the observed-calculated difference. (b) Evolution with Co doping of the cell parameters and volume analyzed from D2B neutron diffraction data at room temperature.

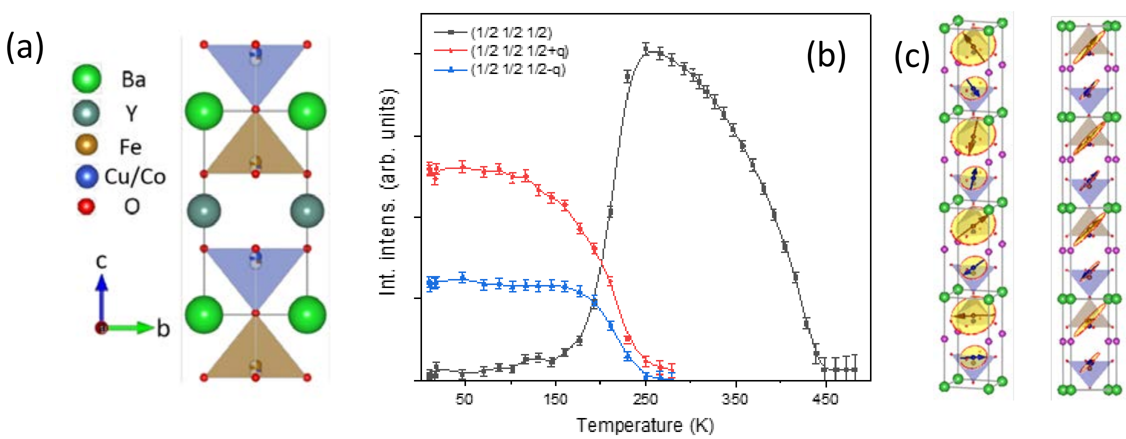

Figure 2. (a) Projection of the *P4mm* structure. (b) Evolution of the CM (collinear) and ICM (spiral) magnetic integrated intensities in one of the samples. (c) Refined spiral magnetic order at 10K.