Evolution of Mn and Co oxidation state on TbMn$_{1-x}$Co$_x$O$_3$ compounds

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Abstract. Structural and electronic properties of TbMn$_{1-x}$Co$_x$O$_3$ samples have been characterized by means of x-ray and neutron diffraction and x-ray absorption spectroscopic techniques. Crystallographic structure was refined from diffraction data, and samples show the orthorhombic distorted perovskite structure ($Pbnm$), being isostructural to TbMnO$_3$, except for $x=0.4, 0.5$ and $0.6$, where an ordered double perovskite structure ($P2_1/n$) is found. The electronic configuration of Mn and Co ions was obtained along the series from the chemical shift of the edge on x-ray absorption spectra, at the Mn and Co K-edges. Our results agree with a charge redistribution between Mn and Co ions, yielding a mixed valence state Mn$^{3+}$/Mn$^{4+}$ and Co$^{3+}$/Co$^{2+}$ for the whole series.

1. Introduction.
The multiferroic state of TbMnO$_3$ is found at low temperatures, below $T_{N1}$=T$_{FE}$=27 K, where a non-collinear magnetic ordering breaks the spatial inversion symmetry allowing a ferroelectric state [1]. The first magnetic transition on this compound takes place at $T_{N1}$=41K, when an antiferromagnetic (AFM) collinear ordering arranges. Magnetoelastic properties are highly correlated in this compound, so the main challenge nowadays is to promote the multiferroic state to higher temperatures, keeping magnetoelastic coupling.

In this work, Mn sublattice has been partially substituted by a magnetic ion, such as Co, in order to enhance magnetic interactions. In other rare earth perovskites, Co is normally trivalent. Co$^{3+}$ shows a $3d^6$ electronic configuration on a CoO$_6$ octahedral environment and can show several spin states depending on the occupation of $t_{2g}$ and $e_g$ orbitals, most of them having a net magnetic moment [2]. There are three configurations that may also change with temperature and composition: low spin (LS), intermediate spin (IS) and high spin (HS) which correspond to $S=0$, $S=1$ and $S=2$ respectively. In addition, Co$^{2+}$ is also a magnetic ion, with $S=3/2$ on its HS configuration.

Previous works on similar La-based compounds claim the evolution of the oxidation state of Mn and Co from Mn$^{3+}$/Co$^{3+}$ to Co$^{2+}$/Mn$^{4+}$ [3]. This would lead to superexchange interactions through oxygen ions. On the other hand, different results are found in the case of LaMn$_{1-x}$Ni$_x$O$_3$ series compounds. Mn$^{3+}$/Mn$^{4+}$ mixed valence state is described for the lower doped compounds, while Ni$^{2+}$/Ni$^{3+}$ appears at higher Ni concentrations [4]. This mixed valence state can lead to a large variety of competitive magnetic interactions, not found on Co$^{2+}$/Mn$^{4+}$ valence state, such as AFM...
superexchange (Ni-O-Ni, Mn\textsuperscript{n+}-O-Mn\textsuperscript{n+}, n=3 or 4), ferromagnetic (FM) superexchange (Ni\textsuperscript{2+}-O-Mn\textsuperscript{4+}) and FM double exchange (Mn\textsuperscript{3+}-O-Mn\textsuperscript{4+}).

Thus, determining the evolution of the oxidation state of Mn and Co is essential to further understand the magnetic properties of TbMn\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} series.

2. Experimental Section.
All samples were synthesized by solid state chemistry procedures. As a first step, stoichiometric amounts of Tb\textsubscript{2}O\textsubscript{7}, MnCO\textsubscript{3} and Co\textsubscript{2}O\textsubscript{4} were mixed, ground and calcined overnight at 1000 °C in air. After that, they were ground, pressed into pellets and sintered at 1200°C for 1 day in air. Then, we repeat the last process, but at 1400 °C for 2 days in Ar atmosphere for x=0.1, 0.2 and air in the case of x=0.3, 0.4, in order to ensure the appropriate oxygen content and the lack of vacancies. O\textsubscript{x} atmosphere was used for higher Co concentrations (x≥0.5). The oxygen content was tested by cerimetric titration and all samples have the correct oxygen content within experimental error (±0.01).

A Rigaku D/max-B diffractometer with a rotating anode was used to preliminarily test the crystallographic structure of the powder samples at room temperature, selecting the Cu K\textsubscript{α} wavelength (λ=1.5418 Å). Neutron diffraction powder experiments were performed at D1B and D2B instruments at ILL (Grenoble, France) to properly determine the crystallographic structure and complement absorption experiments.

Finally, x-ray absorption experiments were carried out at BM25-Spline beam line at the ESRF (Grenoble, France), at the Mn and Co K-edge, with a double crystal Si (111) monochromator. The energy resolution of the beam line is AE/E~10\textsuperscript{-4}. All spectra were collected at room temperature in transmission mode, using ionization chambers as detectors, so that we could measure up to x=0.6 at the Mn K-edge and down to x=0.3 at the Co K-edge. The powder pellets were mixed with cellulose and we used TbMnO\textsubscript{3} (Mn\textsuperscript{3+}) as a reference for Mn K-edge and TbCoO\textsubscript{3} (Co\textsuperscript{3+}) for Co K-edge.

3. Results and discussion.
The crystallographic structure has been refined by Rietveld analyses with FullProf package. X-ray diffraction measurements at room temperature have been successfully refined using a simple perovskite model, space group Pbnm, for the whole series. The evolution of the lattice parameters has been obtained along the series and can be seen on fig. 1. There is a shrinkage of a and b axis as Co concentration increases, being stronger the contraction of b-axis. In both cases, these axes change their contraction rate from x~0.4, being smaller after this concentration of Co. On the contrary, c axis expands up to x~0.4-0.5, when it reaches a maximum and then slightly decreases as Co content increases. The global effect is a contraction of the unit cell volume, with an inflection point for x~0.5.

In this central region, the crystallographic structure change and corresponds to a monoclinic cell, as will be explained hereinafter.

When Mn and Co have different oxidation state they have rather different radius. This fact, as will be probed below, can lead to the ordering of the Mn-Co sublattice in a NaCl structure [5]. In this case, the crystallographic structure is a double perovskite A\textsubscript{2}BB’O\textsubscript{6}, with monoclinic space group P2\textsubscript{1}/n. Neutron diffraction allows distinguishing between Mn and Co, as these ions have very different neutron scattering lengths. The double perovskite structure gives better results for diffraction patterns (not shown here) of intermediate samples (x=0.4, 0.5 and 0.6), with a ~25% of antisites defects, while the rest of the samples are consistent with a simple perovskite structure, as can be seen on figure 1.

The values of B-O distances of BO\textsubscript{6} octahedra can be seen in fig. 2 for the whole series. As Co content increases, BO\textsubscript{6} octahedra tend to be more regular. In the composition range 0.4 ≤ x ≤ 0.6, two octahedra can be differentiated corresponding to the two Wyckoff positions 2d and 2c of the double perovskite. BO\textsubscript{6} octahedron (2d) is composed of ~75% Co atoms and 25% Mn ones. Considering the ionic bond valence model, this corresponds to Co\textsuperscript{2+3} and Mn\textsuperscript{2+8}. Co\textsuperscript{3+0} and Mn\textsuperscript{3+6} is obtained in the case of B’O\textsubscript{6}, with the opposite atom composition. As a first approximation, B and B’ sites favor the
existence of Co$^{2+}$ and Mn$^{4+}$ cations respectively, while misplaced atoms might be favored in the trivalent state.

The oxidation state of Mn and Co has been properly determined by x-ray absorption techniques. Figures 3 and 4 show the normalized x-ray absorption near edge spectra (XANES) measured in transmission at Mn K-edge and Co K-edge respectively. In both cases a shift of the edge at higher energies is observed as Mn is diluted by Co. This chemical shift of the edge is linearly related to the valence state of the absorber atom [6], so that the oxidation state increases when the edge shifts to higher energies, as shown by the arrow on figs. 3 and 4. In addition, the evolution of the pre-peak area at the Co K-edge can be observed in the inset of fig. 4. The integrated absorption of the pre-edge increases as Co content does, so as Co$^{2+}$ tends to Co$^{3+}$ for $x\geq 0.5$. This is related to the hybridization of 3$d$ states of Co and 2$p$ states of O: Co-O covalency increases as the valence state of Co increases.

![Fig. 1. Evolution of the lattice parameters and the unit cell volume along the series. The crystallographic structure obtained for the different $x$ ranges is indicated. Data for $x=0$ is taken from ref. [4].](image1)

![Fig. 2. Interatomic distances in BO$_6$ octahedra obtained from the refinement of neutron diffraction data from D1B. B-O1=Apical. B-O2=Equatorial. $<B$-$O>$= Average.](image2)

![Fig. 3. XANES spectra at the Mn K-edge for $0\leq x \leq 0.6$ measured in transmission.](image3)

![Fig. 4. XANES spectra at the Co K-edge for $0.3\leq x \leq 1$ measured in transmission. Inset: Integrated absorption at the pre-edge region.](image4)
a full charge disproportion is not found along the series (dashed lines). The valence of Mn increases when it is diluted with Co from +3 (TbMnO<sub>3</sub>) up to +3.6 for x=0.5, 0.6, when it tends to saturate. Inversely, Co valence decreases when it is diluted with Mn from +3 (TbCoO<sub>3</sub>) down to 2.4 (x=0.5, 0.4 and 0.2), also tending to saturation.

![Fig. 5. Evolution of the formal valence of Mn and Co along the series. Green triangles represent the weighted average of Mn and Co valences. Dashed lines represent the tendency of a full charge disproportion. Dotted line indicates the average trivalent state.](image)

We can assert then that there is a charge redistribution along the series, and the formal equilibrium Mn<sup>3+</sup>+Co<sup>3+</sup>⇋Mn<sup>4+</sup>+Co<sup>2+</sup> is not completely shifted to the right. This yields to a mixed valence state Mn<sup>3+</sup>/Mn<sup>4+</sup> and Co<sup>3+</sup>/Co<sup>2+</sup>, which is in agreement with the evolution of B-O distances obtained from neutron powder diffraction experiments (table I) and may be due to the existence of antisite defects in the intermediate compounds.

4. Conclusions.

TbMn<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> series has been synthesized by ceramic procedures and all samples are single phase. At intermediate concentrations (x=0.4, 0.5, 0.6) the structure becomes monoclinic P2<sub>1</sub>/n, and the metal transition sublattice is ordered on a double perovskite structure with antisites (~25%). The dilution with Co decreases the distortion on BO<sub>6</sub> octahedra. We have also determined the valence state along the series by x-ray absorption spectroscopy. We found a mixed valence state along the series Mn<sup>3+</sup>/Mn<sup>4+</sup> and Co<sup>3+</sup>/Co<sup>2+</sup> so that the oxidation of Mn<sup>3+</sup> is coupled to the reduction of Co<sup>3+</sup>. The B-O distances obtained by diffraction techniques are in agreement with the electronic information extracted from XANES.

It is noteworthy that several exchange interactions are expected to appear in this series (such as FM superexchange Mn<sup>4+</sup>-O-Co<sup>2+</sup>), which makes it very promising to enhance FM correlations.

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