



	Experiment title: XAFS study of Tb(Mn _{1-x} A _x)O ₃ perovskites (A= Ga, Sc): effect of destabilizing the Mn sublattice on the magnetoelectric coupling.	Experiment number: 25-01-741
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Shifts:	Local contact(s): Felix Jimenez-Villacorta	<i>Received at ESRF:</i>
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Report:

TbMnO₃ with orthorhombic (*Pbnm*) distorted perovskite-structure is a magnetoelectric multiferroic at low temperatures, showing antiferromagnetism (AFM) and ferroelectricity (FE) below 27 K [1]. Mn³⁺ magnetic moments show an AFM sinusoidal order below T_{Mn}~41 K and also Tb³⁺ moments below T_{Tb}~7 K. At 27 K Mn³⁺ moments are reoriented into a cycloidal non-collinear arrangement, leading to FE via Dzyaloshinsky-Moriya interaction. In order to shed light into these striking properties, we have investigated the modification of the structural and magnetic arrangement when diluting the Mn³⁺ sublattice with non-magnetic ions, such as Sc³⁺. All of the samples are isostructural to the parent compound TbMnO₃, crystallizing in an orthorhombic cell with space-group *Pbnm* symmetry. The homovalent substitution of Mn³⁺ with the larger Sc³⁺ ion leads to an increase in both the unit-cell volume and the BO₆ octahedra tilting. The analysis of neutron and x-ray diffraction patterns suggest a continuous evolution from a Jahn-Teller distorted BO₆ octahedron in TbMnO₃ into a nearly regular one in TbScO₃. Here, the new TbMn_{1-x}Sc_xO₃ series has been synthesized and the structural properties have been characterized by x-ray absorption spectroscopy.

The evolution of the Mn local structure after dilution was probed by measuring EXAFS spectra at the Mn *K* edge at 50 K for the whole series. Figure 1 (a) shows the Fourier transform (FT) of the *k*-weighted EXAFS signal calculated between 3 and 12 Å using a sine window. The inset displays a typical EXAFS signal analyzed. The modulus of the FT spectra of all samples shows a main peak at 1.4 Å corresponding to the first Mn-O coordination shell without phase-shift correction. The intensity and shape of this peak is practically independent of the dilution indicating that the oxygen coordination geometry around Mn remains almost constant for the whole series. The contribution from further shells, Mn-Tb, Mn-Mn/Sc, and Mn-O, gives rise to a set of weak and broad peaks between 1.8 and 2.8 Å. Their low intensities suggest a large number of different paths with destructive interferences. This fact is in agreement with the high orthorhombic distortion of their crystallographic structures. Fits for selected compounds are also displayed in Fig. 5(b). In these fits, the starting point for all samples was the crystallographic data of TbMnO₃ at 50 K. The coordination numbers were fixed to their crystallographic values and the amplitude reduction factor s_0^2 was fixed to 0.84 for all samples. As shown on figure 2, all samples show the same distribution of Mn-O

distances composed by two short pairs and one long pair of Mn-O bond lengths. The short distances slightly increase with dilution but the octahedral distortion itself remains for all x value.

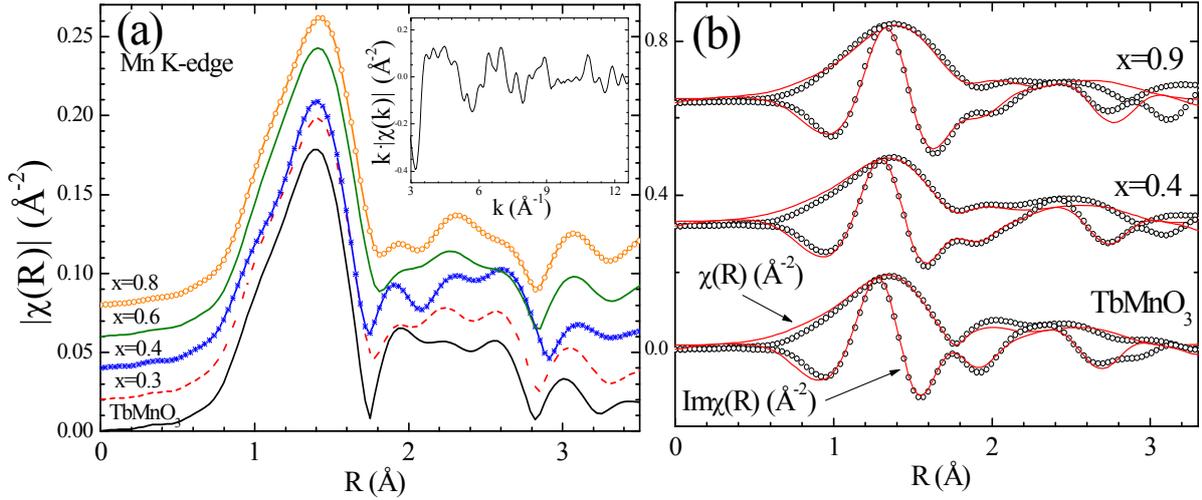


FIG. 1. Left graph: Fourier transform of the experimental k^2 weighted signals at the Mn K edge. Inset: EXAFS spectra k weighted at the Mn K edge of TbMnO_3 sample. Right graph: modulus and imaginary part of the experimental Fourier transforms together with its fit for samples $x=0, 0.4$, and 0.9 at the Mn K edge.

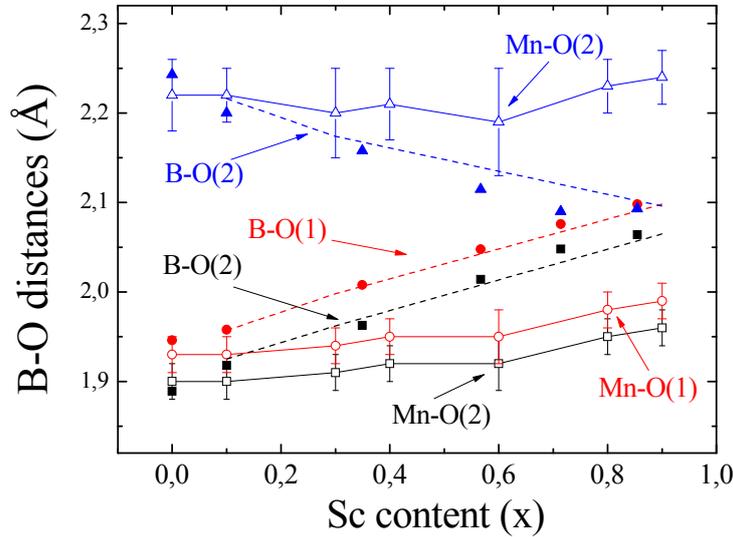


FIG. 6. Evolution of Mn-O distances along the series (open symbols) obtained from EXAFS analysis. The B -O distances calculated by weighted average of the previous Mn-O distances and Sc-O distances (dotted line) are compared to the experimental B -O bond lengths obtained from neutron-diffraction refinements (closed symbols).

The existence of MnO_6 octahedra with a tetragonal distortion in a diluted system is a new and surprising result. Previous findings in $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ revealed that the Jahn-Teller distorted MnO_6 octahedron transforms into a regular octahedron with dilution and this transformation is nearly coinciding with the appearance of long-range ferromagnetism. The overall reduction in such a distortion in the MnO_6 octahedron was explained by an orbital-flipping model [2] whereas the occurrence of ferromagnetism has been recently ascribed to the orbital mixing of Mn orbitals due to the structural bias effect of the orthorhombic cell with $Pbnm$ symmetry.[3] The instability of isolated distorted MnO_6 octahedra was confirmed in a study of $\text{LaB}_{1-x}\text{Mn}_x\text{O}_3$ samples $B=\text{Ga}$ or Sc with a very diluted Mn^{3+} concentration. This suggested that the Mn clusters have to have a minimum size in order to show the tetragonal distortion typical of Jahn-Teller Mn^{3+} ions.[4] The persistence of this type of distortion in the whole $\text{TbMn}_{1-x}\text{Sc}_x\text{O}_3$ series adds a new factor not previously considered, the degree of the anion octahedra tilting.

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