Effects of A-site order on the Mn local structure and polar phases of magnetoelectric $REBaMn_2O_6$ (RE: La, Nd, Sm, Y)

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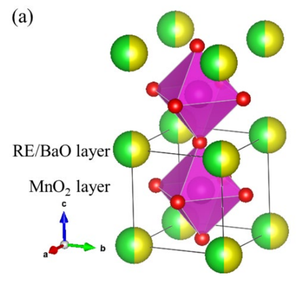
Motivation

Perovskite-type manganese oxides $RE_{1-x}AE_xMnO_3$ (RE = trivalent rare-earth, AE = divalent alkaline-earth) have focused widespread interest in the last decades thanks to the key discovery of their colossal magnetoresistance behavior but also, metal-insulator transitions, thermoelectricity, ferroelectricity and (anti)ferromagnetism. The last types of orderings may appear simultaneously and be coupled in magnetoelectric multiferroics[1]. When divalent AE cation is Ba, the different ionic size favors the ordering of Ba and RE atoms in the A-site of the perovskite-type lattice. In particular, for x=0.5, i.e. $REBaMn_2O_6$ stoichiometry, RE and Ba ions can alternately occupy the A-sites along the *c* axis if the synthesis conditions are properly controlled, showing a complex magnetoelectric phase diagram as a function of the ionic radius of RE atoms and the degree of A-site disorder[2-4].

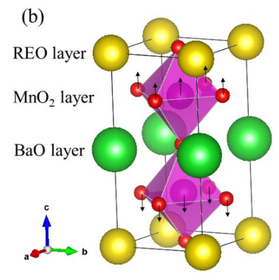
The occurrence of polar phases and, consequently ferroelectricity, in these systems strongly depends on the type of the A-site rare-earth cation and the degree of A-site order, which can break the inversion symmetry at the Mn sites. While characterizing the Mn local structure of the different magnetoelectric phases is key to elucidate the ferroelectric mechanism, this information is very limited in these systems. The ferroelectric mechanism is termed displacive when the structural distortions strictly vanish in the paraelectric phase, and order–disorder when they are non-vanishing but thermally average out to zero in the paraelectric phase. Here, we perform a combined high energy resolution fluorescence detected (HERFD) and total fluorescence yield (TFY) X-ray absorption spectroscopy (XAS) study to understand the alteration of the Mn local structure as a function of temperature, A-site cation size and A-site randomness. The implication of these changes in the occurrence of polar states and the mechanism of the magnetoelectric transitions is determined.

1. Y. Taguchi *et al.*, Physica B **407**, 1685 (2012)
2. J. Blasco, G. Subías, M. L. Sanjuán, J. L. García-Muñoz, F. Fauth & J. García, Phys. Rev. B 103, 064105 (2021)
3. J. Blasco, G. Subías, J. L. García-Muñoz, F. Fauth, M. C. Sánchez & J. García, Phys. Rev. B 103, 214110 (2021)
4. J. Blasco, G. Subías, J. L. García-Muñoz, F. Fauth & J. García, J. Phys. Chem. C 125, 19467 (2021)

A-site disordered



A-site ordered



FE polarization ↑ r (RE^{3+})↓

Experimental Details

CLÆSS beamline @ ALBA

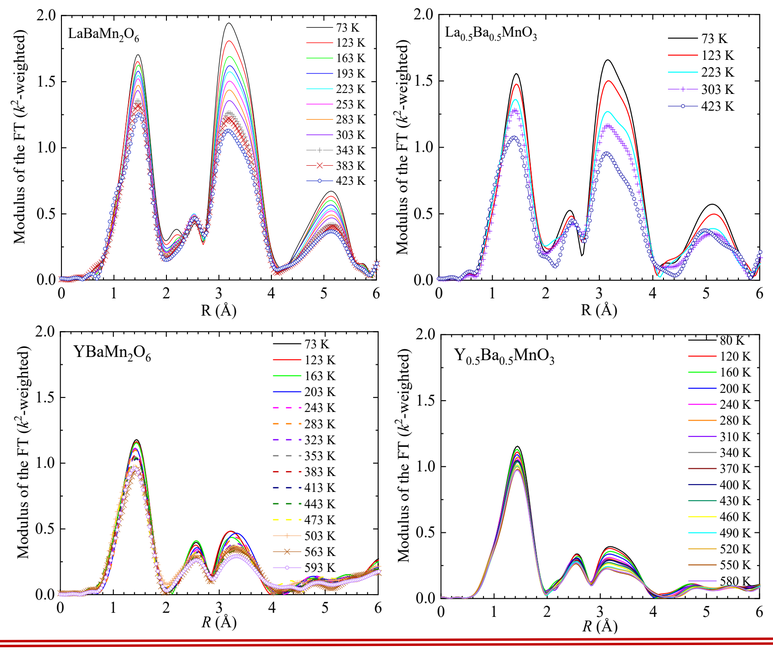
L. Simonelli et al., Cogent Physics (2016), 3: 1231987

$(REBa)^AMn^B_2O_6$ (RE: La, Nd, Sm, Y)
1375 °C reductive atmosphere
+ Topotactic oxidation

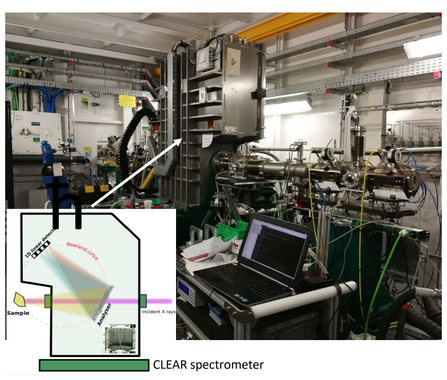
$(RE_{1/2}Ba_{1/2})^AMn^BO_3$ (RE: La, Nd, Sm, Y)
1400 °C reductive atmosphere
+ Quenching
+ Annealing in O_2

XAS experiment:

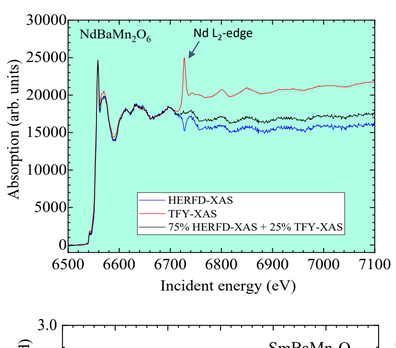
1. RE: La & Y → Transmission Mn K-edge EXAFS

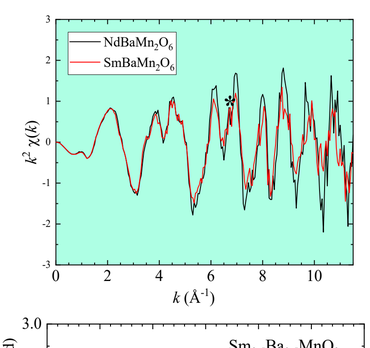


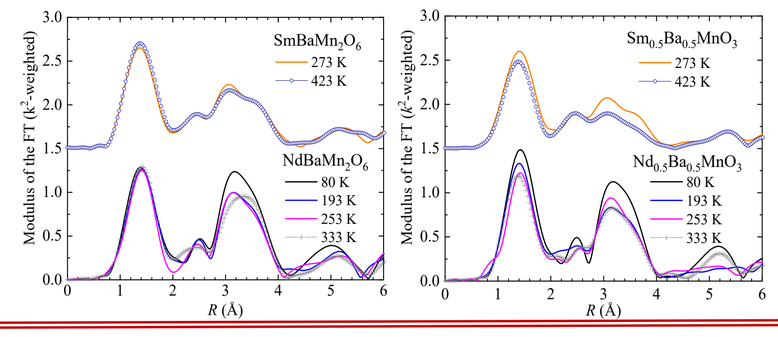
2. RE: Nd & Sm → Mn $K\beta_{1,3}$ HERFD-XAS & TFY-XAS



S. Lafuerza et al., Phys. Rev. B, 93, 205108 (2016)
S. Lafuerza et al., Nanoscale, 12, 16270 (2020)

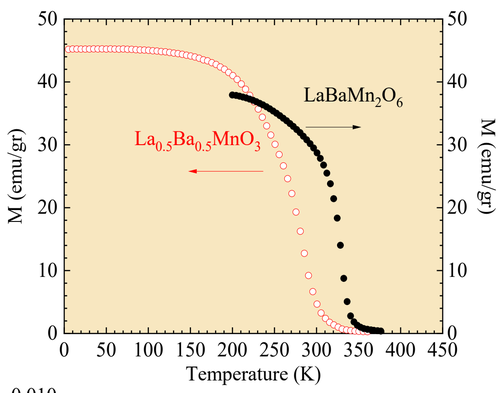


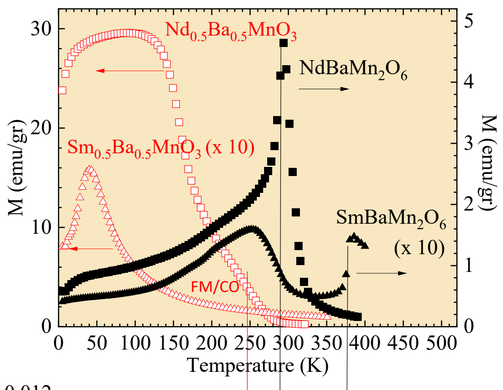


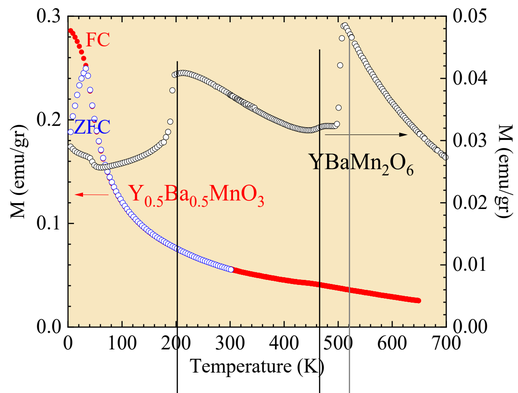


Results & Conclusions (*Subías et al. submitted 2022*)

Magnetic properties:







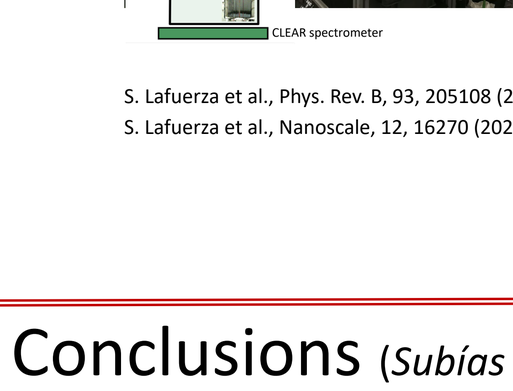
Mn local structure:

Einstein model

$$\sigma^2(T) = \sigma_0^2 + \frac{\hbar^2}{2\mu K_B \theta_E}\coth\left(\frac{\theta_E}{2T}\right)$$

$\theta_E(La_{0.5}Ba_{0.5}MnO_3) = 467 \pm 50\ K$

$\theta_E(LaBaMnO_3) = 467 \pm 50\ K$
σ_0^2 = -0,0015



I. A-site ordered/disordered $\underline{La}BaMn_2O_6$ → FM & non polar phases
↕
Undistorted MnO_6 & No charge localization

II. Large difference in ionic size of A-site RE/Ba cations + A-site disorder → detrimental for long-range FM
↕
Presence of local MnO_6 distortions & Charge localization

Mechanism for the polar-structural-charge localized transitions ?

Displacive
$\Delta S_{CO} = 2 \cdot R \cdot ln2 = 1.39R$
$= 11.53\ J/mol \cdot K$

or

Order - Disorder
$\Delta S_{order-disorder} = R \cdot ln2 = 0.695R$
$= 5.76\ J/mol \cdot K$

III. EXAFS results & Entropy content (ΔS) → $\underline{\text{order-disorder}}$ + displacive mechanisms for polar charge-localized transitions

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