

## Long and short ordering in cationic deficient Manganese related brownmillerites

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Ever since colossal magnetoresistance (CMR) was discovered in  $\text{Ln}_{1-x}\text{AE}_x\text{MnO}_3$  (Ln=lantanide; AE alkaline-earth), establishing the relationship between structure and properties constitutes a prominent place in the landscape of solid-state science because of its intriguing potential applications. The occurrence of different  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratios seems to be responsible of the different magnetic behaviours observed and can be tuned by either changing i) the Ln/AE ratio or ii) the oxygen content, i.e.,  $\text{Ln}_{1-x}\text{AE}_x\text{MnO}_{3-\delta}$ . Although plenty of works has been devoted to the first point, less effort has been devoted to study the effect of the compositional variations at the oxygen sublattice. In spite of the partial break-up occurring at the 3D network of octahedral sharing corners, responsible of the double exchange interactions the oxygen deficient compounds exhibits complex magnetic and electric properties [1].

In this context, we have recently shown the stabilization of a new brownmillerite (B) compound  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{2.5}$  [2], built up of octahedral and tetrahedral layers sharing corners, exhibiting CMR. In this compound  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  oxidation states coexist leading to complex electric and magnetic behaviours. Even more, it is also known that the manganese oxidation state is not the only parameter affecting to the above behavior. Previous studies have shown that the introduction of cation vacancies in  $(\text{La}_{1-x}\text{Ca}_x)_z\text{MnO}_3$  [3], can lead to materials with the same  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  concentration but having different properties. Note that z accounts for the % of cationic vacancies.

In this sense, the aim of this work is studying the effect of the cationic vacancies in the polycrystalline  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{2.5}$  compound. For that purpose, cationic vacancies up to 5% have been introduced in the parent material according to  $(\text{La}_{1-x}\text{Sr}_x)_z\text{MnO}_3$  formula. The prepared compositions for this paper,  $(\text{La}_{0.525}\text{Sr}_{0.475})_{0.99}\text{MnO}_3$  and  $(\text{La}_{0.551}\text{Sr}_{0.449})_{0.98}\text{MnO}_3$ , were selected in order to keep the same  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio respect to the  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  material. Perovskite (P) phases were treated in a Cahn D-200 electrobalance and a topotactic reduction process led to  $(\text{La}_{1-x}\text{Sr}_x)_z\text{MnO}_{2.5}$  samples where the Mn oxidation state should be identical than in  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{2.5}$ . The X-ray diffraction study suggests a B related structure for the above samples. Nevertheless, a clear orthorhombic distortion is observed as the percentage of cationic vacancies increases. At this point a technique able to provide information concerning the vacancy ordering is required. In this sense, a SAED (Selected Area Electron Diffraction) and HRTEM (High Resolution Transmission Electron Microscopy) study has been performed in two samples  $\text{La}_{0.52}\text{Sr}_{0.47}\text{MnO}_{2.5}$  and  $\text{La}_{0.54}\text{Sr}_{0.44}\text{MnO}_{2.5}$  showing long and short range ordering situations for the first and second cases, respectively. For  $\text{La}_{0.52}\text{Sr}_{0.47}\text{MnO}_{2.5}$ , as seen in Fig. 1, SAED patterns are in agreement to the  $\text{Ima}2$  B unit cell. Nevertheless, a more complex situation involving extended defects as a consequence of the disorder intergrowth between P and rock salt blocks appears for higher cationic vacancy content as can be seen in Fig. 2 corresponding to a characteristic image and FFT (Fast Fourier Transform) along  $[100]_c$  (c stands for cubic P) of  $\text{La}_{0.54}\text{Sr}_{0.44}\text{MnO}_{2.5}$  sample.

Mn B compounds have potential for providing a new family of MR materials. In fact, previous resistance measurements indicate the presence of MR in the  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{2.5}$  B related compound [2]. Tunability of cationic vacancies in above composition leads to new Mn oxide materials having the required compositional conditions to exhibit also FM interactions and CMR behaviour.

## References

1. Cortes-Gil et al., Chem. Eur. J., 13: 4246-4252, 2007
2. Cortes-Gil et al., Chem. Eur. J., 17: 2709-2715, 2011
3. Alonso et al., Phys. Rev. B, 64: 1724101-4, 2011

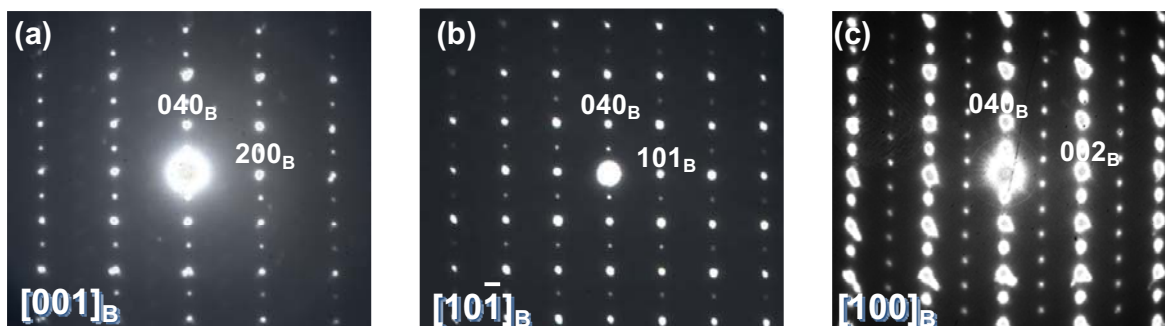


Figure 1. SAED patterns along (a)  $[001]_B$ , (b)  $[10\bar{1}]_B$  and (c)  $[100]_B$  zone axes corresponding to  $\text{La}_{0.52}\text{Sr}_{0.47}\text{MnO}_{2.5}$ .

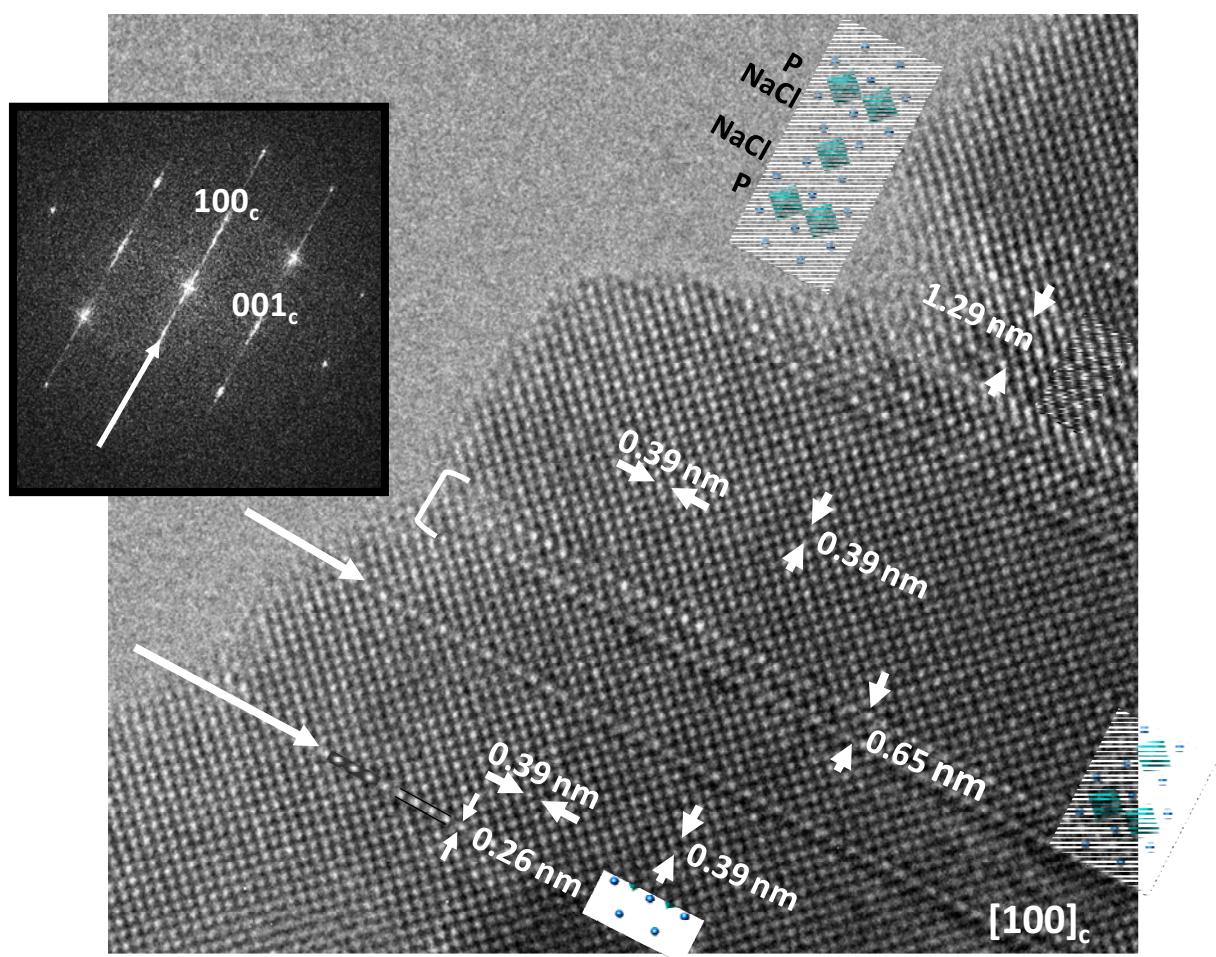


Figure 2. HRTEM image and FFT along  $[100]_c$  corresponding to  $\text{La}_{0.54}\text{Sr}_{0.44}\text{MnO}_{2.5}$ . Extended defects are marked with arrows. Local ordering is shown at the top right of the image.