

*Site-specific magnetically frustrated  $Sr_5Mn_5O_{13}$  and  $Sr_4LaMn_5O_{13}$  perovskites*Leopoldo Suescun<sup>1</sup>, Bogdan Dabrowski<sup>2</sup>, Stanislaw Kolesnik<sup>2</sup>, Kamal Chapagain<sup>2</sup><sup>1</sup>Facultad De Química, Universidad De La República, Montevideo, Uruguay, <sup>2</sup>Physics Department, Northern Illinois University, DeKalb, IL, United States  
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$LaxSr_{1-x}MnO_3$ -d manganites are among the most intensely studied perovskites because of the plethora of interesting properties and potential applications. The possibility of obtaining compounds with the Mn valence that can change between 2+ and 4+ by varying the La and oxygen contents allows for a wide range of magnetic, conducting and dielectric properties. The subtle relations among various degrees of freedom, combined with the flexibility of the perovskite framework made these compounds a very interesting test-case for study of the structure-properties correlations.

The Sr-rich side of the system showed an interesting series of compounds  $(LaxSr_{1-x})_{4+n}Mn_{4+n}O_{10+3n}$  with a systematic progression of oxygen vacancy ordering and the related Mn charge and orbital occupation/ordering [1]. In this series, the La-free compounds ( $x=0$ ) have been observed for  $n=0$  ( $Sr_4Mn_4O_{10}$ ),  $n=1$  ( $Sr_5Mn_5O_{13}$ ) and  $n=3$  ( $Sr_7Mn_7O_{19}$ ) [2]. Only the  $n=0$  and  $n=1$  members have been observed for the La-containing samples ( $x=0.1$  and  $0.2$ ) and only the  $n=1$  member was found for the  $x=0.3$  due to the subtle correlation of Mn charge and oxygen vacancy ordering.

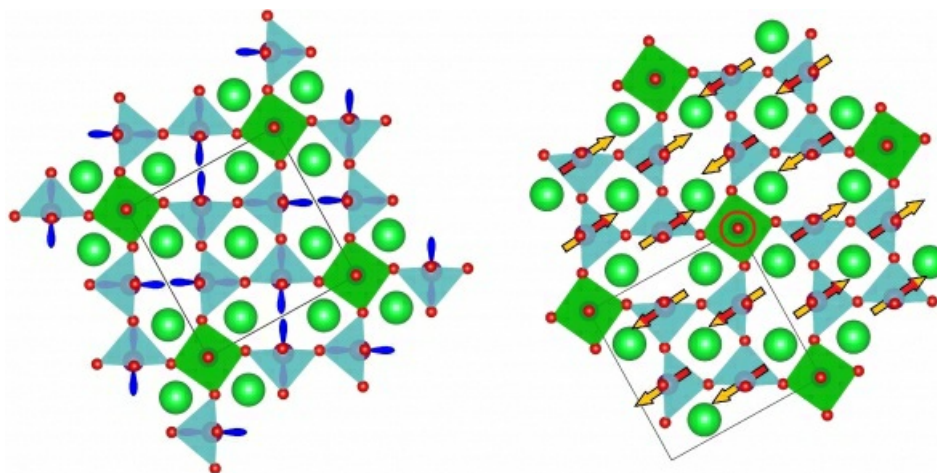
The  $n=1$  member  $(LaxSr_{1-x})_5Mn_5O_{13}$  shows an interesting evolution with  $x$  [3]. The structure (left figure) is formed by a very stable "pinwheel" pattern of  $Mn^{3+}$  pyramids linked by the Mn octahedron, which is the only structural site susceptible to change of valence from  $Mn^{4+}$  ( $x=0$ ) to  $Mn^{4+}/Mn^{3+}$  for  $x=0.1$ ,  $Mn^{3+}$  for  $x=0.2$  and  $Mn^{3+}/Mn^{2+}$  for  $x=0.3$ . The space group symmetry of the compounds changes from  $P4/m$  ( $x=0$ ) to  $P2/m$  ( $x=0.2$ ) with increasing La content to accommodate the Jahn-Teller  $Mn^{3+}$  ion in octahedral environment. This structure was reported to show an unusual averaged compressed  $Mn^{3+}$  octahedral environment, produced by averaging of the elongated octahedra disordered in the  $x$ - $y$  plane [3].

Neutron powder diffraction patterns obtained at 10 K for  $Sr_5Mn_5O_{13}$  and  $LaSr_4Mn_5O_{13}$  compounds showed peaks of the magnetic origin suggesting an antiferromagnetic ordering pattern of spins with propagation vector  $k=(1/2,1/2,1/2)$ . The magnetic structures of both compounds was solved in the  $I2'_1/m$  magnetic space group (#12.3.68), showing that the pinwheel pattern of pyramids with half-occupied  $d_{z^2}$  orbital pointing towards the apex of the pyramids has all  $Mn^{3+}$  cations aligned ferromagnetically. The four close-by clusters, separated by an oxygen vacancy, are antiferromagnetically coupled. The intermediate  $Mn^{4+}/Mn^{3+}$  octahedron is, therefore, sharing corners with two couples of inverted spin pinwheel clusters. Due to the orbital ordering, also associated with the magnetic and oxygen vacancy ordering, the  $Mn^{4+}$  cations in  $Sr_5Mn_5O_{13}$  show only antiferromagnetic interactions with the neighbouring pinwheel clusters, therefore the  $Mn^{4+}$  spins are not able to order magnetically with the two pairs of opposite spins (right figure). The  $Mn^{3+}$  cations in  $LaSr_4Mn_5O_{13}$ , on the contrary, may couple ferromagnetically with two pinwheel clusters (through the half-occupied  $d_{z^2}$  orbital that lays in the  $x$ - $y$  plane), and antiferromagnetically with the second pair (through the empty  $d_{x^2-y^2}$  orbitals), allowing for magnetic ordering. This would require, however a perfect orbital ordering of  $Mn^{3+}$  in the octahedral sites, which is not observed in this compound [2], instead nano-scale magnetically ordered regions with different magnetic orientations are observed.

[1] L. Suescun et al (2008) Chem. Mater. 20, 1636-1645.

[2] L. Suescun & B. Dabrowski (2008) Acta Cryst. B: Structural Science 64, 177-186.

[3] L. Suescun et al. (2009) J. Solid State Chem. 182, 280-288.



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