

Aqueous routes used for the synthesis of nanoscale particles of LiFePO_4 may lead, under specific conditions, to a full solid solution behavior upon Li^+ extraction at ambient temperature, hence favoring an easier monitoring of the state of charge/discharge of the electrode [1]. We demonstrated through neutron diffraction that this behavior is strongly connected with the presence of significant amounts of structural defects within the crystallites ($\text{Li} \rightleftharpoons \text{Fe}$ exchange, vacancies) [2]. We demonstrated as well that it was possible to monitor and adjust the amount of structural defects through careful annealing in air between 140°C and 500°C , up to a composition close to $\text{LiFe}_{0.67}\text{PO}_4$ [3]. An important feature is that these findings suggest unusually high mobility of Fe within the triphylite framework

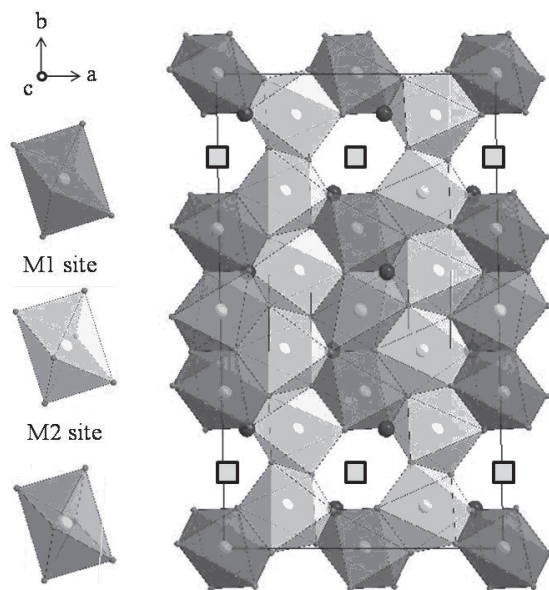


Figure 1: Proposed model for the superstructure of $\text{LiFe}_{23}\text{PO}_4$ built by analogy with the structure of laihunite $\text{Fe}_{2-x}\text{SiO}_4$

The resulting powders show complete new electrochemical features (fig. 1) at various redox steps between 3.5 V and 2.8 V vs Li, associated with partial redistribution of Fe and Li within the octahedral sites, followed by *in situ* Mossbauer spectroscopy and X-ray diffraction. New crystal super-structures [4] with long range ordering of Fe, vacancies and/or Li (fig. 2), determined through electron diffraction and high resolution Synchrotron X-Ray and neutron diffraction will be presented.

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A new homologous series of oxygen vacancy ordered strontium manganese perovskite

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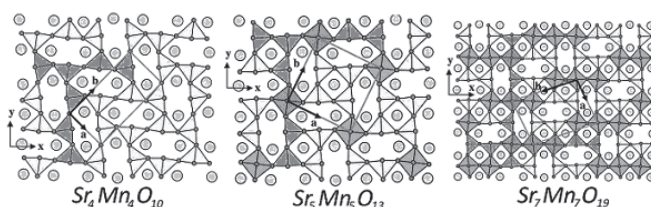
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Perovskite manganites have been extensively studied during last several decades due to a wide range of functional properties like colossal magnetoresistance, mixed ionic-electronic conductivity, and large magnetocaloric effect. Additionally oxygen deficient manganites are relevant as Solid Oxide Fuel Cell cathode materials.

During a systematic study of structural aspects of oxygen deficient $\text{La}_x\text{Sr}_{1-x}\text{MnO}_{3-\delta}$ compounds we determined the structure of a new compound $\text{Sr}_7\text{Mn}_7\text{O}_{19}$ ($\text{SrMnO}_{2.714}$) [1] showing a new oxygen vacancy ordering arrangement. We also found that the previously described vacancy ordered phases $\text{Sr}_2\text{Mn}_2\text{O}_5$ ($\text{SrMnO}_{2.5}$), $\text{Sr}_5\text{Mn}_5\text{O}_{13}$ ($\text{SrMnO}_{2.6}$) and the new phase form a new homologous series of compounds with general formula $\text{Sr}_{4+n}\text{Mn}^{3+}_4\text{Mn}^{4+}_n\text{O}_{10-3n}$ that in certain conditions may accept La substitution [2] and may also be extended to well-known compounds in the $\text{CaMnO}_{3-\delta}$, $\text{LaCuO}_{3-\delta}$ and $\text{NdCuO}_{3-\delta}$ series [3,4,5].

Starting with the $n=0$ member of the series ($\text{Sr}_4\text{Mn}_4\text{O}_{10}$), containing pyramidal Jahn-Teller Mn^{3+} cations, a basic building block for the homologous series is built based on four pyramids lying on the 001 plane with the apex of the pyramids pointing alternatively in the in the [100], [010], [0-10] and [-100] directions in a $p_x p_y p_x p_x$ arrangement. This arrangement repeats in the normal direction of the plane replacing x by y and viceversa. The n^{th} member of the series is built by adding n Mn^{4+} octahedra to the four pyramids keeping the order of the pyramids and the $2/m$ symmetry of the original block. The $n=1$ member $\text{Sr}_5\text{Mn}_5\text{O}_{13}$ is formed with the building block $p_x p_y \text{Op}_y p_x$ while the $n=3$ member $\text{Sr}_7\text{Mn}_7\text{O}_{19}$ is formed by a combination of $p_x p_y \text{OOOp}_y p_x$ and $p_y \text{Op}_x \text{Op}_x \text{Op}_y$ blocks in the x and y direction. The $n=0$ and 1 members of the series are also found in $\text{LaCuO}_{3-\delta}$ and $\text{NdCuO}_{3-\delta}$ systems, while only $n=0$ members are found for $\text{SrCuO}_{3-\delta}$ and $\text{CaMnO}_{3-\delta}$ systems, although many stable compounds with stoichiometries compatible with $n=2$ and 4 have been studied in this latter system.

The lack of observation of $n=2$ and 4 members of the $\text{Sr}_{4+n}\text{Mn}^{3+}_4\text{Mn}^{4+}_n\text{O}_{10-3n}$ series is supposed to be related to the geometrical incompatibility among the two possible $p_x p_y \text{OOOp}_y p_x$ and $p_x \text{Op}_y p_y \text{Op}_x$ building blocks (different from the combination of them in $n=3$ member) and the reduction of stability of structures where two pyramids are linked by the apical oxygen resulting from these blocks. Additionally, A cation size seems to correlate with the lack of observation of other members of the series in the $\text{CaMnO}_{3-\delta}$ system.



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Polyene-diphenylaniline D5 dyes and their role in the efficiency of DSSC solar cells

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