Aqueous routes used for the synthesis of nanoscale particles of LiFePO₄ 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 (Li ↔ 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 LiFePO₄ [3]. An important feature is that these findings suggest unusually high mobility of Fe within the triphylite framework.

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.

Keywords: battery materials, phosphates, diffraction

MS.39.3

A new homologous series of oxygen vacancy ordered strontium manganese perovskite

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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 LaSrₓMnO₃₋δ compounds we determined the structure of a new compound SrₓMnO₃₋δ (SrMnO₃₋δ) [1] showing a new oxygen vacancy ordering arrangement. We also found that the previously described vacancy ordered phases Sr₂MnO₃ (SrMnO₃₋δ), SrₓMnO₃₋δ (SrMnO₃₋δ) and the new phase form a new homologous series of compounds with general formula SrₓMⁿ⁺ₓ⁴⁻ₓMⁿ⁺⁻ₓO₃₋δn, that in certain conditions may accept La substitution [2] and may also be extended to well-known compounds in the CaMnO₃₋δ, LaCuO₃₋δ, and NdCuO₃₋δ series [3,4,5].

Starting with the n=0 member of the series (SrMnO₃₋δ), containing pyramidal Jahn-Teller Mn⁺ⁿ⁺ 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,p,p,p,p,p arrangement. This arrangement repeats in the normal direction of the plane replacing x by y and viceversa. The nᵗʰ member of the series is built by adding n Mn⁺ⁿ⁺ octahedra to the four pyramids keeping the order of the pyramids and the 2/m symmetry of the original block. The n=1 member Sr₄MnO₃₋δ is formed with the building block p,p,p,Op,p, while the n=3 member Sr₄MnO₃₋δ is formed by a combination of p,p,Op,p, and p,p,Op, blocks in the x and y direction. The n=0 and 1 members of the series are also found in LaCuO₃₋δ and NdCuO₃₋δ systems, while only n=0 members are found for SrCuO₃₋δ and CaMnO₃₋δ 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 SrₓMⁿ⁺ₓ⁴⁻ₓMⁿ⁺⁻ₓO₃₋δn series is supposed to be related to the geometrical incompatibility among the two possible p,p,Op,p, and p,p,Op, 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 CaMnO₃₋δ system.

Keywords: homologous series, manganites, perovskites

MS.39.4

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

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It is known that the performance of DSSC solar cells is determined by the quality of the dye sensitizer and the efficiency of the dye regeneration system. Polyalkylthiophene dyes have proved to be very efficient sensizers with high stability. Polyene-diphenylaniline D5 (D5) is one of the most efficient polyenes, but less efficient than DSSC solar cells sensitized with polyalkylthiophene dyes. In this work we have investigated the influence of two types of sensitization on the efficiency of DSSC solar cells.

Keywords: polyene-diphenylaniline D5, DSSC solar cells