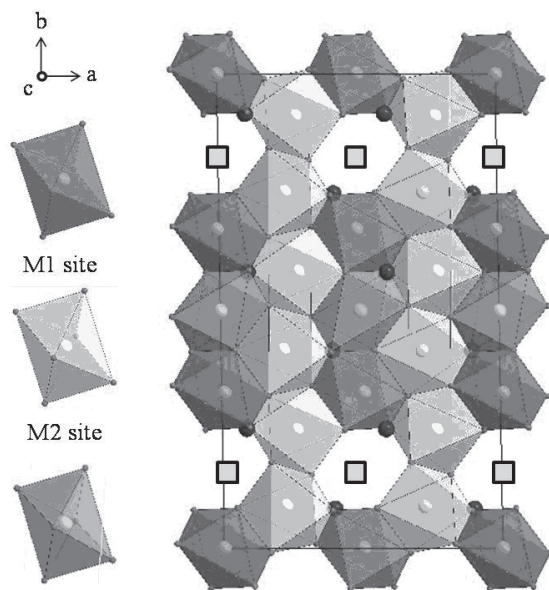


Aqueous routes used for the synthesis of nanoscale particles of  $\text{LiFePO}_4$  may lead, under specific conditions, to a full solid solution behavior upon  $\text{Li}^+$  extraction at ambient temperature, hence favoring an easier monitoring of the state of charge/discharge of the electrode [1]. 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  $140^\circ\text{C}$  and  $500^\circ\text{C}$ , 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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**Keywords:** battery materials, phosphates, diffraction

### MS.39.3

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**A new homologous series of oxygen vacancy ordered strontium manganese perovskite**

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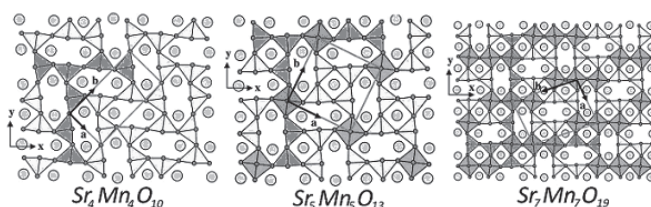
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Perovskite manganites have been extensively studied during last several decades due to a wide range of functional properties like colossal magnetoresistance, mixed ionic-electronic conductivity, and large magnetocaloric effect. Additionally oxygen 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  $\text{Mn}^{3+}$  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  $n^{\text{th}}$  member of the series is built by adding  $n$   $\text{Mn}^{4+}$  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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**Keywords:** homologous\_series, manganites, perovskites

### MS.39.4

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

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Dyes are key elements of dye sensitized solar cells (DSSC). Understanding their chemical properties at the molecular level and their adsorption mechanism on TiO<sub>2</sub> is of paramount importance for DSSC characterization and further developments. The crystal structure of a polyene aniline based dye, named D5 [1], was solved from synchrotron high resolution powder patterns, while that of its precursor without linking moiety was solved by standard single crystal XRD. The two molecules show remarkable differences in their intermolecular interactions and in crystal packing. In the precursor a T-like interaction is observed between pairs of molecules, while in D5  $\pi$ - $\pi$  interactions, together with intermolecular H-bonds between carboxyl groups, impose a planar stacking. However in both structures the packing is driven by the hydrophobic interactions between the phenyl moieties in adjacent molecules. This structural information sheds light on the features of D5 when bonded to TiO<sub>2</sub> (P25) in the working DSSC devices and can help explaining the limited (8%) conversion efficiency. Indeed the strong hydrophobic interactions can interfere with the dye grafting process. After grafting, intermolecular H bonds can not play a role, since the COO<sup>-</sup> is involved in the bond with TiO<sub>2</sub>, but strong lateral interactions between adjacently bonded D5 molecules may facilitate the charge recombination processes that lower the yield of electron injection into the P25 conduction band, with an overall smaller efficiency of DSSC cells.

The adsorption mechanism of D5 on the TiO<sub>2</sub> surface has been characterized by UV-Vis spectroscopy, Grazing Incidence-XRPD and Scanning Electron Microscopy together with elemental analysis by Energy Dispersive Spectrometry (EDS). UV-Vis spectra on the D5 solutions after contact with TiO<sub>2</sub> allowed to determine, by difference, the quantity of adsorbed dye. The experiments were carried out on both P25 powders and on commercial Dyesol glasses, and, using an optimized analytical procedure, the number of adsorbed molecules was determined under different conditions: D5 concentration, contact time and presence of CDCA anti-aggregation agent. Dyesol glasses were also analyzed by GI-XRPD to verify the size of TiO<sub>2</sub> crystallites, while the thickness of the TiO<sub>2</sub> layer was determined by SEM. The elemental analysis by EDS showed that the sulfur signal, only due to D5, is uniformly distributed along the TiO<sub>2</sub> thickness. The results of all these crystallographic and spectroscopic analyses and their relevance for the characterization of TiO<sub>2</sub>-D5 interactions will be presented.

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**Keywords:** DSSC solar cells, D5 dye, intermolecular interactions

## MS.39.5

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### The cation distribution in off stoichiometric CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>

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Chalcopyrite type compound semiconductors with Cu(In,Ga)Se<sub>2</sub> composition are successfully implemented as absorber layers in

thin film solar cells. The stoichiometric compound Cu(In,Ga)Se<sub>2</sub> crystallizes in the tetragonal chalcopyrite type crystal structure with space group *I42d*. Within this crystal structure the monovalent cations (Cu<sup>+</sup>) occupy the 4a site (0 0 0), the trivalent cations (In<sup>3+</sup> and Ga<sup>3+</sup>) are situated on the 4b position (0 0 ½) and the selenium anions are on the 8d site ( $x \frac{1}{4} \frac{1}{8}$ ). The cations are tetrahedrally coordinated by the anions and vice versa.

In general Cu(In,Ga)Se<sub>2</sub> absorber layers exhibit a copper-poor composition (Cu/(In+Ga) < 1), whereby the chalcopyrite type crystal structure still persists but the occupation of the Wyckoff sites may change and various kinds of intrinsic point defects are present within the material. The kind and concentration of these defects strongly correlate with the electronic and optical properties of the final device and the knowledge about them is crucial to tailor high efficient photovoltaic devices made of such compounds.

Distinguishing between isoelectronic species like Cu<sup>+</sup> and Ga<sup>3+</sup> by conventional diffraction techniques, like laboratory X-ray powder diffraction, is almost impossible. Therefore, at first neutron powder diffraction with subsequent Rietveld refinement was applied to evaluate possible cation distribution models for copper – poor CuInSe<sub>2</sub> and CuGaSe<sub>2</sub>, by the method of average neutron scattering length [1]. To decide if Cu<sup>+</sup> and Ga<sup>3+</sup> in Cu-poor CuGaSe<sub>2</sub> are ordered or partially disordered distributed within the structure, anomalous X-ray diffraction experiments were performed complementary to the neutron diffraction experiments.

For the anomalous diffraction experiments synchrotron X-rays with two different wavelengths, close to and far off the Ga-K-absorption edge (10367 eV), were used. This complementary diffraction technique made a differentiation between an ordered and a partially disordered distribution of the cations in copper-poor CuGaSe<sub>2</sub> possible.

The dominant native point defects in copper-poor CuInSe<sub>2</sub> were specified to be copper vacancies (V<sub>Cu</sub>) and In<sub>Cu</sub> anti-site defects. Moreover, the type and density of these isolated native defects is dependent on the Cu/In ratio [2]. The dominating native point defects in copper – poor CuGaSe<sub>2</sub> are copper vacancies and gallium on interstitial position (Ga<sub>i</sub>).

The study presented here identified, by the use of advanced diffraction techniques, possible cationic point defects in off stoichiometric chalcopyrite type compound semiconductors. This knowledge leads to a further understanding of the complex electronic properties of Cu(In,Ga)Se<sub>2</sub> absorber layers in thin film solar cells, which is indispensable to aim in highly efficient photovoltaic devices based on such compounds.

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**Keywords:** semiconductors, anomalous\_diffraction, neutron\_diffraction

## MS.40.1

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### Pressure-induced phase transitions in Na-Au intermetallic compounds

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Sodium and gold are found to react at room temperature under high pressure. We have compressed a mixture of sodium and a fine powder of gold in a diamond anvil cell (DAC), and taken powder x-ray diffraction