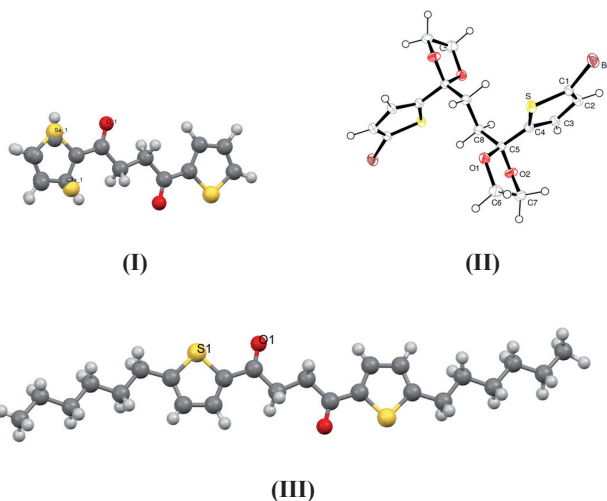


position [2]. In this type of molecules, it is observed, however, that the thiophene ring often shows a disorder [3] even at low temperature, if the adjacent environment allows for free rotation around a single bond. Thus the structural analysis is extremely important for substitution and chain extension at the required position to obtain the required electrochemical efficiency. The experimental analysis of the electronic environment is also desirable to obtain the optimum efficiency of the target molecule. In the meeting, three different representative cases of thiophene based compounds will be presented. The case of *1,4-bis(2-thienyl) butane-1,4-dione* (I), for which the modelling is done for the disordered thienyl group. Secondly, the case of *2, 2'-(1, 2-ethanediyl) bis [2-(5-bromo-2-thienyl)-1, 3-Dioxolane* (II), for which the electron density parameters have been transferred from the ELMAM2 database [4] and lastly, the case of *1,4-bis(5-hexyl-2-thienyl) butane-1,4-dione* (III), whose experimental electron density analysis is underway using MoPro software [5].



[1] M. Grätzel, *Nature*. **2001**, *414*, 338. [2] C. Roux, J.-Y. Bergeron, M. Leclerc, *Macromo. Chem.* **1993**, *194*, 868-877. [3] S. Wang, F. Brisse, F.B. Gariéy, A.D. Bouillud, M. Leclerc, *Acta. Cryst.* **1998**, *C54*, 553-555. [4] S. Domagala, P.M. Munshi, M. Ahmed, B. Guillot, C. Jelsch, *Acta. Cryst.* **2011**, *B67*, 63-78. [5] C. elsch, B. Guillot, A. Lagoutte, C. Lecomte, *J. Appl. Cryst.* **2005**, *38*, 38-54.

Keywords: solar cells, thiophenes, electron density

MS39.P02

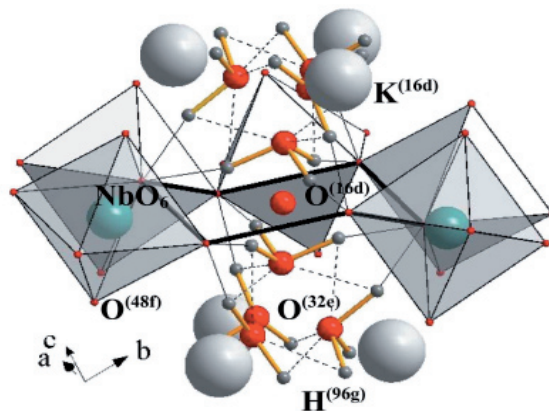
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The exotic ions arrangement in the pyrochlore -type framework of protonic conductor $K_{0.88}Nb_2O_7.58H_{4.28}$ for intermediate temperature PSOFCS

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According to single-crystal, synchrotron powder X-ray diffraction and neutron powder diffraction studies, the novel pyrochlore-type compound contains the water molecules located in 32e sites, the hydroxide ions and potassium ions are located in 16d sites with a significant amount of 'free' protons in 96g sites corresponding to the structural formula $K_{0.88}(OH)_{0.54}H_{1.66}(H_2O)_{1.04}Nb_2O_6$. The total weight loss at temperatures up to 773 K is limited to about 8%, suggesting the oxygen escape from 48f sites can be excluded and 'free' protons must be kept in the structure. The bulk conductivity in ambient air reaches the plateau at $10^{-2} S \cdot cm^{-1}$ for 623 K. Owing to the wide stability range and resistance to water solubility, the compound can be considered as a

candidate to fill the gap for intermediate temperature solid-oxide fuel-cell applications materials. Even more hydrogen-containing materials are prepared with ion exchange for protons.



The protonic sites in hydrothermally grown $K_{0.88}Nb_2O_7.58H_{4.28}$ as extracted from neutron powder diffraction data.

[1] O. Smirnova, N. Kumada, T. Takei, Y. Yonesaki, M. Yashima, N. Kinomura. *Acta Cryst.* **2010**, *B66*, 594-602.

Keywords: protonic conductor, intermediate temperature SOFCs, powder diffraction

MS39.P03

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Rationalising the molecular origins of dyes used in dye sensitized solar cells

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The dye sensitized solar cell (DSC) has been at the forefront of worldwide research since the pioneering work of O'Regan and Grätzel [1] showing that these devices can achieve a power conversion efficiency of over 11%. One of the key aspects controlling the performance of the DSC is the molecular nature of the dye used. However, even after two decades of study, one of the first ever produced dyes for DSC's (N719) still provides record efficiencies. This is puzzling as the DSC field is so driven by economics and Ruthenium, which is contained in N719, is a rare transition metal making it relatively expensive.

We have used X-ray diffraction and accompanying statistical analysis to compare three Ruthenium based dyes and one Iron based dye which are structurally similar to N719 in order to elucidate why it is still one of the best performing dyes to date. Iron and Ruthenium lie in the same group of the periodic table. Consequently the Iron based dye has been considered as a cheaper alternative to Ruthenium based dyes despite affording reduced efficiency.

Our X-ray diffraction studies concentrate on a Ruthenium dye and an Iron dye that have the same principal molecular structure but different counter ions. We also looked at the structural differences of the previously mentioned Ruthenium dye with and without carboxylate groups attached. These structures were all compared to that of N719 both structurally and spectroscopically.

The Cambridge Structural Database (CSD) was then employed

to compare these structures with a range of similar structural motifs present in the literature. Conformational differences between our investigated dyes and those complexes with a different counter ion were revealed. This analysis motivated a general enquiry into the influence of the position of attached ligands on the pyridine unit within all known Ruthenium or Iron based dyes containing three bipyridyl groups. The extent of delocalisation of electron density in these pyridine groups was calculated via a bond length variation analysis [2]. This revealed that our complexes were much less delocalised (~4%) than N719 (up to 37%). This delocalisation of the pyridine ring is attributed to the superior charge transfer properties of N719 and thus its better performance in DSC operation.

This work has contributed to the basic foundation of molecular engineering wherein lies the ultimate goal of being able to tailor dyes to meet a specific component design of a DSC device.

[1] B.O'Regan, M. Grätzel, *Nature* **1991**, *97*, 1102-1111. [2] J.C. Cole, J.M. Cole, G.H. Cross, M. Farsari, J.A.K. Howard, M. Szablewski, *Acta Crystallographica Section B Structural Science* **1997**, 812-821.

Keywords: energy, organometallic, photovoltaic

MS39.P04

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Crystal structure, local atomic order and metastable phases of zirconia-based nanoceramics for Solid-Oxide Fuel Cells

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ZrO₂-based ceramics have many technological uses because of their high ionic conductivity at high temperatures and their excellent mechanical properties. They are usually employed as solid electrolytes in solid-oxide fuel cells (SOFCs). In addition, due to their excellent oxygen-storage capability, ZrO₂-CeO₂ solid solutions are used as SOFC anodes and in three-way catalysis.

Pure ZrO₂ exhibits three polymorphs of monoclinic, tetragonal and cubic symmetries. The monoclinic phase is stable at room temperature and on heating transforms to the tetragonal phase at 1170°C which by further heating transforms to the cubic phase at 2370°C. This phase exhibits a fluorite-type crystal structure and can be fully stabilized at room temperature by doping with other oxides (Y₂O₃, CaO, etc.). The tetragonal phase has a crystal structure similar to the cubic phase, but with its unit cell *c* parameter slightly longer than the other two axes. The tetragonal phase can be retained, under metastable condition, in nanopowders or fine-grained ceramics. Since the monoclinic phase has poor electrical properties, only the high-temperature phases are useful for technological applications.

These materials can exhibit three tetragonal forms, all belonging to the *P4₂/nmc* space group. The stable tetragonal form is called the *t*-form, which is restricted to the solubility limit predicted by the equilibrium phase diagram. There is also a *t'*-form with a wider solubility, but unstable in comparison with the mixture of the *t*-form and cubic phase. Finally, the *t''*-form has an axial ratio *c/a* of unity, but, in this phase, the oxygen atoms are displaced along the *c* axis from their ideal sites of the fluorite-type structure of the cubic phase (8*c* sites of the *Fm3m* space group).

During the last decade, we have investigated the crystallographic

features of a number of ZrO₂-based systems (ZrO₂-CeO₂, ZrO₂-CaO, ZrO₂-Y₂O₃ and ZrO₂-Sc₂O₃). We have mainly focused on the retention of metastable tetragonal forms in nanocrystalline and compositionally homogeneous zirconia-based solid solutions. In this communication, we review the main results of our investigations in a number of nanocrystalline ZrO₂-based solid solutions, most of them obtained by means of X-ray powder diffraction (XPD) and EXAFS techniques at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil). We demonstrate how the use of a high intensity synchrotron source in XPD experiments allows to detect and precisely determine the intensity of very weak Bragg peaks, which are related to small displacements of oxygen atoms in the tetragonal phase, even those observed for the *t''*-form with a cubic unit cell. By analyzing high-temperature XPD data, we determined the influence of the average crystallite size on the features of different phase diagrams of the studied materials. We also discuss our results for a number of ZrO₂-based solid solutions related to (i) the local atomic structure, which yields a new insight on the structural disorder of the oxygen sublattice, and (ii) the mechanisms responsible for the retention of the observed metastable phases.

Keywords: zirconium_oxide, X-ray_diffraction, EXAFS

MS39.P05

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Novel *Pn* Li₂MnSiO₄: synthesis, DFT-aided characterization and charge/discharge

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This abundantly illustrated talk details the two-step synthesis in nano-crystalline form, as well as the DFT-aided characterization of the metastable *Pn* polymorph of Li₂MnSiO₄, a novel cathode material for Li-ion batteries. Contrary to the *Pmn2₁* polymorph which is made of MnSiO₄ layers bonded by van der Waals forces when de-lithiated, the *Pn* polymorph retains a 3-D MnSiO₄ framework. This basic structural difference might lead to different charge/discharge properties in a battery.

Preparation started with the sol-gel synthesis of nano-crystalline *Pn* Na₂MnSiO₄ followed by sintering at 700°C under flowing Ar with 5% H₂. In a second step, site-ordered *Pn*-LiNaMnSiO₄ and *Pn*-Li₂MnSiO₄ were obtained by soft-chemistry ion exchange. The degree of Na exchange was tuned by changing experimental conditions. The nano-crystalline form of the material precluded structure solution of XRD profiles or even Rietveld refinement of atom coordinates. The novel polymorphs were instead conclusively identified from successful Rietveld analyses of experimental profiles by refining only cell parameters, and fixing atom coordinates at values of corresponding crystal structures optimized by DFT with VASP for the various materials. In particular, Li and Na were shown to be ordered among the two possible sites in LiNaMnSiO₄. Spin-polarized optimizations with GGA potentials were performed for cell-and-coordinate calculations. In contrast, "GGA+U" optimizations were performed for total-energy calculations required for enthalpy comparisons in the phase change and for calculation of average electrochemical de-lithiation potentials.

The *Pmn2₁* polymorph of Li₂MnSiO₄ is the stable phase, readily obtainable by sol-gel or hydrothermal synthesis techniques. The thermal stability of each new polymorph was investigated by differential scanning calorimetry (DSC). Upon heating in N₂ at 20°C/min from 100–500°C in DSC experiments, no significant variation was observed for LiNaMnSiO₄. By contrast, a broad exothermic peak from 150–420°C, peaking at 275°C was measured for Li₂MnSiO₄ owing to