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.

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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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ZrO_2-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, ZrO_2-CeO_2 solid solutions are used as SOFC anodes and in three-way catalysis.

Pure ZrO_2 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 (Y_2O_3, 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 (8c sites of the *Fm3m* space group).

During the last decade, we have investigated the crystallographic

features of a number of ZrO_2-based systems (ZrO_2-CeO_2, ZrO_2-CaO, ZrO_2-Y_2O_3 and ZrO_2-Sc_2O_3). 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 ZrO_2-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 ZrO_2-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

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 *Pmn*2₁ 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 *Pmn*2₁ 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

a transformation from Pn to $Pmn2_1$, confirmed by XRD. The enthalpy change was estimated at 4.7±0.2 kJ/mol, which agrees reasonably well with total-energy difference of 4.1 kJ/mol from GGA+U calculations.

The stability of de-lithiated $MnSiO_4$ structures resulting from Li_2MnSiO_4 Pn and $Pmn2_1$ polymorphs was compared by computing *ab initio* elastic coefficients using VASP GGA+U potentials. Results indicated that $MnSiO_4$ arising from them are both soft materials, but their calculated 3D plots of anisotropic tensile modulus or small-shear modulus did not indicate a spontaneous transition to another phase, suggesting stability of both Pn and $Pmn2_1$ $MnSiO_4$ against possible second-order phase transitions that preserve cell translations. The $Pmn2_1$ polymorph is known to be unstable with respect to $C2/m$ $MnSiO_4$, but this first-order transformation would require a rearrangement of atomic bonds, which may or may not happen spontaneously.

Finally, the electrochemical performance of the new polymorphs was assessed and compared to $Pmn2_1$ Li_2MnSiO_4. Most of the electrochemical data on Li_2MnSiO_4 reported in the literature is on the latter polymorph. Here, polymorph-specific features are identified by cyclic voltammetry and galvanostatic cycling.

Keywords: Lithium-ion battery, DFT calculations, Silicates

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Li^+ Ion diffusion and vacancy formation in the $Li_{1-x}FeO_2$ electrode material

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The 'corrugated layer' $Pmmn$ phase of $LiFeO_2$ (a=4.061, b=2.962, c=6.032 Å) is an attractive electrode material for reversible lithium ion batteries, because inexpensive and not toxic [1,2]. The distorted rocksalt superstructure contains alternate Li-O and Fe-O double layers, corresponding to (011) rocksalt planes. We recently proposed a satisfactory interpretation of the complex electrochemical reactions occurring in a $Pmmn$-$LiFeO_2$ cathode, on the basis of first-principles calculations of the corresponding voltages and comparison with data from experimental charge/discharge curves [3]. Here models for Li^+ ion mobility pathways in the (001) lithium layers of stoichiometric and defective $Li_{1-x}FeO_2$ are presented and discussed.

The ground-state crystal energy was computed by DFT (Density-Functional-Theory) methods, based on use of the hybrid B3LYP functional with localized Gaussian-type basis sets [4]. Appropriate supercells were devised as needed, with full least-energy structure optimization. In the defect-free case (x=0), ion diffusion was found to take place cooperatively inside a fraction of 'active' lithium layers, separated by inert ones. This condition is necessary to avoid excessive strain of the crystal structure. The mobility pathway based on a Li bottleneck state in tetrahedral coordination is slightly preferred over that implying an intermediate state with linearly coordinated Li, according to a predicted ΔE_a activation barrier of 0.410 vs. 0.468 eV. The ion diffusivity $D,$ with jump distance of 3 Å, was then calculated in the range between 1.9×10^{-10} and 1.8×10^{-11} cm^2 s^{-1} at 300 K. This corresponds to the behaviour of a satisfactory ion conductor.

For the $Li_{0.75}FeO_2$ deintercalated material a number of low energy vacancy configurations were considered, investigating also the vacancy influence on electron density of states and atomic charge distribution. The most favourable structural arrangements have a vacancy formation energy E_f in the 4.3 to 4.5 eV range. One of them, $P2_1/m$-$Li_{0.75}FeO_2$, was found to favour an ion hopping pathway based on the linear-type bottleneck state, with a quite low activation barrier of 0.30 eV; further, in this case no inert layers are required to limit the structural strain. A significantly improved ion conductivity thus ensues, with respect

to stoichiometric $LiFeO_2$. Accordingly, in the defective material the predicted ionic conductivity at room temperature rises from $10^{-5} \div 10^{-6}$ ($LiFeO_2$) to 4×10^{-4} ohm^{-1}cm^{-1} ($Li_{0.75}FeO_2$). The present results show that, by developing reliable low-energy structural models for the vacancy arrangements in Li-deintercalated phases, it is possible to successfully determine ion mobility pathways and to predict conductivity values in such electrode materials.

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Keywords: first-principles calculations, ion diffusion, lithium material

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Structure and Thermoelectric Properties of Ca-M-Co-O (M=Sr, Zn, and La)

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Thermoelectric research is of increasing importance in the development of technologies for improving vehicular fuel economy and for mitigating green house gas emissions. There is a well-defined need for efficient energy conversion materials and environmentally friendly technologies over the next twenty years. For waste heat energy conversion applications, oxide materials which have high temperature stability are potential candidates. In the Ca-M-Co-O (M=Sr, Zn, and La) systems, in addition to the well-known $Ca_3Co_4O_9$ phase (with misfit layered structure) that exhibits excellent thermoelectric property, other interesting phases include members of the homologous series, $A_{n+2}Co_nCo'O_{3n+3}$ (where A= Sr, Ca, (Ca,Sr) or (Sr,Ca)), which consist of 1-dimensional parallel $Co_2O_6^{6-}$ chains. While the members of the $A_{n+2}Co_nCo'O_{3n+3}$ series have reasonably high Seebeck coefficients and relatively low thermal conductivity, the electrical conductivity needs to be increased in order to achieve higher ZT (figure of merit) values. This paper discusses our phase equilibria/structural/property studies of selected cobaltites, including those in the SrO-CaO-CoO_x, CaO-ZnO-CoO_x, and CaO-La_2O_3-CoO_x systems.

Keywords: thermoelectric, phase-equilibira, structure

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Structural Changes and Voltage Output in Defect Perovskite Cathode Materials

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The development of new high capacity cathodes is becoming increasingly important as currently used materials reach their critical