

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

*Acta Cryst.* (2011) **A67**, C489

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

Diego G. Lamas,<sup>a</sup> Paula M. Abdala,<sup>b,c</sup> Leandro M. Acuña,<sup>c</sup> Ismael O. Fábregas,<sup>c</sup> Rodolfo O. Fuentes,<sup>c</sup> Noemí E. Walsøe de Reca,<sup>c</sup> Márcia C.A. Fantini,<sup>d</sup> Rogério J. Prado,<sup>c</sup> Aldo F. Craievich,<sup>d</sup> <sup>a</sup>Laboratorio de Caracterización de Materiales, Facultad de Ingeniería, Universidad Nacional del Comahue and CONICET, (Argentina). <sup>b</sup>SNBL-ESRF, Grenoble, (France). <sup>c</sup>Centro de Investigaciones en Sólidos, CONICET-CITEDEF, (Argentina). <sup>d</sup>Instituto de Física, Universidade de São Paulo, (Brazil). <sup>e</sup>Instituto de Física, Universidade Federal de Mato Grosso, (Brazil). E-mail: dlamas@uncoma.edu.ar

ZrO<sub>2</sub>-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<sub>2</sub>-CeO<sub>2</sub> solid solutions are used as SOFC anodes and in three-way catalysis.

Pure ZrO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>, 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 *P4<sub>2</sub>/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 ZrO<sub>2</sub>-based systems (ZrO<sub>2</sub>-CeO<sub>2</sub>, ZrO<sub>2</sub>-CaO, ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>-Sc<sub>2</sub>O<sub>3</sub>). 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<sub>2</sub>-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<sub>2</sub>-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

*Acta Cryst.* (2011) **A67**, C489-C490

### Novel *Pn* Li<sub>2</sub>MnSiO<sub>4</sub>: synthesis, DFT-aided characterization and charge/discharge

Patrick H.J. Mercier, Hugues Duncan, Abhinay Kondamreddy, Yvon Le Page, Yaser Abu-Lebdeh, Pamela S. Whitfield, Isobel J. Davidson, National Research Council Canada, Ottawa, Ontario, (Canada). E-mail: patrick.mercier@nrc-cnrc.gc.ca

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 Li<sub>2</sub>MnSiO<sub>4</sub>, a novel cathode material for Li-ion batteries. Contrary to the *Pmn2<sub>1</sub>* polymorph which is made of MnSiO<sub>4</sub> layers bonded by van der Waals forces when de-lithiated, the *Pn* polymorph retains a 3-D MnSiO<sub>4</sub> 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* Na<sub>2</sub>MnSiO<sub>4</sub> followed by sintering at 700°C under flowing Ar with 5% H<sub>2</sub>. In a second step, site-ordered *Pn*-LiNaMnSiO<sub>4</sub> and *Pn*-Li<sub>2</sub>MnSiO<sub>4</sub> 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 LiNaMnSiO<sub>4</sub>. 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 *Pmn2<sub>1</sub>* polymorph of Li<sub>2</sub>MnSiO<sub>4</sub> 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 N<sub>2</sub> at 20°C/min from 100–500°C in DSC experiments, no significant variation was observed for LiNaMnSiO<sub>4</sub>. By contrast, a broad exothermic peak from 150–420°C, peaking at 275°C was measured for Li<sub>2</sub>MnSiO<sub>4</sub> owing to