

In-situ diffraction experiments were performed on SOFC under standard operating conditions, more specifically during successive cycles of reduction and reoxidation at  $\sim 850$  °C.

The experiment was performed with the spiral slit set-up at beamline ID15 at the ESRF and an X-ray wavelength of  $\lambda = 0.173$  Å.

The strain distribution within the three constituent layers of the SOFC was determined from the distortion of the monitored Debye-Scherrer-rings.

**Keywords:** solid oxide fuel cell, residual stress measurement, in-situ observation

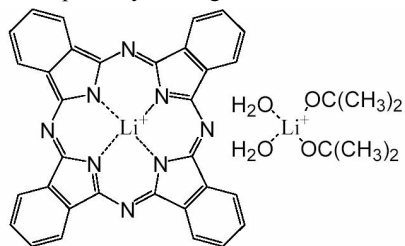
#### P.11.13.2

*Acta Cryst.* (2005). A61, C401

##### A Crystallographic Examination of Dilithium Phthalocyanine

David A. Grossie<sup>a</sup>, William A. Feld<sup>a</sup>, Lawrence Scanlon<sup>b</sup>, Giselle Sandi<sup>c</sup>, Zdzislaw Wawrzak<sup>d</sup>, <sup>a</sup>Department of Chemistry, Wright State University. <sup>b</sup>AFRL, PRPS, WPAFB. <sup>c</sup>Chemistry Division, Argonne National Laboratory. <sup>d</sup>DuPont–Northwestern–Dow Collaborative Access Team, Argonne National Laboratory. E-mail: david.grossie@wright.edu

Dilithium phthalocyanine is a compound that shows promise as the dielectric for lithium-lithium ion batteries. The compound forms small, flakey crystals from the few solvents in which it can be dissolved. Experimental evidence indicates that the lithium atoms within the solid structure migrate in the presence of an electric field. The determination of the crystal and molecular structure was initiated so as to determine the pathways through which the lithium ions move.



A=12.8017(6), b=14.3637(7), c=17.3859(8),  $\alpha$ =101.5838(9),  $\beta$ =94.1351(9),  $\gamma$ =92.3054(9), V=3118.7(3),  $\lambda$ =0.71073Å, T=173K, R<sub>int</sub>=0.0187, R<sub>1</sub>=0.0484, wR<sub>2</sub>=0.1351, S=1.046, Obs=18798, Par=1116.

**Keywords:** battery materials, crystal structure determination, lithium batteries

#### P.11.13.3

*Acta Cryst.* (2005). A61, C401

##### Site Preference of Valence Ions in Fe<sub>1+x</sub>Co<sub>2-x</sub>O<sub>4</sub> (0 ≤ x ≤ 1)

Takeshi Ohno<sup>a</sup>, Norio Shimizu<sup>a</sup>, Koichi Ohkubo<sup>a</sup>, Takayasu Hanashima<sup>b</sup>, Kouji Yamawaki<sup>a</sup>, Satoshi Sasaki<sup>a</sup>, <sup>a</sup>Materials and Structure Lab., Tokyo Institute of Technology. <sup>b</sup>PPL, Kusatsu, Shiga, Japan. E-mail: ohno@lipro.msl.titech.ac.jp

Iron cobaltites show the ferrimagnetism to have a spinel structure, where Co and Fe ions occupy tetrahedral A and octahedral B sites in various valence states. Therefore, the determination of cation distribution between the two kinds of sites is indispensable to the interpretation of the magnetic properties of cobaltites.

Fortunately, we succeeded to synthesize single crystals of Fe<sub>1+x</sub>Co<sub>2-x</sub>O<sub>4</sub> (x = 0.2) by the hydrothermal reaction. The site occupancy of Fe and Co ions was first determined by the single-crystal synchrotron X-ray diffraction method, where the anomalous scattering effect was used at the Co K absorption edge ( $\lambda = 1.6182$  Å) in the BL-10A station of the Photon Factory. Then, the electronic information from X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) spectra was utilized for determining the valence states of Fe and Co ions. The absorption experiments were performed at both Fe K and Co K edges at BL-3A. It was found that all Fe ions exist as trivalent ions in Fe K XANES spectra, while the valences of Co ions were uniquely obtained from the intensity variation of XMCD signals in the solid solutions [1].

Based on the full determination for x = 0.2 sample, the most plausible chemical formula and magnetic structures have been

suggested through the solid solution of Fe<sub>1+x</sub>Co<sub>2-x</sub>O<sub>4</sub> (0 ≤ x ≤ 1).

[1] Kita N., Shibuichi N., Sasaki S., *J. Synchrotron Rad.*, 2001, 8, 446.

**Keywords:** cation distribution, cobalt compounds, X-ray magnetic circular dichroism

#### P.11.13.4

*Acta Cryst.* (2005). A61, C401

##### Structures of Defect Perovskites Suitable for Li Ion Intercalation

Siebert Schmid, School of Chemistry, The University of Sydney, Sydney, Australia. E-mail: s.schmid@chem.usyd.edu.au

The phase Sr<sub>7</sub>Zr<sub>4</sub>Nb<sub>6</sub>O<sub>30</sub> in the SrO-ZrO<sub>2</sub>-NbO<sub>2.5</sub> system was recently discovered in our laboratories. X-ray diffraction patterns have shown that the compound Sr<sub>7</sub>Zr<sub>4</sub>Nb<sub>6</sub>O<sub>30</sub> forms a cubic perovskite substructure with an additional modulation (satellite reflections at  $\frac{1}{2}\langle 111 \rangle_p$ ). This compound is analogous to the perovskite Sr<sub>x</sub>NbO<sub>3</sub>, 0.7 ≤ x ≤ 1, which exists over a significant range of composition [1]. In contrast to our new phase Sr<sub>x</sub>NbO<sub>3</sub>, 0.7 ≤ x ≤ 1, does not display additional ordering (no satellite reflections were found despite intensive searching). Therefore it is likely that the additional reflections for our new phase are due to Nb/Zr ordering.

If x in the Sr<sub>x</sub>NbO<sub>3</sub> solid solution equals 1 all the niobium is in oxidation state +IV. Reducing the amount of strontium leads to vacancies on that site and to a corresponding amount of Nb<sup>5+</sup> required for charge balance. The vacancies on the Sr site allow Li to be intercalated electrochemically. In Sr<sub>7</sub>Zr<sub>4</sub>Nb<sub>6</sub>O<sub>30</sub>, all Nb<sup>4+</sup> has been replaced by Zr<sup>4+</sup>, which allows syntheses to be carried out in air at high temperature. Preliminary investigations [2] have shown that a significant amount of Li can be intercalated, which would make that compound suitable as a cathode in a Li ion battery. The apparent reversibility of the intercalation process is another indication that this new phase might be suitable for that application.

[1] Hessen B., Sunshine S. A., Siegrist T., Jimenez R., *Mater. Res. Bull.*, 1991, 26, 85. [2] Schmid S., Kuhn A., unpublished.

**Keywords:** defect perovskite, lithium intercalation, lithium battery

#### P.11.14.1

*Acta Cryst.* (2005). A61, C401

##### Residual Stress Distribution Near HA Coating Interface on Titanium Alloy Substrate

Adele Carrado<sup>a</sup>, Vesna Stanic<sup>b</sup>, Vincent Ji<sup>c</sup>, Wilfrid Seiler<sup>c</sup>, Jacques Werckmann<sup>a</sup>, Sebastian Joulié<sup>a</sup>, <sup>a</sup>IPCMS, Strasbourg, France. <sup>b</sup>Turbocoating SpA, Parma, Italy. <sup>c</sup>LM3 ENSAM, Paris, France. E-mail: adele.carrado@ipcms.u-strasbg.fr

Titanium alloys (Ti-6Al-4V) are largely used to realise fixed and mobile biomechanical prostheses, to be implanted for long times inside the human body, such as dental implants and hip prostheses. In order to prevent damage due to the relevant mechanical stresses and corrosive environment inside the human body, coatings are usually applied to provide a surface with properties such a good biocompatibility, corrosion protection, wear resistance, high strength and low cost. Hydroxyapatite (HA, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>), as the major mineral component of bones and teeth, is used in implants as a coating, obtained by vacuum plasma spray deposition process. Although it has excellent bioactivity HA has poor intrinsic mechanical properties, so it is often coated on metallic substrates. This creates a device that combines good surface bioactivity with the strength of the metallic substrate.

A mechanical characterisation of the HA, coated on Ti-6Al-4V substrate is fundamental for the determination of the characteristics that the material provides from a functional point of view. Together the determination of microstructural features, it is very important to evaluate the residual stresses (RS) induced by deposition process, due to the different thermo-physical properties of the substrate and coating, as RS strongly influence the wear resistance of the coating. In this paper, X-ray diffraction stress in the ceramic coating and in Ti-6Al-4V substrate are presented and related to other experimentally determined microstructural parameters.

**Keywords:** TEM characterization, residual stress analysis, X-ray diffraction