

(Grenoble) ( $\lambda=0.3748$  Å) at 25° and 250°C, respectively, suggests that the coefficient of thermal expansion is highest for samples with low iron substitution. Split of triangular Cu2 positions increases with temperature and the half-occupied Cu2 positions from different coordination triangles approach one another, down to 2.70-2.75 Å in tennantite at 250°C. There is insignificant residual electron density between the split Cu2 half-sites in tetrahedrite at 25°C and its increase with temperature is moderate. The inter-site density is substantially higher in tennantite and it increases considerably with temperature, especially in the low-Fe sample.

#### MS17 P23

##### Ion exchange properties for lamellar oxides

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The investigations about materials dealing with energy have shown that the oxides with a layer structure are potential candidates for solid state electrolytes and for electrodes. In this respect, attention has been focussed on protonic oxides owing to their stability at rather high temperature. Moreover these latter compounds are characterized by their ability to accommodate in the interlayer space ions of different shapes and sizes. They offer the possibility to synthesize some partially exchanged compounds. During this work reactions of some K<sup>+</sup> and Na<sup>+</sup> salts (1) with the layered niobic acid HNb3O8 (2) in different ratio (1)/(2) were studied. The partial exchange reaction increases the spacing between the inorganic sheets is discussed in terms of ion size and state of hydration.

#### MS17 P24

**Temperature dependent stability field of nanodomain structures in PZT ceramics using synchrotron powder diffraction** Kristin A. Schoenau<sup>a</sup>, Michael Knapp<sup>b</sup>, Hans Kungl<sup>c</sup>, Michael J. Hoffmann<sup>c</sup>, Mario Maglione<sup>d</sup>, Hartmut Fuess<sup>a</sup> <sup>a</sup>Materials Science, Darmstadt University of Technology, Germany. <sup>b</sup>CELLS, Barcelona, Spain. <sup>c</sup>Institute of Ceramics in Mechanical Engineering, University of Karlsruhe, Germany <sup>d</sup>ICMCB-CNRS, Université Bordeaux I, France.

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**Keywords:** ferroelectric oxides, in situ synchrotron x-ray powder diffraction, phase stability, nanodomains,

Extraordinarily high piezoelectric properties of ferroelectric lead zirconate titanate, PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> (PZT), at its so-called morphotropic phase boundary (MPB) between tetragonal and rhombohedral symmetry have raised interest on the structural properties of this compositional area in last years. Discussions involved a coexistence of tetragonal and rhombohedral structures as well as the existence of a monoclinic phase [1]. Recent studies using high-resolution synchrotron x-ray powder diffraction in combination with TEM and EPR at ambient temperature [2, 3] were able to correlate XRD observation with a nanodomain structure. The internal symmetry of the nanodomains is difficult to determine due to strong coherence effects in diffraction experiments, which is in

correspondence with findings for relaxor ceramics using martensitic theory [4]. The fraction of nanodomains within the material besides tetragonal microdomains can be derived using a two-phase Rietveld fit. To investigate the stability field of these nanodomains with changes in temperature dependent on sample composition, in situ diffraction experiments on powders were conducted in transmission mode at the beamline B2, Hasylab, Hamburg Germany. Various parameters derived from Rietveld refinement are found to reflect the changes in domain structure. There are e.g. pronounced changes in volume strain of the tetragonal phase accompanied by the observation of a plateau in the evolution of the c/a-ratio of the tetragonal phase, as seen in Fig.1, which classify the stability range of the nanodomains.

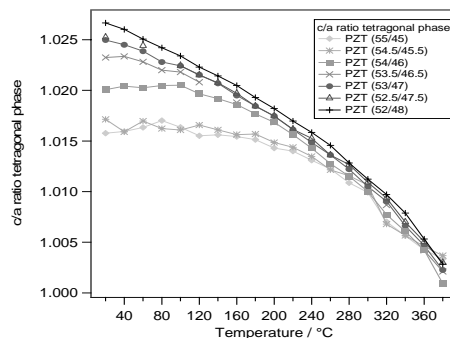


Fig. 1: Temperature-dependent evolution of the tetragonal c/a-ratio for samples out of the compositional range of the MPB.

- [1] Glazer, A. M.; Thomas, P.A.; Baba-Kishi, K. Z.; Pang, G. K. H.; Tai, C. W.; *Phys. Rev. B* 70, 184123 (2004)
- [2] Schmitt, L.A., Schönau, K.A.; Theissmann, R.; Fuess, H.; Kungl, H.; Hoffmann, M.J.; *J. Appl. Phys.* 101, 074107 (2007).
- [3] Schönau, K.A.; Schmitt, L.A.; Knapp, M.; Fuess, H.; Eichel, R.-A.; Kungl, H.; Hoffmann, M.J. *Phys Rev B*, 2007, 75(14) in press.
- [4] Jin, Y.M.; Wang, Y.U.; Khachatryan, A.G.; Li, J.F.; Viehland, D.; *J. Appl. Phys.*, 2003, 94 (5), 3629

#### MS17 P25

**Peculiarity of polymerization of the fullerite C<sub>60</sub> in a hexagonal form.** N.R. Serebryanaya<sup>a</sup>, G.A. Dubitsky<sup>a</sup>, V.D. Blank<sup>a</sup>, B.N. Mavrin<sup>b</sup>, E.A. Skryleva<sup>c</sup>, E.V. Skokan<sup>d</sup>, V.V. Aksenkov<sup>a</sup>, <sup>a</sup>TISNCM, Troitsk, Russia, <sup>b</sup>Institute of Spectroscopy, Troitsk, Russia, <sup>c</sup>Moscow Institute of Steel and Alloys, Russia, Department of Chemistry, MSU, Russia. E-mail: [nadya@ntcstm.troitsk.ru](mailto:nadya@ntcstm.troitsk.ru)

**Keywords:** fullerenes, polymerization, high pressure

2D polymerized phases of the hexagonal closed-packed (hcp) modifications of fullerite C<sub>60</sub> have been manufactured after the high-pressure-high-temperature treatment at 4 GPa and different temperatures. Polymeric phases of the hcp-form are compared with the polymeric phases of fcc-form obtained at the same conditions. Polymeric phases of both C<sub>60</sub> forms have been investigated by X-ray diffraction, X-ray photoelectron (XPS) and Raman spectroscopy methods.

At 450° C the hcp-form is transformed into 2D polymeric rhombohedral phase as the fcc-form. The Raman spectra confirmed that 2D polymeric structures of C<sub>60\_hcp</sub> (orthorhombic and rhombohedral structures) are the same as these of C<sub>60\_fcc</sub>. Unit-cell parameters of 2D polymeric structures of C<sub>60\_hcp</sub> and C<sub>60\_fcc</sub> are calculated.

The essential differences in polymerization of  $C_{60\_hcp}$  are a preservation of hcp-structure up to  $200^{\circ}\text{C}$  and the enormous broadening of diffraction peaks of the polymerized phases. Diffractograms of the polymeric phases of  $C_{60\_hcp}$  contain halos.  $C_{60\_hcp}$  polymers are less stable than fcc polymers. The destruction point of 2D polymerized structure  $C_{60\_hcp}$  is  $600^{\circ}\text{C}$ , the total destruction of fullerene molecules is observed at  $800^{\circ}\text{C}$ . The fullerene molecules of 2D polymeric structures of  $C_{60\_fcc}$  are destroying at  $950^{\circ}\text{C}$ . XPS measurement has shown that the shape of molecules polymerized changes.

#### MS17 P26

##### Rietveld refinement of the x-ray diffraction pattern of $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$ layered oxide

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**Keywords:** Rietveld Refinement, Functionally graded Materials, Energy storage

The  $\text{AMO}_2$  compounds such as  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  are important prototypes for modern high energy density battery materials awaiting commercial application as a large scale [1-2]. Many years ago, we have investigated the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  solid solution and shown that the  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  composition presents the best electrochemical cycling properties. Nevertheless, this phase shows a low electronic conductivity which contributes to the decrease of the electrochemical properties upon cycling [3]. The substitution of  $\text{Mn}^{4+}$  for  $\text{Ni}^{3+}$  and  $\text{Co}^{3+}$  in this phase leads to the presence of both  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  which makes easier the electronic hopping and enhances the electronic conductivity. The  $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$  oxide was prepared at three different temperatures:  $S_1$  ( $900^{\circ}\text{C}/1\text{h}$ ),  $S_2$  ( $900^{\circ}\text{C}/12\text{h}$ ) and  $S_3$  ( $1000^{\circ}\text{C}/12\text{h}$ ) with the aim to show the effect of the thermal treatment on the cationic structural distribution. Indeed,  $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$  compound crystallizes in the trigonal system (space group R-3m) that belongs to the  $\alpha\text{-NaFeO}_2$  structure type. Some transition metal is invariably found in the lithium layer (3a site) displacing that lithium to the transition metal layer (3b site). A full Rietveld refinement of the X-ray diffraction pattern of  $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$  compound was performed to determine the degree of cation mixing. The splitting of the (018)/(110) doublet and the intensity ratio of the (003)/(104) diffraction lines superior to unity suggests a good 2D character of the structure. The resulting data shows that only 0.03  $\text{Ni}^{2+}$  are presents in the lithium site for  $S_1$  sample, whereas for  $S_2$  and  $S_3$  samples, the degree of cation mixing is 0.06 and 0.12 respectively. This result is confirmed by the continuous increase of the  $\text{MO}_2$  (M :  $\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}$ ) slab thickness, given by  $2(1/3-z_{\text{oxygen}})c_{\text{hex}}$ , as a results of the increase of the  $\text{Li}^+/\text{Ni}^{2+}$  mixing leading to the decrease of the covalency within the slab. Structural features deduced from this study were correlated to the electrochemical behaviour of the three studied samples. Presence of  $\text{Ni}^{2+}$  ions in lithium plane clearly reduce the electrochemical capacity and the rate capability as a results of  $\text{Li}^+/\text{Ni}^{2+}$  electrostatic repulsion during the intercalation process.

[1]Tanaka T. et al., 2001, J.Power Sources, 97, 2-6.

[2] Saadoune I. et al., 1997, J. Mater. Chem., 7, 2505-2511.

[3] Saadoune I. et al., 1996, J. Mater. Chem., 6, 193-99.

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#### MS17 P27

**The  $\text{Li}_2\text{FeSiO}_4$  structure under battery cycling** Anton Nyten, Torbjörn Gustafsson & Josh Thomas, Ångström Advanced Battery Centre, Department of Materials Chemistry, Uppsala University, Sweden.

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**Keywords:** Li-ion battery; cathode material; in situ XRD

$\text{Li}_2\text{FeSiO}_4$  has recently emerged as a promising new cathode material for Li-ion battery applications [1,2]. The lithium-ion extraction/re-insertion mechanism in the material has sub-sequently been shown to be somewhat complex, involving some type of structural rearrangement – mainly taking places during the first cycle [3]. This is the prime focus of the work reported here.

$\text{Li}_2\text{FeSiO}_4$  powder was prepared by the solid-state reaction of  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Li}_2\text{SiO}_3$ ; the powders were thoroughly mixed with a carbon precursor (10 wt.%) and heated at  $700^{\circ}\text{C}$  for 20 h under a flow of  $\text{CO}/\text{CO}_2$ . The electrodes studied here by *in situ* powder XRD comprised  $\text{Li}_2\text{FeSiO}_4$ :CB:EPDM in a 80:10:10 ratio. Electrochemical cycling was performed in galvanostatic mode at  $60^{\circ}\text{C}$ . “Coffee-bag” type cells were prepared inside an Ar-filled glove-box with lithium metal as anode and 1M LiTFSI in EC:DEC 2:1 as electrolyte. Cells were tested in the voltage range 2.0 - 3.7 V at a C/25 rate on a Digatron BTS-600 battery tester. The *in situ* XRD profiles were measured on a STOE PSD powder diffractometer.

All samples contain a small amount of impurities, mainly FeO (~5wt.%). The crystal system of the as-prepared  $\text{Li}_2\text{FeSiO}_4$  has been confirmed to be orthorhombic, space-group:  $\text{Pmn}2_1$ ;  $Z=2$ ,  $a=6.2667(5)\text{Å}$ ,  $b=5.3296(5)\text{Å}$ ,  $c=5.0147(4)\text{Å}$ ,  $V=167.5(3)\text{Å}^3$ , with the Li, Fe and Si atoms all tetrahedrally coordinated to four oxygen; see Fig. 1. However, a few weak reflections in the diffractogram indicate the presence of a superstructure ordering dependant upon the thermal history of the sample. A fully refined structure of this compound has yet to be reported.

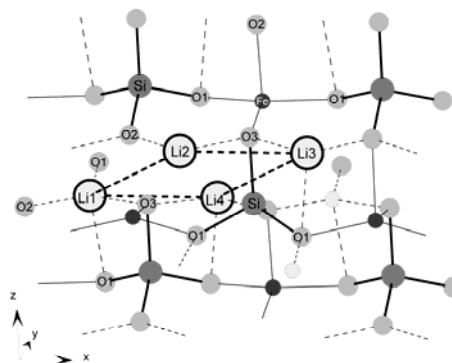


Fig. 1. The crystal structure of  $\text{Li}_2\text{FeSiO}_4$

During the first electrochemical cycle, a shift in the potential plateau from 3.1 to 2.8 V indicates an interesting rearrangement of the structure, presumably involving a phase transition to a more stable structure.