

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

MS39.P06

Acta Cryst. (2011) A67, C490

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

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The ‘corrugated layer’ $Pmnm$ 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 $Pmnm$ - $LiFeO_2$ 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} cm² 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⁻¹cm⁻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

MS39.P07

Acta Cryst. (2011) A67, C490

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-equilibria, structure

MS39.P08

Acta Cryst. (2011) A67, C490-C491

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

energy density limit. Further, for application in electric vehicles there is increasing focus on producing a low cost, highly stable battery with high capacity. In line with this has been the re-emergence of aqueous electrolyte based cells [1]. Defect perovskite structures such as $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$ and $\text{Li}_{3x}\text{La}_{0.33-x}\text{NbO}_3$ present a possible choice of cathode for these cells due to their ideal voltage range, high ionic conductivity, structural flexibility and high intercalation limits [2-3]. However, in order to further develop the properties of defect perovskites a thorough understanding of the structural changes which occur during lithium intercalation and how these affect the electrochemical properties is essential.

We have previously synthesised the defect perovskite compounds $\text{Sr}_{0.8}\text{Ti}_{0.6}\text{Nb}_{0.4}\text{O}_3$ (STN) and $\text{Li}_{0.18}\text{Sr}_{0.66}\text{Ti}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (LSTN). While STN intercalated only a small amount of lithium via chemical means, LSTN readily intercalated lithium. A combination of neutron diffraction studies and bond valence calculations has provided significant insight into the early stages of structural changes during intercalation as well the diffusion properties of the material.

Both STN and LSTN have been able to intercalate lithium electrochemically exhibiting a sloping discharge profile between 1 – 2 V (Fig. 1). This type of voltage profile would normally be associated with solid solution type intercalation behaviour. However, both in-situ neutron and ex-situ synchrotron diffraction experiments have revealed multiphase intercalation behaviour.

This contribution will address the structural changes which occur in STN and LSTN during chemical and electrochemical intercalation and the connection of these structural changes to the observed properties.

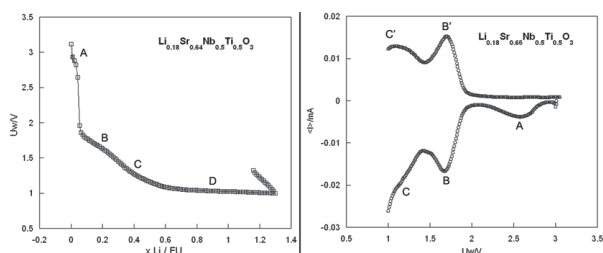


Figure 1: Cyclic voltammogram showing the voltage output during intercalation into LSTN and the location of several electrochemical processes.

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Keywords: battery, perovskite, diffusion

MS39.P09

Acta Cryst. (2011) A67, C491

Structure and dehydrogenation properties on ammine borohydride system as hydrogen storage materials

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Complex metal hydride materials have received a great deal of attention owing to their high gravimetric hydrogen contents [1, 2]. Recently several novel ammine borohydride complex materials, which contain high wt % hydrogen, have been synthesized. The use of ammonia complex of metal borohydrides $\text{Me}(\text{BH}_4)_x \cdot n\text{NH}_3$ (Me = Li, Mg, Al, Zn, Ca) has shown to be a considerable strategy for achieving improved

dehydrogenation mechanism by the interaction between NH_3 and BH_4 molecules. Several compounds release most of hydrogen at a relatively low temperature with no undesirable gas emission. The structures have subsequently been solved by synchrotron powder diffraction method. First principles calculations were performed using density functional theory (DFT), with the projected augmented wave method, to evaluate the electronic properties. The ground state structures are subjected to full structural optimization. The chemical bonding of the material has been analyzed by means of electron localization function (ELF). The development of materials which allow the low temperature release of a large volume of hydrogen is significant, thereby demonstrating the potential of to be used as solid hydrogen storage.

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Keywords: hydrogen storage, crystal structure, powder diffraction

MS39.P10

Acta Cryst. (2011) A67, C491-C492

Altering the properties of metal borohydrides by substitution

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Effective hydrogen storage is one of the bottlenecks for widespread use of hydrogen as a clean energy carrier. Hydrogen storage in solids, most notably metal hydrides, is the only option which can potentially meet the requirements for volumetric hydrogen density. To achieve high gravimetric hydrogen densities, the research focuses on light element such as aluminum and boron. However, no complex hydride with suitable stability and high hydrogen content has yet been found.

The heavy intermetallic hydrides have highly tunable properties by metal substitution over wide compositional ranges, but this possibility is lacking for complex metal hydrides which take stoichiometric metal compositions. However, the use of anion substitution has turned out to be a viable method to change the stability of metal hydrides, e.g. by partly substituting H^- by F^- in Na_3AlH_6 [1].

The system $\text{NaBH}_4 - \text{NaCl}$ has been investigated by powder (lab and synchrotron) X-ray diffraction (PXD), powder neutron diffraction (PND) and various thermal methods. A continuous range of chlorine substitution in NaBH_4 , $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ ($0 < x < 1$) has been obtained by ball-milling mixtures of NaBH_4 and NaCl up to 24 hours. The $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ phases take NaCl-type structures and show almost ideal Vegard's law behavior. In-situ SR-PXD shows a gradual depletion in BH_4^- upon thermal decomposition and hydrogen release and NaCl is the only crystalline final decomposition product. The changes in thermal stability upon chlorine substitution are small, with only a slight stabilization with increasing chlorine content. On the other hand, a drastic change in the order-disorder temperature is observed. Hydrogen ordering in NaBH_4 induces a phase transition from cubic to tetragonal symmetry around 190 K, however, no phase transformation was observed in $\text{Na}(\text{BH}_4)_{0.75}\text{Cl}_{0.25}$ down to 9 K by PND. Phase transformations in more dilute systems are under investigation.

Halide substitution in $\text{Ca}(\text{BH}_4)_2$ mixed with calcium halides has been investigated by in-situ SR-PXD. No substitution of BH_4^- by Cl^- is observed in the low-temperature modification $\alpha\text{-Ca}(\text{BH}_4)_2$, but an appreciable chlorine substitution is observed into the high-temperature phase $\beta\text{-Ca}(\text{BH}_4)_2$. No substitution with bromide or iodide was achieved.