PS10.13.11 CRYSTAL STRUCTURE OF $Li_{6-3x}Al_xGe_2O_7$ PREPARED VIA A SOL-GEL METHOD. H. S. W. Chang, J. C. Wang, K. Guo, L. S. Liou, C. M. Tsai, Department of Chemistry, Soochow University, Taipei, Taiwan, 11102, ROC

A new phase of $Li_{6-3x}Al_xGe_2O_7$ ($x \approx 0.1$)has been synthesized via a sol-gel method. The compound has a $Li_6Ge_2O_7$ related monoclinic structure, but with double cell volume. A hexagonal tunnel formed honeycomb structure, along b-axis, was found in the lattice. It also shown every two of seven hexagonal tunnels contain lithium ions in the tunnels. The properties of the lithium ions, in the tunnels, are believed different from that of the lithium ions form the hexagonal frame work structure. The lithium ions, within the tunnels, are surrounded by two boat form twisted hexagonal layers. Each layer contain three oxygen atoms. The distance between the lithium ion and the six oxygen atoms, on two adjacent layers, are around (a) first layer: 1.992(27), 1.983(31), and 3.079(21) Å, and (b) second layer: 2.056(27), 2.153(26), and 3.487(27) Å. This shows the location of lithium ions in the tunnels are close to the wall of the tunnel. The honeycomb structure and the bonding of the lithium ions can very possibility make them mobile lithium ions. The lithium ions are expected to move in the tunnels and make the obtained $Li_{6-3x}Al_xGe_2O_7$ ($x \approx 0.1$) a possible new material for lithium ion conductor.

The structure of the compound was determined by single-crystal data and refined to R=0.0449 for 2252 reflections. The crystallographic data are; Monoclinic, $P2_1/c$, a=16.2430(10), b=5.400(10), c=15.8161(10) Å, β=118.490(0)°, and Z=8.

PS10.13.12 NEUTRON RIETVELD ANALYSIS OF FAST ION CONDUCTING Ca-DOPED $(Y_{0.95}Ca_{0.05})_2Ti_2O_7$ PYROCHLORE. Kevin Eberman, Per Önnerud, Bernhardt J. Wuensch, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, USA, Judith K. Stalick, Reactor Radiation Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

$Y_2Ti_2O_7$ which crystallizes with the $A_2B_2O_7$ pyrochlore structure type is a good oxygen ion conductor. Ca-doping this material causes a jump in ionic conductivity of three orders of magnitude. It has been suggested that the doping creates vacancies at oxygen sites to compensate the negative relative charge of the calcium substituting for yttrium on the A site, however, Ca-doping might also promote Frenkel disorder placing oxygen on a normally unoccupied site. If doping sets the charge neutrality condition, we expect the oxygen vacancy concentration to be half the calcium concentration ($[V_O^{\cdot\cdot}] = [Ca_{Y'}]/2$). Rietveld powder-profile analysis of the data collected with 1.5405-Å thermal neutrons has been used to determine the site occupancy of oxygen. The anion array consists of three independent sites O(1), O(2), and O(3), at positions 48f, 8a, and 8b respectively. Positions 48f and 8a are completely occupied in the fully ordered pyrochlore leaving 8b completely unoccupied. The structure seems fully ordered with 0.05 Ca substituted on the A site, with no detectable occupancy of the normally unoccupied O(3) site.

PS10.13.13 THE EFFECT OF POTASSIUM ON THE PHYSICAL, CHEMICAL AND STRUCTURAL PROPERTIES OF ELECTROLYTIC MANGANESE DIOXIDE (EMD). V.Ichharam, A.W.Bryson, D.Levendis, F.Crundwell, Centre for Molecular Design, University of the Witwatersrand, Private bag 3, Wits, 2050, Gauteng, South Africa

EMD is used as a cathode material in batteries. X-ray powder diffraction was used to analyse the structure of K^+ doped EMD. Results confirm that K^+ induces cryptomelane formation. The current work shows that K^+ induces the formation of two structural forms of cryptomelane. These structural forms are the monoclinic and tetragonal forms which have similar unit cell parameters. XRD analysis of solid EMD fragments showed that cryptomelane tends to form on a relatively pure γ-MnO_2 substrate. Supporting data was obtained using Energy Dispersive X-ray Analysis (EDXA). XRD data along with data reported in the literature (Kao *et al.*) and data obtained from techniques such as BET surface area measurement and standard compositional analysis techniques permitted a structural model for K^+ doped EMD to be proposed. In this model K^+ ions are located primarily in tunnels of the cryptomelane structure which forms a part of the EMD matrix.

Kao, W.H. *et al.* (1987). *J.Electrochem.Soc.* **134**(6). 1322-1325; (1992) *J.Electrochem.Soc.* **139**(5). 1223-1226.

PS10.13.15 SOLID OXIDE FUEL CELL MATERIALS SYNTHESIS FROM AQUEOUS SOLUTIONS. Takeshi Yao, Akira Ariyoshi and Takashi Inui, Faculty of Engineering, Kyoto University, Kyoto 606 Japan

Novel methods for synthesizing ZrO_2 crystals and $LaMeO_3$ (Me=Cr, Mn, Fe, Co) perovskite crystals from aqueous solutions at ordinary temperature and pressure were discovered. These methods are expected to be applied to film preparations. ZrO_2 and $LaMeO_3$ perovskites now are paid great attentions as the electrolyte, the cathode or the interconnection materials for solid oxide fuel cells (SOFC). The thin film shapes are desirable, however, the usual manufacturing methods such as CVD, sputtering, sol-gel, etc. have some disadvantages. Methods for forming films from aqueous solutions are advantageous because of lower cost, requirement of no vacuum or no high temperature and applicability to films with wide areas and/or complicated shapes.

1. ZrO2 crystals synthesis

Boric acid was added into the sodium hexafluorozirconate solution, the fluoride ion was consumed by the formation of BF_4^-, then the hexafluorozirconate ion was hydrolyzed to ZrO_2 in order to increase the amount of the fluoride ion. The X-ray diffraction peaks were strong and sharp enough to confirm the high crystallinity. In SEM photograph, there observed particles gathering, growing connecting and uniting each other to form a film like aggregates.

2. $LaMeO_3$ perovskite crystals synthesis

The valence state control of the transition metal ions was important and a sophisticated technique was contrived. Powder of $LaMeO_3$ perovskite produced by the usual solid state reaction was dissolved in hydrofluoric acid solution which is expected to neither oxidize nor reduce the transition metal ions, then the solution of metal fluoride having the same valence states as those in the perovskite crystal was obtained. Boric acid was added into the solution, then $LaMeO_3$ perovskite crystal was formed by the similar mechanism as that of the ZrO_2 synthesis. The high crystallinity was indicated by the strong and sharp X-ray diffraction peaks. In the SEM photographs, there observed highly dispersed particles about 1~5 μm on the substrates.