MS17-P3 Defect flourite *vs* pyrochlore: the $M_2 M'_2 O_7$ case

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In recent times we have prepared a considerable number of mixed metal oxides with the a $M_2M'_2O_7$ stoichiometry. Our interest principally being to investigate the thermoresponsive behaviour of these materials via VT-PXRD methods and to assess their potential as energy materials in Solid Oxide Fuel Cells (SOFC's).

Crystallographically, the defect fluorite structure with space group *Fm3m* (No 225) and pyrochlore structures with space group *Fd3m* (No 227) are isometric. In the defect fluorite (DF) phase, the M and M' cations are completely disordered and oxygen atoms are evenly distributed into all the tetrahedral sites formed by cations. Each oxygen position having a 7/8 occupancy, and hence the description as a 'defect fluorite' phase. The pyrochlore (P) phase is a superstructure of the DF phase with the *a*-axis doubled. Upon heating the DF phase converts to the P phase and although there are a number of reports in the literature reporting on this phase transition, the detailed phase behaviour of most of these materials remain relatively unexplored. Further heating in our experience has occasionally resulted into the decomposition of the mixed metal oxide into simpler, primary oxides.We have focused our studies on materials prepared via the sol-gel method. Typically materials are prepared as the DF phase and then subsequently converted to the P phase by heating. The materials produced have been extensively characterised via VT-PXRD, COXA, Rietveld, Raman, TGA and EIS. Our over aim being to comprehensively understand the phase property relationships of these materials, and to use this to determine ideal candidate materials for making proof of concept SOFC's

Selected results of the study are to be presented. Including thermal expansion coefficients of materials studied and a COXA study of the phase transition.

Keywords: Defect Flourite, Pyrochlore, VT-PXRD, SOFC's

MS17-P4 Phase behaviour and thermal transformations within the $Cu^{I/II}X_2(PO_4)_3$ [X = Ti, Zr, Hf & Sn] series

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The sodium zirconium phosphate (NZP) family is of academic and industrial importance. The $[Zr_2(PO_4)_3]^-$ is composed of a rigid framework containing channels that are suitable for occupation by numerous cations.[1] This structure is unique and a large number of elemental substitutions are possible.[2] A further consequence thereof is that NZP and many of its analogues possess a number of commercially useful physical properties, for example, low thermal expansion behaviour, fast alkali transportation as well as exhibiting mild oxidative catalytic behaviour. In the present study substitutions at the tetrahedral site were investigated for a series of $Cu^{I/II}X_2(PO_4)_3$ [X = Ti, Zr, Hf & Sn] compounds. It has previously been shown that $Cu^{I}Zr_2(PO_4)_3$ and several of its analogues may be unstable to thermal treatment in air.[3] This is attributed to the migration of Cu(I) cations from the framework structure.[4] The chemical, catalytic and ionic properties of the $CuX_2(PO_4)_3$ type phases have previously been reported.[5] Citing a lack of structural data in the literature there is as a consequence no quantitative description of the phenomena that occur during thermal treatment. The purpose of this study was thus to examine possible structural and compositional changes and their relation to the thermal stability of these compounds. Transformations that were achieved with the $Cu^{I/II}X_2(PO_4)_3$ series are displayed below in Figure 1. Significant results will be presented.

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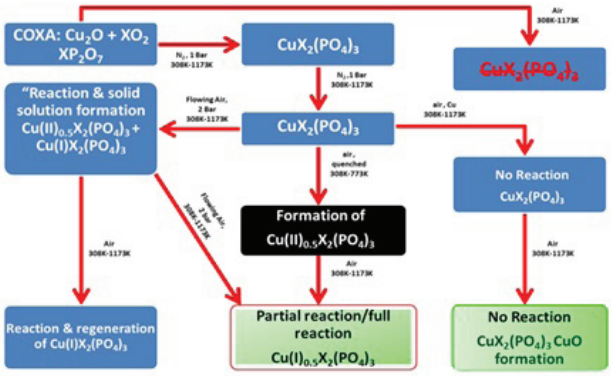

Figure 1. Structural and chemical transformations observed within the $Cu^{I/II}X_2(PO_4)_3$ [X = Ti, Zr, Hf & Sn] series

Keywords: framework materials, thermal stability

MS17-P5 Real-time XRD nd XAS investigation on the influences of vanadium additives to the structural chemical state evolutions of $LiFePO_4$ of a lithium-ion

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The influence of adding vanadium on the structure evolution and electrochemical performance of $LiFePO_4$ were systematically investigated by *in-situ* x-ray powder diffraction and x-ray absorption near edge structure spectroscopy. Our results indicate that the addition of a small amount of vanadium (less than at 1%) significantly reduces the formation of non-crystalline (highly disordered) triphylite and remnant heterosite phases in the cathode of battery especially at higher C rates. By adding vanadium, the cycle stability of $LiFePO_4$ cathode is improved by 14.9% compared to that of pristine $LiFePO_4$ cathode in the batteries. Such an enhancement could be attributed to the improved ion diffusion kinetics and reduced inactive $LiFePO_4$ in cathode by the reversible excess charge – vacancy effects of supervalent-vanadium additive in cathode during electrochemical redox cycles. The most interesting point is the difference between diffraction intensity ratio determined by XRD and ratio of oxidation state of Fe ion determined XAS. Without V additives, this difference is much larger after cycling, which implies the disorder irreversible phase persists.

Keywords: lithium ion battery, XRD, XAS, phase transition