Poster Presentation

MS15.P03

Transformation from pyrochlore to fluorite by diffraction and X-ray spectroscopy

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We have studied the long-range average and local structures in a number of zirconium containing materials of the type A2B2O7 (A = Ln or Y; B = Zr, Hf or Sn) using synchrotron X-ray and neutron powder diffraction and X-ray absorption spectroscopy. Studies of the system Gd2-xTbxZr2O7 include neutron diffraction data, obtained at λ ≈ 0.497 Å to minimise absorption, not only provide evidence for independent ordering of the anion and cation sublattices, but also suggest that the disorder transition across the pyrochlore-defect fluorite boundary of Ln2Zr2O7 is rather gradual. In general we observe that while the diffraction data indicate a clear phase transition from ordered pyrochlore to disordered defect-fluorite at specific compositions corresponding to a critical ionic radius ratio of the A and B cations (rA/rB) x ~ 1.0-1.2, X-ray absorption near-edge structure (XANES) results reveal a gradual structural evolution across the compositional range. These findings provide experimental evidence that the local disorder occurs long before the pyrochlore to defect-fluorite phase boundary as determined by X-ray diffraction, and the extent of disorder continues to develop throughout the defect-fluorite region. Where possible the experimental results were supplemented by ab initio atomic scale simulations, which provide a mechanism for disorder to initiate in the pyrochlore structure. Further, the coordination numbers of the cations in both the defect-fluorite and pyrochlore structures were predicted, and the trends agree well with the experimental XANES results. X-ray absorption measurements at the Zr L3-edge, which showed a gradual increase in the effective coordination number of the Zr from near 6-coordinate in the pyrochlore rich samples to near 7-coordinate in the defect fluorites.

[1] *E. Reynolds et al Inorganic Chemistry 2013 52 8409-8415,* ***[2]*** *P.E.R Blanchard et al J. Chem Soc., Dalton Transactions 2013 42 14875-14882,* ***[3]*** *z. Zhang et al J. Physical Chemistry C 2013 117 26740-26749*

Keywords: Phase Transformation, Neutron Powder Diffraction, X-ray absorption spectroscopy