Pyrochlore disorder: a combined experimental and atomistic simulation study

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Pyrochlore ceramics ($A_2B_2O_7$) are considered to be promising host phases for the immobilization of Pu and fission products with respect to nuclear waste management [1,2]. Due to their high radiation tolerance ZrO_2 based pyrochlores undergo a phase transition to the less ordered defect fluorite structure, rather than amorphizing. Probing the nature and the driving forces of this order/disorder transition is a prerequisite to understand the high stability of these potential host phases for high level nuclear waste.

Here, the structural transition of a $Nd_{2x}Zr_{1-x}O_{2+x}$ system was followed by combining experimental and theoretical approaches. Partial substitution of Nd by the B-site cation Zr led to $(Nd,Zr)_2Zr_2O_{7+x}$ compounds which exhibit already partial disorder. At 1600 °C the transition of the pyrochlore to the defect fluorite structure was determined by XRD to occur at around 19 mol% Nd_2O_3. High temperature oxide melt solution calorimetry determined a transition enthalpy of ~30 kJ/mol. *Ab initio* calculations of both phases were performed using quasi-random structures, assuming a random distribution of the excess Zr on the A-site and additional oxygen at former oxygen vacancy sites. Full disordering was assumed for a defect fluorite phase. The predicted formation enthalpies of the structural model are in excellent agreement with our experimental results, probing the model to be suitable to estimate standard thermodynamic properties of such pyrochlore phases. In consistency with our XRD results the computed differences in free energies of pyrochlore and defect fluorite predict the structural transition around 20 – 23 mol% Nd_2O_3.

This combined experimental and atomistic modelling study on the order/disorder transition of pyrochlore allows us to develop a molecular process understanding for the pyrochlore/defect fluorite transition, which is a prerequisite for their potential application as nuclear waste forms.

[1] Ewing *et al*. (2004) *J. Appl. Phys* **95**, 5949-5971.
[2] Finkeldei *et al*. (2014) *Appl. Geochem* **49**, 31-41.