

HYDRATION IN FLUORITE-RELATED RARE-EARTH CERATES

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Key Words: $\text{La}_2\text{Ce}_2\text{O}_7$, $\text{Nd}_2\text{Ce}_2\text{O}_7$, fluorite, hydration, protons.

Hydration enthalpy and water uptake in $\text{La}_{2-x}\text{Nd}_x\text{Ce}_2\text{O}_7$ series ($x = 0.0, 0.5, 1.0$ and 2.0) have been measured using combined thermogravimetry (TG) and differential scanning calorimetry (DSC), TG-DSC. The DSC data unambiguously yield standard molar hydration enthalpies of around -74 kJ/mol independent of water uptake.

The TG results however needs interpretation according to a model, and it is clear that they cannot be fitted to a classical model of hydration of all disordered oxygen vacancies. Instead, the hydration appears to be limited to a small fraction of the free vacancies. Hydration further decreases as the Nd content (x) and long range order increases and regions of disorder decrease.

We propose a new model explaining why hydration occurs only in a small fraction of the nominally free vacancies: The higher basicity of La/Nd compared to Ce enables hydration, and high coordination with La/Nd around OH is needed to stabilize the proton/hydroxide in order to obtain exothermic hydration. The statistical variation of coordination around oxygen sites in a disordered fluorite oxide creates a limited number of such oxide ions sites which results in limited hydration.

It is expected that this new purely statistical approach to interactions in special cases of heavily defective compounds may apply to rationalize unexpected defect behavior also in other systems.

