Energetics of UO_2-Solid Solutions with CaO and Y_2O_3

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Doped UO_2 with two-, three- and four-valent metals has been attracting interest for decades primarily because of its relevance to nuclear fuels and reactor accidents, but also because of potential industrial usage. Although early work measured vapor pressure in such solid solutions, direct calorimetric measurements of enthalpies of formation have been hampered by the refractory nature of such oxides. Here we present first measurements, by high temperature oxide melt solution calorimetry, of the enthalpy of formation of the systems UO_2-CaO and UO_2-$YO_{1.5}$. The results obtained show that UO_2-CaO solid solution is slightly more exothermic in enthalpy (by – 2 kJ/mol for the composition $(UO_{2.22})_{0.861\pm0.0062}(CaO)_{0.14\pm0.02}$) relative to its constituent oxides, whereas UO_2-$YO_{1.5}$ solid solution is significantly more stable (67 kJ/mol for the composition $(UO_{2.32})_{0.34\pm0.03}(YO_{1.5})_{0.66\pm0.07}$) than a mechanical mixture of binary oxides. Relationships between the energetics and the cation size of th dopant in the fluorite structure will be discussed together with a comparison to the previously reported vapor pressure data. It is clear that the formation of defect clusters and short-range order has a major stabilizing effect in the yttrium-containing system.