Thermodynamic Study of Zirconium and Hafnium Boranate - $Zr(BH_4)_4$ and $Hf(BH_4)_4$

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The storage of hydrogen is a necessary step to achieve the transition of the German energy sector from fossil fuels to renewable energy sources [1]. Transition metal boranates may contribute to reach this goal. A concept to reduce the often very high decomposition temperatures of boranates is that of thermodynamic tuning using mixtures with other (complex) hydrides [2,3]. In respect to the rehydrogenation and dehydrogenation of complex hydrides in general, Zr and Hf compounds are known to exhibit catalytic acivity [4]. Combing these thermodynamic and catalytic aspects, $Zr(BH_4)_4$ and $Hf(BH_4)_4$ may be interesting candidates to design valuable hydrogen storage systems. Unfortunately, no thermodynamic data are available for these materials, which are prerequisit for thermodynamic calculations. Therefore, we conducted a calorimetric and DFT study to provide them.

$Zr(BH_4)_4$ and $Hf(BH_4)_4$ have been synthesised by solid state metathesis [5] instead by wet chemistry. The high vapor pressure and low boiling point of both compounds [6] allows to separate easily the product by destillation from the by-product.

The heat capacities of the compounds were measured between 5 °C and 35 °C using a Setaram DSC-111. TG-DSC-MS measurements and Hess law were employed to determine the enthalpy of formation at 298.15 K. Furthermore, DFT calculations were performed to obtain the standard entropy at 298.15 K of both compounds. Finally, our data were optimised by the CALPHAD method based on experimental vapor pressure measurements [6] and own measurements of the enthalpy of fusion as well as the temperature of fusion. With these data it is possible to perform thermodynamic calculations in regard to the decomposition behaviour of both compounds.

References

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