

Pr(BH₄)₃ - polymorphic transitions and a hint of stepwise negative thermal expansion

Wednesday, 26 June 2019 10:00 (20 minutes)

In this work, praseodymium(III) borohydride, Pr(BH₄)₃, and the isotopically enriched analogue, Pr(11BD₄)₃, are prepared by two routes. The first approach started by mechanochemical synthesis of PrCl₃ and LiBH₄, and extraction of LiCl [1], while the second approach, shows a new route and proceeded via a solvate complex, Pr(11BD₄)₃S(CH₃)₂ starting from the metal Pr itself. α -Pr(BH₄)₃ is isostructural with cubic unit cells (Pa-3) stable at room temperature (RT) and unit cell volume per formula unit (V/Z) of 180.1 and 175.8 Å³, respectively. Heating α -Pr(BH₄)₃ to T = 190 °C, p(Ar) = 1 bar, introduces a transition to a rhombohedral polymorph, r-Pr(BH₄)₃ (R $\bar{3}$ c) with smaller unit cell volume and denser structure, V/Z = 156.06 Å³. However, heat treatment of α -Pr(BH₄)₃, at T = 190 °C, p(H₂) = 40 bar facilitates reversible formation of another three cubic polymorph, denoted β , β' -Pr(BH₄)₃ and β'' -Pr(BH₄)₃ (Fm $\bar{3}$ c). Moreover, the transition β - to β' - to β'' - is considered a rare example of stepwise negative thermal expansion, which we pursue to validate via PDF analysis. For Pr(BH₄)₃, 2/3 of the sample take this route of transformation whereas in argon only 5 wt%, and the remaining transforms directly from alpha- to r-Pr(BH₄)₃. The β -polymorphs are porous with V/Z = 172.4 and 172.7 Å³ for β'' -Pr(BH₄)₃, and are stabilized by the elevated hydrogen pressures. The polymorphic transitions occur due to rotation of RE(BH₄)₆ octahedra without breaking or forming chemical bonds. Structural DFT optimization reveals decreasing stability of α -Pr(BH₄)₃ > β -Pr(BH₄)₃ > r-Pr(BH₄)₃.

Primary author: HEERE, Michael

Presenter: HEERE, Michael

Session Classification: Science group meetings 1