Expansion of the hydride chemistry – new materials based on mixed anionic hydrides

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Within the last decade, mixed anionic hydrides have gained multiple attraction as a materials class due to some of their unique properties[1]. For instance, fast hydride ion conduction[2], tunable optical properties[3], but also superconductivity[4] were found. Overall, most of these materials are oxy hydrides with isolated oxide ions. Hydridic materials with complex oxoanions are however scarce and the reductive nature of hydrogenation reactions often require carefully designed synthetic routes to accomplish such compounds. To date, only a handful of mixed anionic hydrides with complex (oxo-)anions are reported, with several hydride-to-anion combinations yet unknown. With the ambition to expand the family of mixed anionic hydrides, we established three hitherto unknown hydride-to-anion combinations. Here, we present $Sr_5(PO_4)_3H$[5] as the first phosphate hydride, $Sr_5(BO_3)_3H$[6] the first borate hydride and lastly we introduce Na_3SO_4H[7] as the first sulfate hydride. The materials are either accessible *via* mechanochemical synthesis routes or *via* solid-state reactions under controlled conditions. Structure determination of the unprecedented materials are carried out by the means of laboratory powder X-ray diffraction and complementary neutron powder diffraction of the deuterated analogues. Further prove of the abundance of hydride ions next to different complex anions is provided by ^{1}H MAS NMR spectroscopy and vibrational analysis in combination with DFT-calculations.

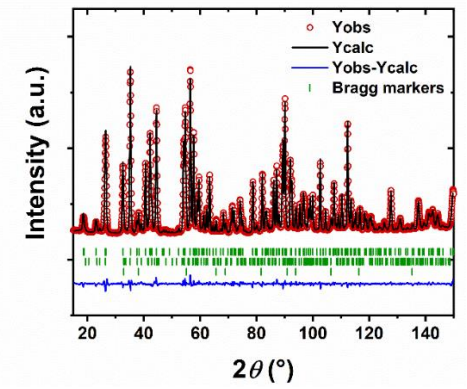

Fig 1 Rietveld refinement plot of Na_3SO_4D. Bragg markers from top to bottom: Na_3SO_4D (92.2(9) wt.%), Na_2SO_4 (*Cmcm*) (6.3(7) wt.%), NaD (1.5(2) wt.%)

In summary we opened up the door to new hydridic materials containing complex (oxo-)anions next to hydrides. While the phosphate hydrides and borate hydrides might be suited as host materials for lanthanide activated luminescence, sulfate hydrides might be utilized as approach to introduce polarizable anions in solid-state ionic conductors. Applying the described sophisticated synthesis methods, more mixed anionic hydrides within these materials classes with potentially desirable properties are expected to be discovered and explored.

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