Project H-4: Zintl phase hydrogen absorbing compounds

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Since Bogdanonvic' reported the reversible hydrogenation of $NaAlH_4$ with catalysts, alanates have attracted remarkable attention. However, at this moment only $NaAlH_4$ among alanates is a potential candidate for practical applications. The objective of this project is to synthesize new type of hydrides with Al-H bonding. We started from an alloy $SrAl_2$. This alloy of $SrAl_2$ is the Zintl phase compound in which Al^- forms a three-dimensional infinite network [1, 2].

We have synthesized $SrAl_2H_2$ by hydrogenation of $SrAl_2$ at 5MPa hydrogen pressure below 473K. $SrAl_2H_2$ is also Zintl phase compound that consists of Sr^{2+} cations and two-dimensional infinite $[AlH^-]_n$ anions. $SrAl_2H_2$ crystallizes with a new trigonal structure in space group $P\bar{3}m1$ (164), cell parameters: a = 0.45283(1) nm, c = 0.47215(2) nm (hydride), a = 0.45253(1) nm, c = 0.47214(2) nm (deuteride), Z = 1. We also synthesized the higher hydride Sr_2AlH_7 under a hydrogen pressure of 7 MPa at 543 K for 10 days. Sr_2AlH_7 crystallizes with a new monoclinic structure in space group $I2$ (No. 5): a = 1.2575(1) nm, b = 0.9799(1) nm, c = 0.79911(8) nm, α = 100.270(4)° (hydride), Z = 8.

The alkali earth element Ba does not form $BaAl_2$ but Ba_7Al_{13}. We synthesized a new type of hydride, $BaAlH_5$, by hydrogenation of Ba_7Al_{13} under a hydrogen pressure of 7 MPa at 513 K for 5 days. It crystallizes with a new orthorhombic structure in the space group $Pna2_1$, cell parameters: a = 0.9194(1) nm, b = 0.70403(9) nm, c = 0.51061(6) nm (deuteride). The crystal structure of $BaAlH(D)_5$ (Fig. 1) contains Al-centered deuterium octahedra $[AlD_6]$, which share one-corner and form one-dimensional zigzag chains along the crystallographic c axis (Fig. 2). Because of this interesting arrangement of hydrogen atoms, $BaAlH_5$ has a larger H/M ratio than the conventional alanates such as $NaAlH_4$ and Na_3AlH_6. If some light elements can be used as substitutes for Ba, the weight percent of hydrogen will increase considerably.

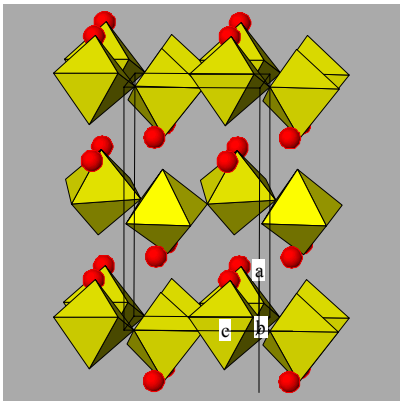

Fig. 1 Crystal structure of $BaAlH_5$. Spheres are Ba and the $[AlH_6]$ octahedra are centered by Al.

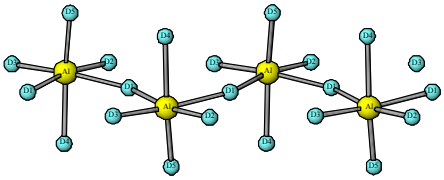

Fig. 2 The zigzag chain of $[AlH_6]$ in $BaAlH_5$.

References

1. S.M. Kauzlarich, Zintl compounds, in: R.B. King (Ed.), *Encyclopedia of Inorganic Chemistry*, Vol. 8, Wiley, 1994, p. 4467ff, and Refs. therein.
2. G. Cordier, E. Czech, H. Schafer, *Z. Naturforsch*. **37b** (1982) 1443.