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Structural Investigation of Intermediates and End Products in the Synthesis of Ti-doped Alkali Metal-Aluminum Hydrides

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Background

The group of Prof. B. Bogdanovic' has developed a novel medium-temperature reversible hydrogen storage material utilizing Ti-catalyzed hydriding and dehydriding reactions of $NaAlH_4$ and Na_3AlH_6. Ti doping renders the normally nonreversible $NaAlH_4$ and Na_3AlH_6 hydrides reversible, thus making them good candidates for reaching the IEA Task 12 target for hydrogen storage capacity. However, the kinetics are low. This project aimed at identifying and structurally characterizing the constituents participating in the reactions, in order to make reasonable judgments toward the future design of improved catalysts. The phases of the hydrogenated samples were identified at Stockholm University from Guinier-Hägg x-ray diffraction patterns, thus confirming the reactions and reversibility of the metal-aluminum hydrides in the samples supplied by the Max Planck Institute.

Results and discussion

High-resolution x-ray diffraction was used in an effort to identify the catalyst and, possibly, intermediate species. Among the identifiable x-ray lines from starting materials and end products, a number of unidentified lines were consistently found in samples taken at different reaction stages. Unfortunately, the low x-ray intensity of the extra lines, combined with overlap from the main phases made identification impossible.

The main outcome of the project was that the hydriding-dehydriding reactions could be monitored by observing the relative x-ray intensity of their phases in samples taken at various stages of the reaction. A detailed structural determination of Na_3AlH_6 was made, by combining x-ray and neutron diffraction [1]. It was previously suggested that Na_3AlH_6 is isostructural with the low-temperature phase of Na_3AlF_6 and space group symmetry $P2_1/n$. However, with the trial and error indexing program TREOR, the best figure of merit for the Guinier-Hägg x-ray diffraction patterns was obtained for an ortorhombic unit cell: M_{20}= 35. However, four extremely weak lines in the diffraction pattern could only be indexed with a P-centered cell, so we decided to synthesise the deuteride, Na_3AlD_6, and to collect a neutron diffraction pattern in order to find the true symmetry by a full structural determination (Figure 1).

From Guinier-Hägg x-ray powder diffraction patterns, the cell parameters were determined to be a = 5.408(2), b = 5.538(2) and c = 7.757(2) [Å and β = 89.83(2)^o]. In a Rietveld refinement of the neutron diffraction data (Figure 1), the best criteria of fit were not found for *Immm* nor for a P-centered cell, but for the monoclinic space group $P2_1/n$. The sample also contained some NaD, which was included in the refinements as a second phase. The structural parameters for Na_3AlD_6 are listed in Table I below.

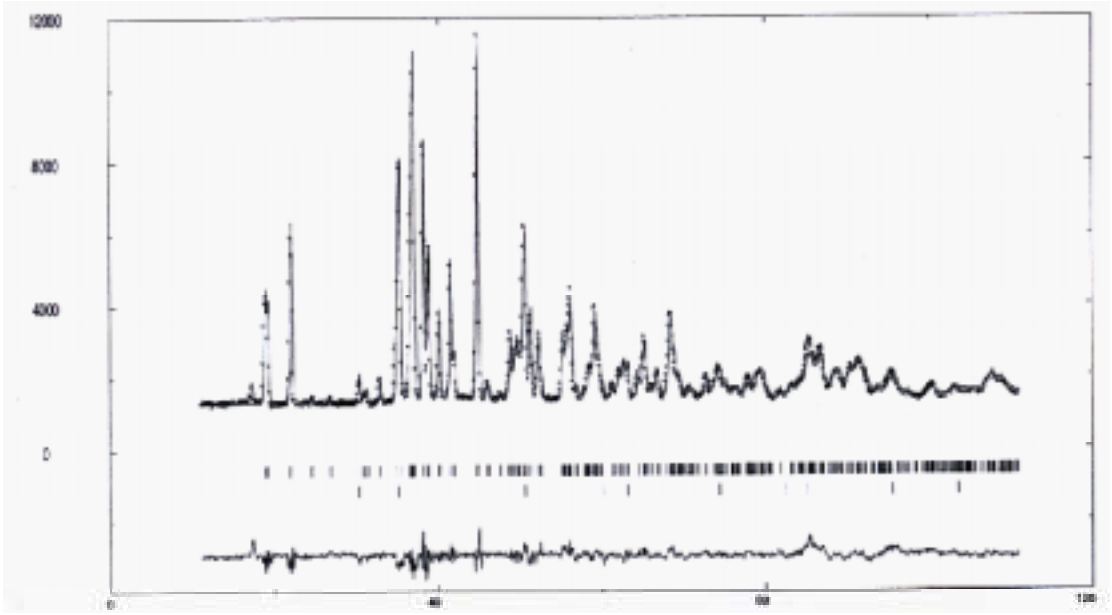

Figure 1 - The observed and calculated diffraction patterns from the Reitveld refinement on Na_3AlD_6 in the space group $P2_1/n$ (no.14). Also included in the refinement was NaD.

Relative Intensity

Table I: Structural parameters for Na_3AlD_6 refined from powder neutron diffraction data in space group $P2_1/n$ (no.14), Z=2, to R_F = 6.2, R_B =7.9 and R_W =13.3%. The estimated standard deviations are given in brackets.

Atom	Site	x	y	z	B_{iso}
Na1	2b	0	0	1/2	2.49(5)
Na2	4e	-0.006(5)	0.461(4)	0.252(5)	2.49(5)
Al	2a	0	0	0	1.16(5)
D1	4e	0.091(3)	0.041(3)	0.215(3)	3.1(1)
D2	4e	0.234(3)	0.328(3)	0.544(3)	3.1(1)
D3	4e	0.154(3)	0.266(3)	0.944(3)	3.1(1)

Reference

[1] E. Rönnebro, D. Noréus, K. Kadir, A. Reiser and B. Bogdanovic', J. Alloys and Comp. **299** (2000) 101.