Project 16 – Leader: Etsuo Akiba (Japan), e-mail: akiba@nimc.go.jp

Synthesis and Crystal Structural Analysis of New Ternary Hydrides Based on Hydride-Fluoride Similarity

E. Akiba, H. Enoki, Q-A. Zhang and F. Gingl
National Institute of Materials and Chemical Research
Tsukuba, Ibaraki, Japan

Introduction

Aluminum hydrides such as $NaAlH_4$ have received new attention recently after the discovery that doping with Ti compounds can significantly improve their kinetic properties [1]. Ti doping makes these materials possible candidates for reversible hydrogen storage applications.

One of the authors has developed a Hydrides and Fluorides Database (HFD) based on the similarity in crystal structures of these two families of compounds [2]. During our investigation, using the HFD to find a new class of hydrogen storage compounds, we found several new phases in the Sr–Al–H system. Here we report on the synthesis and the structure determination of the first of these new ternary hydrides, namely $SrAl_2H_2$. $SrAlH_2$ and its hydrides are Zintl compounds. The Zintl compounds are made up of electropositive elements that donate their electrons to the electronegative elements that, in turn, use them to form the correct number of bonds such that each element has a filled shell. This is the first finding that a Zintl compound absorbs hydrogen and its hydride is also Zintl phase.

Experimental Details

$SrAl_2$ was prepared by arc melting stoichiometric amounts of the elements. After remelting several times to ensure homogeneity, the ingots were ground to powders with a particle size smaller than 100μm. Samples of 1–2 g were loaded into stainless steel containers and placed in stainless steel autoclaves. Hydrogenation reactions were carried out at 50 bar hydrogen pressure by slowly raising the reaction temperature from 100ºC to 200ºC in steps of 10–20ºC/day. The products were dark gray and sensitive to moisture.

Results and Discussion

The hydrogenation reaction of $SrAl_2$ was studied by *in situ* X-ray powder diffraction. During the experiment, the hydrogen pressure was kept at 50 bar and the temperature was raised from 40°C to 350°C in steps of 5°C. The *in situ* X-ray powder patterns measured at temperatures between 150°C and 350°C are shown in Figure 1.

$SrAl_2$ hydride/deuteride crystallizes with a new trigonal structure in space group *P*3*m*1 (164); cell parameters: a = 4.5283(1) Å, c = 4.7215(2) Å (hydride), a = 4.5253(1) Å, c = 4.7214(2) Å (deuteride), Z = 1. The main feature of this structure is a two dimensional polymer Zintl anion, in which one H atom is covalently bonded to each Al atom. $SrAl_2H_2$ is the first example of a Zintl-phase hydride (the first Zintl phase in which hydrogen atoms are part of the Zintl anion).

Conclusions

A new class of hydrogen absorbing materiald has been found. A Zintl-phase alloy, $SrAl_2$, can form a Zintl hydride anion with the Al-H bonding, which is formed by a breaking of Al–Al bonds and replacement of one Al neighbor by a hydrogen atom. The alloy was synthesized by a conventional arc-melting method, but the hydride forms an Al-H bond that is very similar to that of alanates. The work on the Zintl phase hydrides will be continued in the next stage of the IEA activities.

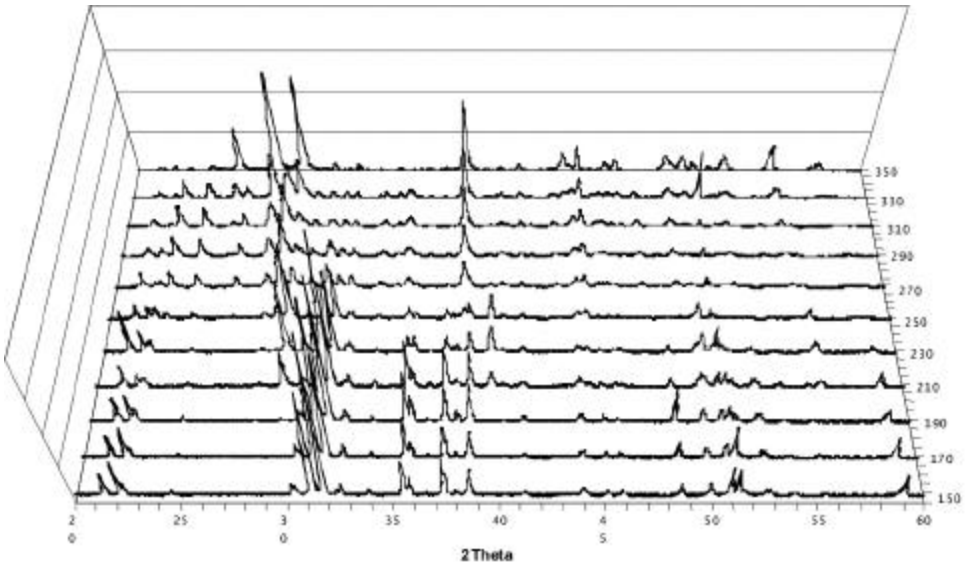

Figure 1 - In situ X-ray powder diffraction patterns between 150°C and 350°C, recorded during hydrogenation of $SrAl_2$ at 50 bar hydrogen pressure.

References

[1] B. Bogdanovic and M. Schwickardi, J. Alloys Comp., **253–254** (1997) 1.
[2] F. Gingl, L. Gelato, K. Yvon, J. Alloys Comp., **253-254** (1997) 286.