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Structural determination of $NaAl_2Ga_2$ intermetallic compound having the $ThCr_2Si_2$ type structure

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ABSTRACT

$NaAl_2Ga_2$ intermetallic compound has been synthesized by direct combination of the elements in the atomic ratio Na:Ga:Al = 1:2:2. Guinier–Hägg X-ray and neutron powder diffraction determined a $ThCr_2Si_2$ type structure for the new compound with tetragonal unit cell axis $a = 4.1817(5)$ and $c = 11.388(2)$ Å.

1. Introduction

The alanates i.e. $NaAlH_4$ and Na_3AlH_6 have attracted considerable interest as possible reversible hydrogen storage systems, since Bogdanović et al discovered that a titanium containing catalyst could significantly improve the usually sluggish hydrogen/dehydrogenation reactions [1]. The Al–H bond is, however, rather weak and the equilibrium pressure is high and not affected by the added Ti-catalyst, the role of which is still also a matter of controversy [2]. The high equilibrium pressure necessitates impractical high hydrogen absorption pressures. In an effort to reduce these we started to investigate new ternary systems where aluminum was partially substituted by gallium. $NaGaH_4$ can for example be made at more moderate hydrogen pressures [3]. During this we came across a new $NaAl_2Ga_2$ intermetallic compound that was found not to absorb hydrogen but formed the interesting $ThCr_2Si_2$ type structure [4]. The inter-atomic distances of $NaAl_2Ga_2$ was compared to similar compounds with the same of structure type like $CaAl_2Ga_2$ and $CeAl_2Ga_2$ [5,6].

2. Experimental

The starting sodium metals ingots with 99% purity Al powder and Ga-metal (99.9%) were all obtained from Aldrich. Binary NaH/D was synthesized by direct combination of the elements.

Initially the ternary compound was prepared by sintering (~2 g) tablets pressed 0.5 MPa of the Na or NaH/D with aluminum and gallium powder in the atomic ratio Na, Ga and Al 2:1:1, as we wanted to test if mixed hydrides existed with compositions in the regime $NaAl_xGa_{1-x}H_4$. The tablets were heat treated in a tube furnace at 603 K and at 5 MPa of hydrogen gas for 12 h. A stainless steel encapsulated thermocouple was inserted in close contact with the reacting tablet to record the sample temperature. After cooling under hydrogen, the samples were crushed and a small volume was removed for X-ray analysis. X-ray diffraction photographs were obtained from a subtraction-geometry Guinier–Hägg focusing camera, using strictly monochromated [7] Cu $K\alpha_1$ radiation. A single-coated X-ray film (CEA Reflex 15) was used in all the work. The films were evaluated by means of a computer-controlled single-beam microdensitometer designed for the scanning analysis of X-ray powder photographs [8]. The θ scale was calibrated by means of the internal (silicon) standard technique, using a parabolic correction curve.

The initial results showed a not fully reacted sample. New tablets were made of the powder and reheated as described above and the temperature was raised stepwise to 723 K after reacting at this temperature the X-ray diffraction pattern consisted of diffraction lines of from NaH and a set of unidentified lines. By reducing the initial NaH content to correspond to a composition $NaAl_2Ga_2$ an almost single phased sample remained with an X-ray diffraction pattern dominated by the unknown set of diffraction lines. No variation in the peak positions of the unknown phase was observed as a function of the changes in the starting composition, indicating that the new phase has almost no range of homogeneity. We also cycled the hydrogen pressure while monitoring the sample temperature. No evolution of any reaction heat could be observed that could be associated to some hydrogen/dehydrogenation reaction taking place in the sample. This indicates that the new compound probably does not react with hydrogen at least for a hydrogen pressure up to 5 MPa and at temperatures between room temperature and 723 K.

But to anyhow localize possible hydrogen atoms in the structure we prepared a sample for neutron diffraction using deuterium instead of hydrogen in a corresponding synthesis. The resulting neutron diffraction pattern was recorded at the R2 reactor in Studsvik using a cylindrical vanadium sample holder (Ø = 5 mm) and a neutron wavelength of 1.47 Å.

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Table 1
Observed, calculated, 2θ, d-values and intensities for $NaGa_2Al_2$ by using Guinier–Hägg X-ray diffraction Cu $K\alpha_1$ radiation and with Si as the internal standard at 293 K. $M(20) = 62$.

h	k	l	$2\theta_{obs}$	$2\theta_{cal}$	d_{obs}	I_{obs}	I_{cal}
0	0	2	15.531	15.550	5.7009	2	1
1	0	1	22.599	22.634	3.9313	100	100
1	1	0	30.171	30.201	2.9597	33	41
0	0	4	31.359	31.397	2.8502	3	4
1	0	3	31.794	31.813	2.8122	50	49
1	1	2	34.120	34.140	2.6256	72	60
2	0	0	43.230	43.236	2.0911	63	65
1	1	4	44.113	44.123	2.0513	70	64
1	0	5	45.308	45.303	1.9999	56	59
0	0	6	47.899	47.890	1.8976	7	6
2	1	1	49.340	49.344	1.8455	22	26
2	1	3	54.659	54.668	1.6778	19	22
2	2	0	62.822	62.801	1.4780	23	24
2	1	5	64.408	64.412	1.4454	41	47
0	0	8	65.548	65.524	1.4230	5	7
2	0	6	66.497	66.479	1.4050	12	11
3	0	1	67.675	67.663	1.3833	3	6
3	1	0	71.247	71.256	1.3225	3	8
3	0	3	72.194	72.131	1.3075	2	6
3	1	2	73.435	73.457	1.2884	13	17
1	0	9	78.946	78.996	1.2117	7	9
3	1	4	79.934	79.926	1.1992	32	34
3	0	5	80.784	80.768	1.1887	5	15
2	0	8	81.803	81.787	1.1765	13	19
2	2	6	82.710	82.667	1.1658	4	8
3	2	1	83.705	83.766	1.1545	8	9

3. Results and discussion

3.1. Crystal structure

Using the TREOR program [9] and the least-square refinements program PIRUM [10], the X-ray powder pattern of the unknown $NaAl_2Ga_2$ phase could be indexed on the basis of a tetragonal unit cell with Table 1 $a \times$ the $c/a = 2.72$ ratio, and we suspected the new intermetallic compound to be isotypic with the $ThCr_2Si_2$ structure, described in the space group $I4/mmm$ (139) [11].

The positions of the heavy atoms were found by direct methods (SHELXS)[12] and subsequent Rietveld refinements RIET94 [13–14] and FULLPROF [15] based on X-ray and neutron powder patterns of $NaGa_2Al_2$ gave the atomic coordinates listed in Table 2. The final Rietveld R-values were: $R_B = 2.5\%$, $R_F = 3.0\%$, $R_{WP} = 6.1\%$, $S = 1.2$. (cf. Fig. 2).

The adjustable parameters a, c and z_{Ga} for this structure type compare well with those of $BaMg_2Si_2$ [16] with the coordination polyhedra locating aluminum in a tetrahedral site of Ga atoms and the large Na atom in a 16-fold coordination polyhedron, the dimensions of which are defined by the Ga–Ga and Al–Ga contacts. The Ga atoms are located in a square anti-prism [Al_2–Ga_2]. The dimensions of this anti-prism are directly related to the cell parameters with the height of the Ga atom defined by the free parameter z_{Ga} Fig. 1.

Table 2
Crystallographic parameters for $NaGa_2Al_2$ in space group $I4/mmm$ (139) and $Z = 2$.

Atoms	Site	Metal atom position			$B_{ISO}(Å)^2$	*Occ*
		x	y	z		
Na	*2a*	0	0	0	1.4(1)	1
Ga1	*4e*	0	0	0.3912(1)	1.10(1)	1
Al	*4d*	0	1/2	1/4	0.62(1)	0.92
Ga2	*4d*	0	1/2	1/4	0.62(1)	0.08

Bragg RB = 2.5%, R–F = 3.0%, R–WP = 6.1%, S = 1.2.

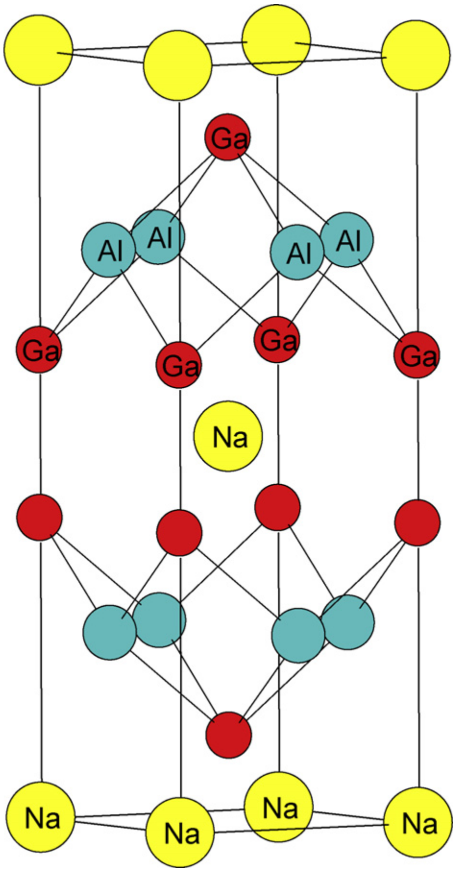

Fig. 1. Crystal structure of $NaGa_2Al_2$ intermetallic compound, in $ThCr_2Si_2$ type.

A comparison of I_{obs} with I_{cal} for $NaGa_2Al_2$ (see Table 1) is leading to the conclusion of a fully ordered atom distribution of all components (see also Table 2). No remaining scattering density was observed in Fourier maps calculated from the observed intensities obtained after the final refinements indicating that deuterium was not absorbed Fig. 2.

According to data in Table 3, the inter-atomic distances Na–(Al,Ga) and Ga–Al are slightly longer than in the same type of structure like $CeAl_2Ga_2$ where, Ce–Al and Ga–Al distances are 3.45 Å and 2.58 Å respectively.

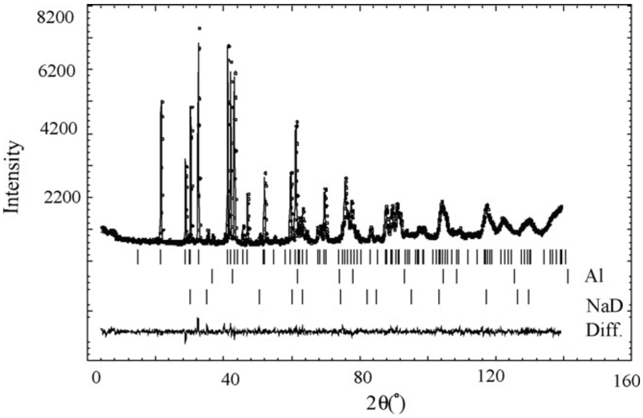

Fig. 2. Rietveld fitted profile and difference plot for $NaGa_2Al_2$. The neutron diffraction data is obtained at room temperature with a wavelength = 1.47 Å. The refined weight percentage are from the top 98% for $NaGa_2Al_2$ and below the impurity phases are less than 1% for Al and NaD respectively.

Table 3
Inter-atomic distances and unit cell dimensions in (Å) of $NaGa_2Al_2$ compared to compounds with the $ThCr_2Si_2$ type structure.

Formula	Unit cell (Å)	Metal-distance(Å)	*c/a*	*V* (Å^3)	Reference
$NaGa_2Al_2$	*a* = 4.1817(5)			199	
	c = 11.388(2)		2.7		
Na–Ga1	3.2060(3)				
Na–(Al,Ga2)	3.5323(4)				
Ga1–Ga1	2.4778(4)				
Ga1–Al	2.6377(3)				
Al–(Al,Ga2)	2.9569(4)				
$CaGa_2Al_2$	*a* = 4.278(1)			202	[5]
	c = 11.015(2)		2.57		
Ca–Ga1		3.268			
Ca–(Al,Ga2)		3.487			
Ga1–Ga1		2.475			
Ga1–Al		2.622			
Al–(Al,Ga2)		3.025			
$CeGa_2Al_2$	*a* = 4.203(3)			194	[6]
	c = 10.955(2)		2.6		
Ce–Ga1		3.219			
Ce–(Al,Ga2)		3.452			
Ga1–Ga1		2.476			
Ga1–Al		2.582			
Al–(Al,Ga2)		2.972			

We also performed a differential thermal analysis (DTA) scan up to 773 K under Ar gas atmosphere, whereby no enthalpy change was observed, which could indicate release of hydrogen or a structural phase transformation. This indicates that $NaGa_2Al_2$ is rather stable intermetallic compound that is not willing to absorb hydrogen. This is also understandable with respect to the limited numbers of electrons that can be donated from the single Na atom to the Al–Ga polyhedra. The existence of this stable non-hydrogen absorbing phase will also be limiting for the search of new quaternary hydrides when trying to modify alanates by Ga additions.

4. Conclusion

In this study we have shown that $NaAl_2Ga_2$ can easily be produced by sintering Na or NaH with Ga and Al metals in a 1:2:2 atomic ratio. Also if the initial composition of the reactants varied around this ratio, the 1:2:2 compound easily formed and always with the same unit cell axes lengths. The $NaAl_2Ga_2$ showed no reaction with hydrogen gas up to 5 MPa pressures at temperatures between room temperature up to 723 K.

Although the inter-atomic distances Na–Al and Ga–Al are slightly long they are comparable to a number of compounds with similar structure type and without transition metal that has been reported to crystallize in the same type of structure like $CaAl_2Ga_2$ and $CeAl_2Ga_2$. No disproportion or phase transformation of the alloy was observed by X-ray diffraction after differential thermal analysis up to 773 K under Ar gas atmosphere. All this taken together indicate that $NaAl_2Ga_2$ is a fairly stable ternary compound, the existence of which will create difficulties to attempts to improve hydrogen storage properties of $NaAlH_4/Na_3AlH_6$ by gallium doping.

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