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Thermodynamical stability and electronic structure of a perovskite-type hydride, $NaMgH_3$

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Abstract

Thermodynamical stability and electronic structure of a perovskite-type hydride, $NaMgH_3$, exhibiting reversible decomposition and recombination reactions, were studied experimentally. $NaMgH_3$ decomposes in two steps accompanying hydrogen desorption reactions, and the enthalpy change (ΔH) and the entropy change (ΔS) are calculated to be $\Delta H_{(1)} = -93.9(6)$ kJ/mol H_2 and $\Delta S_{(1)} = -116.2(9)$ J/K mol H_2 for the first step, and $\Delta H_{(2)} = -102.2(4)$ kJ/mol H_2 and $\Delta S_{(2)} = -125.9(6)$ J/K mol H_2 for the second step, respectively. Maximum entropy method (MEM)/Rietveld analysis of synchrotron X-ray diffraction profiles indicated that $NaMgH_3$ contains two hydrogen anions at the different occupation sites.

Keywords: Hydrogen storage materials; Mechanical alloying; Crystal structure and symmetry; Synchrotron radiation; X-ray diffraction

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1. Introduction

Some ternary hydrides exhibit the perovskite structures expressed as ABH_3, where A and B are monovalent and divalent cations, respectively. The formation abilities of perovskite-type hydrides have been explained on the basis of the geometric factors for the ions at the octahedral and cubo-octahedral sites in the perovskite structure [1,2], as shown by the quadrilateral region in Fig. 1. The Goldschmidt tolerance factors range from $t = 0.9$–1.0, assuming a radius of 0.140 nm for hydrogen anion [1–3] and using the Shannon effective ionic radii [4]. In fact (inverse) perovskite structures have been reported for $NaMgH_3$, $KMgH_3$, $RbCaH_3$, $CsCaH_3$, $SrLiH_3$, $BaLiH_3$, $CaCoH_3$ and $CaNiH_3$ [1–3,5–10], as represented by the closed circles in the region indicated in Fig. 1.

We are interested in light-weight hydrides with perovskite-type structures as possible hydrogen storage materials [1,2,5,6]. So far, we reported the reversible hydrogen desorption/absorption reactions in $NaMgH_3$ from the hydrogen pressure–composition (p–c) isotherm at 673 K and the X-ray diffraction profiles [6]. The decomposition reaction of $NaMgH_3$, accompanying the desorption reaction with approximately 6.0 mass% of hydrogen, proceeds in the following two steps:

$$NaMgH_3 \rightarrow NaH + Mg + H_2 + \Delta H_{(1)} \tag{1}$$

$$NaH + Mg + H_2 \rightarrow Na + Mg + 3/2H_2 + \Delta H_{(2)} \tag{2}$$

Here, $\Delta H_{(1)}$ and $\Delta H_{(2)}$ are the enthalpy changes in the reactions (1) and (2), respectively.

For achieving the further development of the perovskite-type hydrides as possible hydrogen storage materials, more detailed studies from the fundamental point of view are necessary. In order to clarify the fundamental properties of the perovskite-type hydride, $NaMgH_3$, we examine both the thermodynamical stability of the hydrides by measuring the p–c isotherms at three different temperatures, and also the electronic structure by analysing synchrotron radiation X-ray diffraction profiles.

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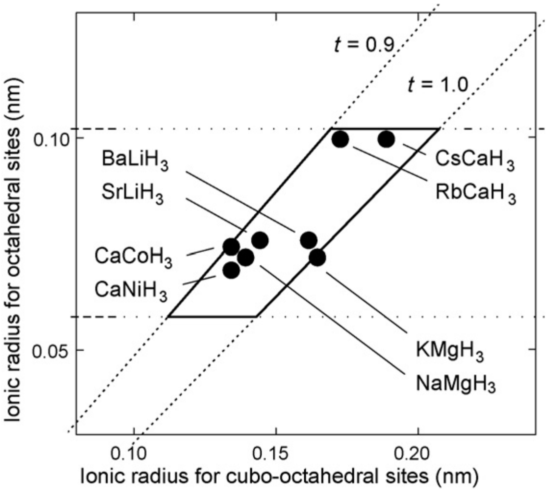

Fig. 1. Formation abilities of the perovskite-type hydrides using the Goldschmidt tolerance factors [1,2]. The quadrilateral region represents the ionic radii of octahedral and cubo-octahedral sites, suggesting the formation region of the (inverse) perovskite-type hydrides.

2. Experimental procedure

Powders of NaH (95% purity) and MgH_2 (90% purity and 10% Mg) were purchased from Sigma–Aldrich Inc., as starting materials. The mixture weighing approximately 300 mg was mechanically milled to obtain $NaMgH_3$ by planetary ball milling with 20 steel balls (7 mm in diameter) in a hardened steel vial (30 cm^3 in volume) for 20 h at 1 MPa of hydrogen at ambient temperature.

The *p*–*c* isotherm measurements of the as-milled sample were carried out in desorption process at 653, 673 and 693 K.

The as-milled sample was then heat-treated for 3 h at 5 MPa of hydrogen at 673 K, for obtaining the sample with larger crystallite sizes and less lattice strains. The sample powders of less than 75 μm were put into glass capillaries (0.2 mm in diameter). The synchrotron radiation X-ray diffraction measurements were carried out at the beam-line BL19B2 in SPring-8. The atomistic and electronic structures were analysed by maximum entropy method (MEM)/Rietveld method [11], using computer programs RIETAN-2000 [12] and PRIMA [13].

The samples were always handled in a glove box filled with purified argon (dew point below 183 K), ensuring no exposure to air before and during the preparations/measurements.

3. Results and discussion

The *p*–*c* isotherms of the as-milled $NaMgH_3$ were measured at 653, 673 and 693 K, as shown in Fig. 2. Two plateau pressures were clearly observed in the hydrogen desorption reaction at each temperature. Two third of the desorbed hydrogen (about 4.0 mass%) is attributed to the reaction (1) and the rest (about 2.0 mass%) to the reaction (2) [6].

The enthalpy change, ΔH, and the entropy change, ΔS, in the reactions (1) and (2) were calculated by using the van't Hoff plot shown in Fig. 2 and summarised in Table 1. The values of $\Delta H_{(1)}$ and $\Delta H_{(2)}$ are −93.9(6) and −102.2(4) kJ/mol H_2 for the reactions (1) and (2), respectively. The former value is between the reported ones, −114.1 kJ/mol H_2 for NaH [14] and −74.5 kJ/mol H_2 for MgH_2 [15], and the latter value is comparable to the reported one for NaH. The values of $\Delta S_{(1)}$ and $\Delta S_{(2)}$ are −116.2(9) and −125.9(6) J/K mol H_2 for the reactions (1) and (2), respectively. These are comparable to the standard entropy of hydrogen, −130 J/K mol H_2, corresponding mostly to the change from molecular hydrogen gas to dissolved solid hydrogen in metal–hydrogen systems.

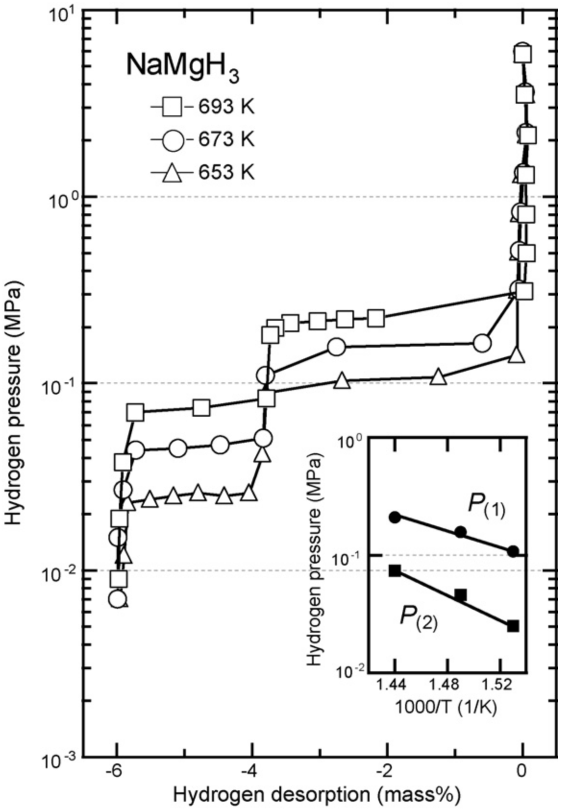

Fig. 2. Hydrogen pressure–composition (*p*–*c*) isotherm of $NaMgH_3$ in the hydrogen desorption process at 653, 673 and 693 K. Inset shows van't Hoff plot of $NaMgH_3$.

Next, we investigated occupation sites and ionicities of hydrogen in $NaMgH_3$. The X-ray diffraction profiles of $NaMgH_3$ analysed by the Rietveld method are shown in Fig. 3. The weighted profile reliability factor, R_{wp}, and the expected reliability factor, R_e, were 2.62 and 1.67% in the Rietveld analysis, respectively. This sample includes approximately 5.3 mass% of NaH and 9.3 mass% of MgH_2, both as the starting materials unreacted, and a small amount of amorphous-like MgO. The crystal structure of the main phase, $NaMgH_3$, was identified as

Table 1
Enthalpy change, ΔH, and entropy change, ΔS, in hydrogen desorption reactions of $NaMgH_3$

	$NaMgH_3$		NaH [13]	MgH_2 [14]	NaH + MgH_2 [7]
	Reaction (1)	Reaction (2)			Mixture
ΔH (kJ/mol H_2)	−93.9(6)	−102.2(4)	−114.1	−74.5	−87.7
ΔS (J/K mol H_2)	−116.2(9)	−125.9(6)	−164.4	−135.1	−154.6

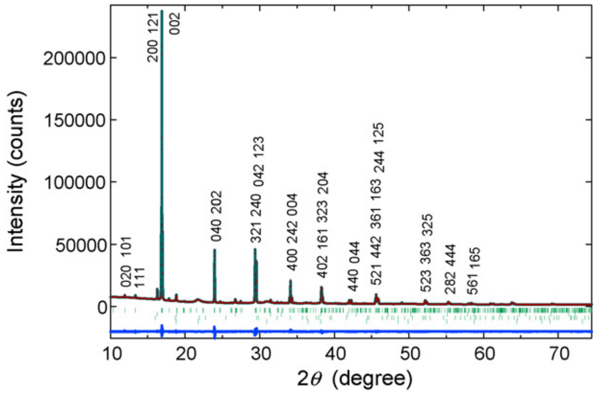

Fig. 3. The X-ray diffraction profiles of $NaMgH_3$ and the result obtained by Rietveld analysis in space group *Pnma* (no. 62). The X-ray diffraction profiles were measured with a 0.01° step from 10.0 to 75.0° in 2θ at room temperature by incident X-ray wavelength 0.0798 nm.

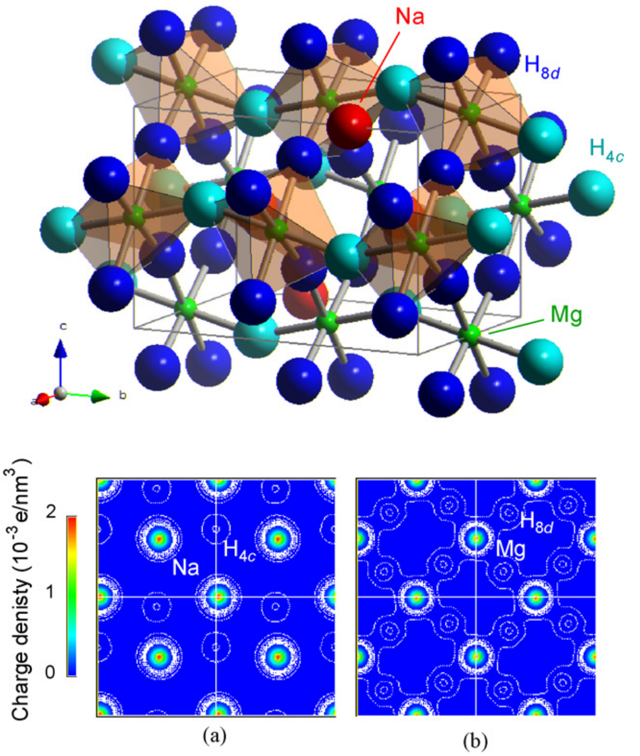

Fig. 4. Crystal structure and MEM charge density maps of $NaMgH_3$ at room temperature: (a) (0 4 0) plane and (b) (0 2 0) plane. The MEM charge density analysis was carried out in 108 × 152 × 108 pixels per orthorhombic lattice. The contour lines are drawn from 0.0 to 2.0 at 0.2×10^{-3} e/nm^3 intervals. These figures were drawn with VENUS developed by Dilanian and Izumi.

Table 3
Ionicities in $NaMgH_3$ refined by MEM analysis and references

	$NaMgH_3$	NaH [17]	MgH_2 [16]
Na	1.00+	0.99+[a]	–
Mg	1.97+	–	1.91+
H	0.23−, 0.13−	–	0.26−

[a] Theoretical calculation.

$GdFeO_3$-type structure [6,7], and the parameters are refined as listed in Table 2. We refer to hydrogen at tetrahedral 4*c*-site composed of 2Na2Mg and octahedral 8*d*-site composed of 4Na2Mg as H_{4c} and H_{8d}, respectively. H_{4c} and H_{8d} are the nearest neighbour hydrogen from Na and Mg, and they correspond to one third and two third of the total hydrogen in $NaMgH_3$, respectively.

The MEM charge density maps of (0 4 0) plane and (0 2 0) plane are shown in Fig. 4. The weighted reliable factor, R_{wf}, was 1.9% in Rietveld/MEM analysis. The charge density distributions of Na and Mg are localised within the sphere of the averaged radii, 0.105 and 0.090 nm, and most of the charge density distributions of H_{4c} and H_{8d} are located in the radii of 0.120 and 0.110 nm, respectively. By estimating the number of electrons within the Na, Mg, H_{4c} and H_{8d} region, the ionicities are expressed as $Na^{1.00+}$, $Mg^{1.97+}$, $H_{4c}^{0.23-}$ and $H_{8d}^{0.13-}$, respectively. Since these values are similar to $Na^{0.99+}$ in NaH [16] and $Mg^{1.91+}$ in MgH_2 [17] as shown in Table 3, Na and Mg in $NaMgH_3$ are almost ionised as Na^+ and Mg^{2+}. Moreover, H_{4c} and H_{8d} at the different occupation sites are suggested to be anions. By theoretical prediction using energy density analysis [18,19], the atomisation energies for H_{4c} and H_{8d} are 3.10 and 2.84 eV in $NaMgH_3$, which are comparable to 2.96 eV for hydrogen in MgH_2. These values imply that the stabilities of H_{4c} and H_{8d} are almost same.

The fundamental properties of the perovskite-type hydride, $NaMgH_3$, obtained in the present study would be useful in devel-

Table 2
Atom sites in $NaMgH_3$ (*a*: 0.54596(2), *b*: 0.76982(4), *c*: 0.54086(2) nm) and $NaMgD_3$ (*a*: 0.5465(5), *b*: 0.7694(2), *c*: 0.5412(1) nm) [7] refined by Rietveld analysis in space group *Pnma* (no. 62)

	Atom	Site	*x*	*y*	*z*	*B*
This work	Na	4*b*	0.0213(4)	1/4[a]	0.0045(5)	1.77(1)
	Mg	4*c*	0[a]	0[a]	1/2[a]	0.84(1)
	H_{4c}	4*c*	−0.004(4)	1/4[a]	0.606(3)	5.0[a]
	H_{8d}	8*d*	0.256(10)	−0.002(7)	0.779(6)	5.0[a]
Rönnebro et al. [7]	Na	4*b*	0.015(2)	1/4	−0.018(2)	1.1(7)
	Mg	4*c*	0	0	1/2	3(1)
	H_{4c}	4*c*	0.064(1)	1/4	0.483(1)	2.9(8)
	H_{8d}	8*d*	0.292(1)	0.040(1)	0.708(1)	2.9(8)

The estimated standard deviations are shown in parentheses.
[a] Fixed in the Rietveld refinement.

oping the related perovskite-type hydrides as a new family of light-weight hydrogen storage materials.

4. Summary

Thermodynamical stability and electronic structure were investigated by the *p*–*c* isotherms of and charge density distributions in the perovskite-type hydride, $NaMgH_3$. Decomposition reaction of $NaMgH_3$, accompanying desorption reaction with approximately 6.0 mass% of hydrogen, proceeds in two steps. The enthalpy changes, $\Delta H_{(1)}$ and $\Delta H_{(2)}$, are calculated to be $-93.9(6)$ and $-102.2(4)$ kJ/mol H_2, and the entropy changes, $\Delta S_{(1)}$ and $\Delta S_{(2)}$, to be $-116.2(9)$ and $-125.9(6)$ J/K mol H_2, for the first and the second step reactions, respectively. The charge density distributions indicated that $NaMgH_3$ contains two hydrogen anions at the different occupation sites.

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