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Tetracalcium trimagnesium tetradecahydride, $Ca_4Mg_3H_{14}$: the first ternary alkaline earth hydride

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Abstract

The title compound and its deuteride, $Ca_4Mg_3D_{14}$, were prepared from CaMg alloy at 410(10) °C (deuteride: 458(8) °C) under 53(3) bar hydrogen (95(5) bar deuterium) pressure and characterized by X-ray and neutron powder diffraction. The compound crystallizes with a new hexagonal structure type (space group $P\bar{6}2m$ (No. 189); lattice parameters at 20 °C: $a=6.3056(2)$ Å, $c=6.8820(2)$ Å (hydride), $a=6.2902(2)$ Å, $c=6.8540(3)$ Å (deuteride), $Z=1$) which contains an ordered array of four symmetry-independent deuterium atoms having respectively tetrahedral (D1: [3Ca, 1Mg]; D2: [4Ca]), trigonal bipyramidal (D3: [2Ca, 3Mg]) and triangular (D4: [3Mg]) metal coordinations. The metal–deuterium bond distances range from 1.85 to 2.44 Å (Mg–D) and from 2.29 to 2.48 Å (Ca–D).

1. Introduction

During the synthesis of quaternary transition metal hydrides containing two alkaline earth elements [1–3], we have observed evidence for the formation of a ternary alkaline earth hydride phase of reported composition "$MgCaH_{3.72}$" [4]. In this paper we report on the structural characterization of this compound. Its correct chemical formula is $Ca_4Mg_3H_{14}$. It crystallizes with a new hexagonal structure type which combines structural features of the binary hydrides MgH_2 and CaH_2. $Ca_4Mg_3H_{14}$ is the first structurally characterized ternary alkaline earth hydride. Ternary hydrides based on alkaline and alkaline earth elements have been known for some time. Examples are $BaLiD_3$ [5] and $Rb_4Mg_3H_{10}$ [6].

2. Experimental details

2.1. *Synthesis*

Binary CaMg alloys were prepared by induction melting of 1:1 mixtures of the elements (calcium: CERAC, −4 mesh, 99.5%; magnesium: CERAC,

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$\frac{1}{8}$ inch, 99.99%). The two-phase samples ($CaMg_2$, calcium) were powdered in an argon-filled glove-box and placed in a high temperature, high pressure autoclave. After evacuating to 10^{-5} bar and flushing with argon, the autoclave was charged with hydrogen gas to an initial pressure of 35 bar. During heating at 420 °C the hydrogen pressure increased to 55 bar. After 6 days at a temperature of 410(10) °C and a hydrogen pressure of 53(3) bar, the autoclave was cooled to room temperature and opened in an argon-filled glove-box. For the preparation of the deuteride samples the reaction was kept at 458(8) °C and a deuterium pressure of 95(5) bar for 7 days. The final products are light grey in colour and sensitive to air.

Attempts were also made to synthesize the ternary hydride from 1:1 mixtures of the binary hydrides (465(5) °C, 97(3) bar hydrogen, 5 days). However, the samples obtained by this method contained more impurity phases than products synthesized by alloy hydrogenation under the same conditions and thus were not further investigated.

2.2. *X-ray diffraction*

The hydride samples were characterized by X-ray powder diffraction at room temperature (Guinier camera, Cu $K\alpha_1$ radiation, sealed capillaries; Guinier diffractometer [7], using silicon as external standard ($a = 5.4308$ Å)). The patterns showed a new phase and small quantities of CaH_2, MgH_2 and magnesium as impurity phases. The positions and intensities of the main phase peaks were in good agreement with the pattern reported for "$CaMgH_{3.72}$" (hexagonal lattice with cell parameters $a = 6.300(1)$ Å, $c = 6.882(1)$ Å [4]). There were no systematic absences. The metal atom substructure was solved from a Patterson map calculated with XTAL [8] in the space group $P6/mmm$ (No. 191) [9]. A preliminary structure model based on two symmetry-independent calcium sites and one magnesium site as refined by the Rietveld method [10] converged at the residuals $R_B = 14.2\%$ and $R_F = 16.6\%$. However, subsequent neutron diffraction experiments showed (see below) that the true space group symmetry was $P\bar{6}2m$ (No. 189) [9]. Thus the Mg atom was allowed to shift away from the position ($\frac{1}{2}$,0,0) to 0.5489(6),0,0), giving a better fit of $R_B = 10.8\%$ and $R_F = 12.8\%$. The observed, calculated and difference X-ray patterns are shown in Fig. 1. The low-temperature X-ray pattern of the deuteride sample ($T = 8$ K; $a = 6.2857(2)$ Å, $c = 6.8706(3)$ Å) showed no evidence for a structural phase transition.

2.3. *Neutron diffraction*

The distribution of hydrogen atoms in the structure was established from a deuterated sample by neutron powder diffraction on the DMC powder diffractometer [11] at the reactor SAPHIR at PSI Villigen (Ge(311) monochromator, $\lambda = 1.7008$ Å, angular range 3.0°–134.8°, angular step $\Delta(2\theta) = 0.1°$, $(\sin\theta/\lambda)_{max} = 0.543$ Å^{-1}, $T = 20$ °C). The sample (2 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and measured in the high-intensity mode for 14 h. The transmission factor was measured ($\mu R = 0.097$) and the data were corrected accordingly. Profile refinements

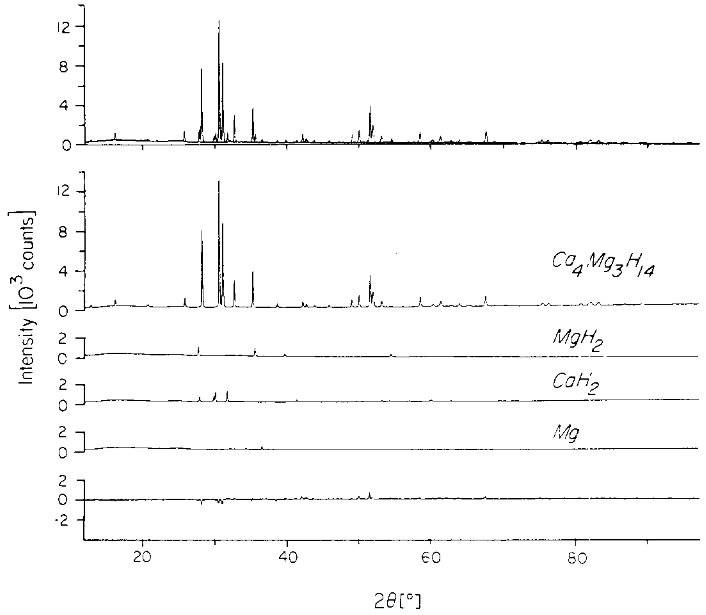

Fig. 1. Observed (top), calculated (middle) and difference (bottom) X-ray patterns of $Ca_4Mg_3H_{14}$ containing CaH_2, MgH_2 and magnesium impurity phases; Cu $K\alpha_1$ radiation.

TABLE 1

Refinement results on neutron diffraction data for $Ca_4Mg_3D_{14}$ ($T = 20$ °C; estimated standard deviations in parentheses)

Atom	Site	x	y	z	B_{iso} (Å^2)
Ca1	2*e*	0	0	0.2684(7)	1.05(4)
Ca2	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	B_{Ca1}
Mg	3*f*	0.5519(4)	0	0	0.85(5)
D1	6*i*	0.6103(2)	0	0.2748(2)	2.08(3)
D2	3*g*	0.2619(4)	0	$\frac{1}{2}$	B_{D1}
D3	3*f*	0.2296(5)	0	0	B_{D1}
D4	2*c*	$\frac{1}{3}$	$\frac{2}{3}$	0	B_{D1}

Space group $P\bar{6}2m$ (No. 189).
Cell parameters: $a = 6.2902(2)$ Å, $c = 6.8540(3)$ Å.
$R_B = 3.4\%$, $R_P = 2.3\%$, $R_{wp} = 3.0\%$, $R_{exp} = 1.2\%$ for 79 reflections.
Form of the temperature factor: $T = \exp[-B_{iso}(\sin^2\theta/\lambda^2)]$.

were performed by using the programme DBW3.2S [10] modified for simultaneous treatment of several phases. The structures of four phases were refined: the ternary deuteride $Ca_4Mg_3D_{14}$ with four symmetry-independent deuterium sites, binary MgD_2 [12], binary CaD_2 [13] and MgO. The following 32 parameters were allowed to vary: four scale factors, three peak width parameters, the theta zero position, eight cell parameters ($Ca_4Mg_3D_{14}$: two; MgD_2: two; CaD_2: three; MgO: one) and 16 atomic parameters ($Ca_4Mg_3D_{14}$:

TABLE 2

Interatomic distances (Å) shorter than 3 Å for $Ca_4Mg_3D_{14}$ (estimated standard deviations in parentheses)

Ca1–3 D2	2.287(4)	D2–2 Ca1	2.287(4)
3 D3	2.339(4)	2 Ca2	2.354(3)
3 D1	2.452(2)	4 D1	2.658(3)
		2 D1	2.681(2)
Ca2–3 D2	2.354(3)	2 D2	2.854(3)
6 D1	2.482(2)		
		D3– Mg	2.027(5)
Mg–2 D4	1.845(5)	2 Ca1	2.339(4)
2 D1	1.919(1)	2 Mg	2.441(2)
D3	2.027(5)	2 D4	2.481(3)
2 D3	2.441(2)	2 D3	2.502(4)
		4 D1	2.846(1)
D1– Mg	1.919(1)		
Ca1	2.452(2)	D4–3 Mg	1.845(5)
2 Ca2	2.482(2)	3 D3	2.481(3)
2 D2	2.658(3)	6 D1	2.707(2)
D2	2.681(2)		
2 D4	2.707(2)		
2 D3	2.846(1)		

13 positional, three isotropic displacement parameters). Preliminary refinements showed that the occupancy factors of the four deuterium sites did not differ significantly from 100%. Thus they were fixed at unity in the final refinement. Results are summarized in Table 1. Bond distances and a list of deuterium–deuterium contact distances are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 2.

3. Results and discussion

The ternary deuteride $Ca_4Mg_3D_{14}$ is identical to the hexagonal "$MgCaH_{3.72}$" phase reported in 1978 by Japanese workers [4]. Its structure combines features of the binary deuterides CaD_2 and MgD_2. Both calcium atoms have tricapped trigonal prismatic deuterium coordinations. One of the deuterium atoms (D2) has tetrahedral calcium coordination similar to that in CaD_2 ($PbCl_2$-type structure), whereas another deuterium atom (D4) has triangular magnesium coordination similar to that in MgD_2 (rutile-type structure). The remaining deuterium atoms have tetrahedral (D1) and trigonal bipyramidal (D3) metal coordinations, whereas magnesium has pentagonal bipyramidal deuterium coordination. The bond distances, [Mg–D] = 1.85–2.44 Å, [Ca–D] = 2.29–2.48 Å, and shortest deuterium–deuterium contact distances, [D–D] = 2.48 Å, are consistent with those in the binary deuterides (CaD_2:[Ca–D] = 2.24 Å, [D–D] = 2.66 Å [13]; MgD_2:[Mg–D] = 1.95 Å, [D–D] = 2.47 Å [12]) and those observed in ternary deuteride structures [14].

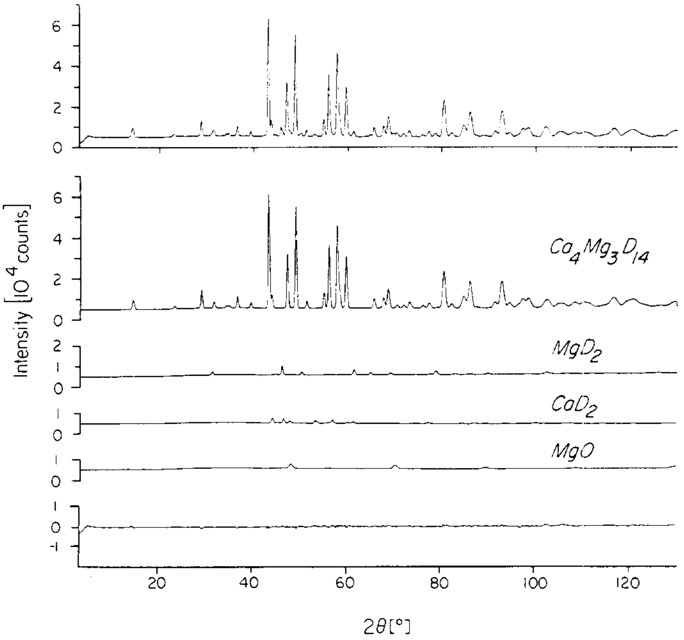

Fig. 2. Observed (top), calculated (middle) and difference (bottom) neutron patterns of $Ca_4Mg_3D_{14}$ containing CaD_2, MgD_2 and MgO impurity phases; $\lambda = 1.7008$ Å.

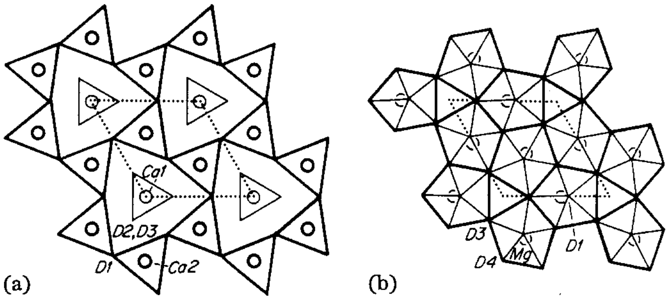

Fig. 3. Deuterium coordination polyhedra around the metal atoms in hexagonal $Ca_4Mg_3D_{14}$, projected along [0001]: (a) tricapped trigonal prisms around Ca1 (thin lines) and Ca2 (thick lines); (b) pentagonal bipyramids around Mg. Ca1 in $z = 0.27$, Ca2 in $z = \frac{1}{2}$, Mg in $z = 0$, D1 in $z = 0.27$, D2 in $z = \frac{1}{2}$, D3 and D4 in $z = 0$.

The arrangement of the deuterium coordination polyhedra around the metal atoms in $Ca_4Mg_3D_{14}$ is shown in Fig. 3. The Ca2-centred tricapped trigonal prisms share edges along the prism axis (D1), thus forming open nets which run parallel to the hexagonal base (thick lines in Fig. 3(a)), whereas those around Ca1 share triangular faces (D2, D3), thus forming columns along [0001] (thin lines in Fig. 3(a)). The magnesium-centred pentagonal bipyramids (Fig. 3(b)) share four base edges with each other, whereas the fifth is shared with a base of the Ca1-centred tricapped trigonal prisms. The apices of the pentagonal bipyramids (D1) form the triangular faces of the Ca2-centred tricapped trigonal prisms.

The existence of $Ca_4Mg_3D_{14}$ is an important step towards the synthesis of new quaternary transition metal hydrides of interest for hydrogen storage.

Acknowledgments

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