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High-pressure synthesis and crystal structures of new ternary caesium magnesium hydrides, $CsMgH_3$, $Cs_4Mg_3H_{10}$ and Cs_2MgH_4

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Abstract

The title compounds were synthesized by heating stoichiometric mixtures of the binary hydrides (deuterides) to 820 K in a multi-anvil press at 30 kbar pressure. X-ray and neutron powder diffraction on the deuterides at ambient conditions indicates rhombohedral symmetry for $CsMgH_3$ (space group *R-3m*, $a=6.2521(6)$, $c=22.382(3)$ Å, $BaRuO_3$ type structure), orthorhombic symmetry for $Cs_4Mg_3H_{10}$ (*Cmca*, $a=6.2569(9)$, $b=14.743(2)$, $c=13.791(2)$ Å, $Cs_4Mg_3F_{10}$ type structure), and tetragonal symmetry for Cs_2MgH_4 (*I4/mmm*, $a=4.3264(5)$, $c=14.760(2)$ Å, K_2NiF_4 type structure). The compounds contain octahedral $[MgH_6]^{4-}$ anions and have considerably better volume efficiencies for hydrogen storage than those containing tetrahedral $[MgH_4]^{2-}$ anions that are synthesised under hydrogen gas pressure.

Keywords: $CsMgH_3$; $Cs_4Mg_3H_{10}$; Cs_2MgH_4; High-pressure phase; Caesium magnesium hydrides; Neutron powder diffraction; Crystal structure

1. Introduction

The Cs–Mg–H system contains two known ternary hydride phases, Cs_2MgH_4 [1] and Cs_3MgH_5 [2]. The compounds were synthesized at relatively low hydrogen gas pressures (typically 100 bar) and found [3] to crystallise with the orthorhombic β-K_2SO_4 and the tetragonal Cs_3CoCl_5 type structures, respectively. Both compounds are saltlike and contain tetrahedral $[MgH_4]^{2-}$ anions. In this work we show that at least three more ternary hydride phases can be stabilised in this system by application of hydrostatic pressure. Their structures contain octahedral $[MgH_6]^{4-}$ anions and show considerably better volume efficiencies for hydrogen storage than those containing tetrahedral $[MgH_4]^{2-}$ anions.

2. Experimental

Samples were synthesized by heating mixtures of the binary hydrides (deuterides) at various stoichiometries ($CsH:MgH_2=2:1$, 1:1,1:2) up to 820 K in a multi-anvil press at 30 kbar for 180 min. The reaction products were white and pyrophoric. X-ray powder diffraction (Phillips PW 1820, CuKα radiation, sealed sample holder) showed the presence of at least three ternary hydride phases: $CsMgH_3$ having the trigonal $BaRuO_3$ type structure [4] (space group *R-3m*, four cation and two anion sites), $Cs_4Mg_3H_{10}$ having the orthorhombic $Cs_4Mg_3F_{10}$ type structure [5] (space group *Cmca*, four cation and four anion sites), and Cs_2MgH_4 having the tetragonal K_2NiF_4 type structure type (space group *I4/mmm*, two cation and two anion sites). The samples also contained unreacted CsH, α-MgH_2 and γ-MgH_2, and the impurity phase MgO. The ternary hydride phases always coexisted and neither one could be obtained as a single phase product. Attempts to obtain any one of them by solid state reaction under hydrogen gas pressure failed. The cation positions were refined by FULLPROF [6]. Neutron powder diffraction data were collected on two deuteride samples having molar ratios of $CsD:MgD_2=2:1$ (sample 1) and 1:1 (sample 2) on the high-resolution powder diffractometer HRPT [7] at SINQ (PSI-Villigen, $T=293$ K, sample 1: $\lambda=1.886$ Å, $2\theta_{max}=158.95°$, step size=0.05° in 2θ; sample 2: $\lambda=2.45$ Å, $2\theta_{max}=164.85°$, step size=0.1°). Sample 1 contained as majority phases $Cs_4Mg_3D_{10}$ and Cs_2MgD_4 for which the structures were refined by taking as starting parameters the

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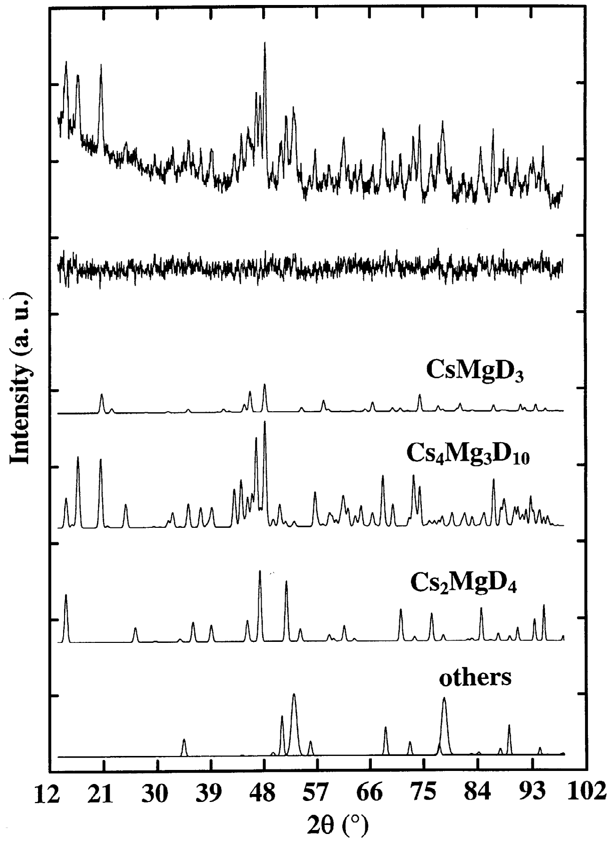

Fig. 1. Observed (top), difference (middle) and calculated (bottom) neutron powder diffraction patterns for sample 1 (nominal Cs/Mg=2), λ=1.886 Å.

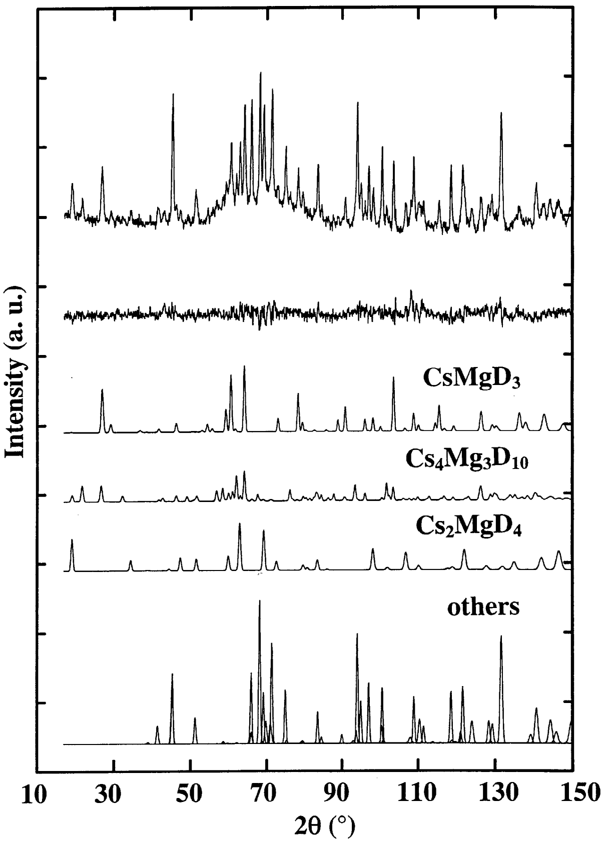

Fig. 2. Observed (top), difference (middle) and calculated (bottom) neutron powder diffraction patterns for sample 2(nominal Cs/Mg=1), λ=2.45 Å.

metal positions obtained from the X-ray refinements and the anion positions reported for the fluoride analogue $Cs_4Mg_3F_{10}$ [5] and the isostructural deuteride Cs_2CaD_4 [8], respectively. The sample also contained small amounts of $CsMgD_3$, MgD_2 and MgO. For $CsMgD_3$, the anion positions of the $BaRuO_3$ type structure were taken as starting parameters for deuterium. The following 40 parameters were allowed to vary: one zero correction, six background, five scale factor, three profile parameters, seven lattice parameters (two for $CsMgD_3$, three for $Cs_4Mg_3D_{10}$, two for Cs_2MgD_4), eighteen positional parameters (two for $CsMgD_3$, fourteen for $Cs_4Mg_3D_{10}$, two for Cs_2MgD_4). Sample 2 contained $CsMgD_3$, $Cs_4Mg_3D_{10}$ and Cs_2MgD_4 as majority phases, and CsD, MgD_2, γ-MgD_2, MgO and V (sample holder) as minority phases. For $CsMgD_3$ the previously refined atomic parameters were taken as starting values and for the other deuteride phases the parameters were fixed at those obtained during refinement of sample 1. A total of 29 parameters were allowed to vary: one zero correction, eight scale factors, eight profile parameters (three for the $CsMgD_3$ phase and five for the seven secondary phases), two lattice parame-

Table 1
Cell parameters[a], volume differences[b] and hydrogen densities

Ternary hydride and deuteride	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Δ*V* [b] (%)	Hydrogen density (g H_2 l^{-1}) (wt.%)
$CsMgH_3$	6.2521(6)	–	22.382(3)	757.7	−12.3	60.0 1.89
$CsMgD_3$	6.2337(2)	–	22.307(1)	750.7	−12.4	–
$Cs_4Mg_3H_{10}$	6.2569(9)	14.743(2)	13.791(2)	1272.1	−10.0	52.7 1.64
$Cs_4Mg_3D_{10}$	6.239(1)	14.712(2)	13.750(2)	1262.0	−10.0	–
Cs_2MgH_4	4.3264(5)	–	14.760(2)	276.3	−14.3	48.5 1.18
Cs_2MgD_4	4.3135(5)	–	14.726(3)	274.0	−14.3	–

[a] For hydrides from X-ray data, for deuterides from neutron data.

[b] Relative difference of the molar volume of the ternary hydrides (deuterides) as compared to the weighted sum of the molar volumes of the binary hydrides (deuterides).

Table 2
Refinement results on neutron powder diffraction data for $CsMgD_3$ (sample 2)

Atom	Site	*x*	*y*	*z*	B_{iso}
Cs1	6*c*	0	0	0.2111(15)	2.2(6)
Cs2	3*a*	0	0	0	2.2(6)
Mg1	6*c*	0	0	0.3760(15)	1.4(5)
Mg2	3*a*	0	0	1/2	1.4(5)
D1	18*h*	0.138(2)	2*x*	0.5596(7)	2.5(4)
D2	9*e*	1/2	0	0	3.7(6)

$T=293$ K; space group *R-3m* (No. 166); $Z=9$; e.s.d. values in parentheses; $R_B=12.2\%$; $R_p=3.4\%$; $R_{wp}=4.4\%$; $S=1.65$.

ters, four positional parameters, and six isotropic temperature factors. The observed, calculated and difference neutron powder diffraction patterns are shown in Figs. 1 and 2. Cell parameters are given in Table 1, refinement results are summarised in Tables 2–4 and selected interatomic distances are listed in Table 5.

3. Results and discussion

The present deuterides are high-pressure phases that do not form under ordinary gas pressure conditions. $CsMgD_3$ is the first deuteride known to crystallize with the trigonal $BaRuO_3$ type structure. While its calcium analogue $CsCaH_3$ [9] adopts the cubic perovskite type structure, its Rb analogue $RbMgH_3$ [9] adopts the 6H variant of the hexagonal perovskite type structure. $Cs_4Mg_3D_{10}$ is the second ternary hydride known to crystallize with the orthorhombic $Cs_4Mg_3F_{10}$ type structure, the other being the Rb analogue $Rb_4Mg_3D_{10}$ [10]. Cs_2MgD_4 crystallizes with the tetragonal K_2NiF_4 type structure, in contrast to its orthorhombic low-pressure polymorph that adopts the β-K_2SO_4 type structure. The only other isostructural deuteride known is the calcium analogue Cs_2CaD_4.

Table 3
Refinement results on neutron powder diffraction data for $Cs_4Mg_3D_{10}$ (sample 1)

Atom	site	*x*	*y*	*z*	B_{iso}
Cs1	8*f*	0	0.253(2)	0.397(2)	3.0
Cs2	8*f*	0	0.449(2)	0.138(2)	3.0
Mg1	8*f*	0	0.112(2)	0.157(2)	2.0
Mg2	4*a*	0	0	0	2.0
D1	16*g*	0.212(2)	0.104(2)	0.038(1)	4.0
D2	8*f*	0	0.250(2)	0.150(2)	4.0
D3	8*f*	0	0.474(2)	0.356(2)	4.0
D4	8*e*	1/4	0.101(2)	1/4	4.0

$T=293$ K; space group *Cmca* (No. 64); $Z=4$; e.s.d. values in parentheses; $R_B=10.8\%$; $R_p=1.9\%$; $R_{wp}=2.4\%$; $S=1.3$.

Table 4
Refinement results on neutron powder diffraction data for tetragonal Cs_2MgD_4 (sample 1)

Atom	site	*x*	*y*	*z*	B_{iso}
Cs	4*e*	0	0	0.358(2)	3.0
Mg	2*a*	0	0	0	2.0
D1	4*e*	0	0	0.137(2)	4.0
D2	4*c*	0	1/2	0	4.0

$T=293$ K; space group *I4/mmm* (No. 139), $Z=2$; e.s.d. values in parentheses; $R_B=11.2\%$, $R_p=1.9\%$; $R_{wp}=2.4\%$; $S=1.3$.

All high-pressure phases in the Cs–Mg–D system contain octahedral $[MgD_6]^{4-}$ anions, in contrast to the low-pressure phases that contain tetrahedral $[MgD_4]^{2-}$ anions. As shown in Fig. 3 the octahedra in $CsMgD_3$ and

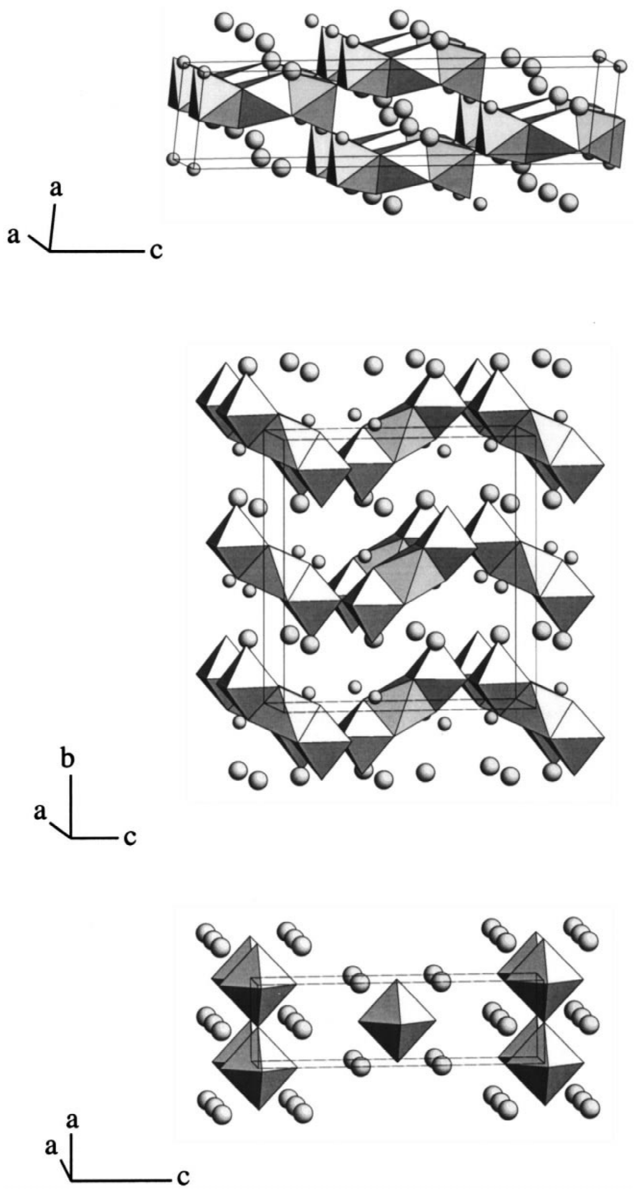

Fig. 3. Connectivity of magnesium centred deuterium octahedra in rhombohedral $CsMgD_3$ (top), orthorhombic $Cs_4Mg_3D_{10}$ (middle) and tetragonal Cs_2MgD_4 (bottom). Cs atoms shown as large (Cs1) and small (Cs2) circles.

Table 5
Selected interatomic distances (Å)[a]

$CsMgD_3$		$Cs_4Mg_3D_{10}$				Cs_2MgD_4	
Cs1–3D1	3.14(3)	Cs1–2D1	2.97(3)	D1–Mg2	2.08(2)	Cs–4D2	3.00(2)
6D1	3.15(2)	2D1	3.16(3)	Mg1	2.11(2)	4D1	3.051(1)
3D2	3.27(3)	2D2	3.185(8)	D1	2.65(2)	D1	3.26(3)
Mg1	3.68(5)	D3	3.31(4)	D3	2.74(3)	4Mg	3.70(1)
3Mg2	3.733(9)	2D4	3.39(3)	D4	2.93(1)	Cs	4.18(4)
3Cs1	4.11(2)	D2	3.39(4)	D2	2.96(3)	Mg–2D1	2.01(2)
Cs2–6D2	3.1171(2)	D2	3.48(4)	Cs1	2.97(3)	4D2	2.1568(2)
6D1	3.19(1)	2Mg1	3.82(2)	Cs2	3.11(3)	8Cs	3.70(1)
6Mg1	3.723(9)	2Cs1	4.22(3)	Cs1	3.16(3)	D1–Mg	2.01(2)
6Cs1	4.52(2)			Cs2	3.20(3)	4D2	2.95(2)
Mg1–3D1	2.04(2)	Cs2–D2	2.94(3)	D2–Mg1	2.03(3)	4Cs	3.051(1)
3D2	2.07(3)	D3	3.03(4)	Cs2	2.94(3)	Cs	3.26(3)
Mg2	2.77(3)	2D1	3.11(3)	2D1	2.96(3)	D2–2Mg	2.1568(2)
Cs1	3.68(5)	2D4	3.12(3)	2Cs1	3.185(8)	4D1	2.95(2)
Mg2–6D1	2.00(2)	2D3	3.142(4)	Cs1	3.39(4)	4Cs	3.00(2)
2Mg1	2.77(3)	2D1	3.20(3)	Cs1	3.48(4)		
6Cs1	3.733(9)	Mg1	3.70(4)				
D1–Mg2	2.00(1)	Cs2	4.07(4)				
Mg1	2.07(3)	Mg1–2D4	2.02(1)	D3–Mg2	2.01(3)		
2D1	2.58(2)	D2	2.03(3)	Mg1	2.03(3)		
2D2	2.91(2)	D3	2.03(3)	2D1	2.74(3)		
Cs1	3.14(3)	2D1	2.11(2)	2D4	2.83(3)		
2Cs1	3.15(2)	Mg2	2.72(2)	Cs2	3.03(4)		
Cs2	3.19(1)			2Cs2	3.142(4)		
D2–2Mg1	2.04(2)			Cs1	3.31(4)		
4D1	2.91(2)	Mg2–2D3	2.01(3)	D4–2Mg1	2.02(1)		
2Cs2	3.1171(2)	4D1	2.08(2)	2D3	2.83(3)		
2Cs1	3.27(3)	2Mg1	2.72(2)	2D1	2.93(1)		
				2Cs2	3.12(3)		
				2Cs1	3.39(3)		

[a] E.s.d. values in parentheses; D–D distances only shorter than 3 Å listed.

$Cs_4Mg_3D_{10}$ are joined by faces to trimers that are linked over corners to three-dimensional networks. In Cs_2MgD_4 the octahedra are joined by corners to two-dimensional slabs. As expected, the Mg–D bond distances in the octahedral anions of $CsMgD_3$ (2.04, 2.07 Å), $Cs_4Mg_3D_{10}$ (2.01–2.11 Å) and Cs_2MgD_4 (2.01, 2.16 Å) are longer than those in the tetrahedral $[MgD_4]^{2-}$ anions of Cs_3MgD_5 (1.84 Å) and the low-pressure modification of Cs_2MgD_4 (1.82–1.88 Å). Caesium is coordinated by up to twelve deuterium atoms at distances in the range 3.12–3.27 Å ($CsMgD_3$), 2.94–3.48 Å ($Cs_4Mg_3D_{10}$) and 3.00–3.26 Å (Cs_2MgD_4). The deuterium atoms occupy various more-or-less distorted octahedral holes in the metal atom networks and have always one or two magnesium atoms in their co-ordination sphere. All D–D distances are longer than 2.5 Å.

The molar volumes of the present high-pressure hydrides are lower by up to 14% compared to the weighted sums of the binary hydrides (see ΔV values in Table 1). The hydrides synthesised under lower (hydrogen gas) pressure generally show smaller (or no) volume contraction (Cs_3MgH_5: $\Delta V = -0.3\%$, orthorhombic Cs_2MgH_4: $\Delta V = +3.8\%$). As a consequence, the hydrogen densities in the high-pressure phases (see Table 1) are considerably higher than those in the low-pressure phases (for example 48 g H_2 l^{-1} for the high-pressure and 40 g H_2 l^{-1} for the low-pressure modification of Cs_2MgH_4).

Finally, the only fluorine analogue known among the present hydrides is orthorhombic $Cs_4Mg_3F_{10}$ [5]. Fluorine analogues for trigonal $CsMgH_3$ and tetragonal Cs_2MgH_4 are only known for divalent metal cations such as in $CsCoF_3$ [11], Cs_2AgF_4 [12] and Cs_2HgF_4 [13]. Previous studies on pressure effects in perovskite fluorides such as $CsMF_3$ (M=Mn, Fe, Co, Ni, Zn, Mg [14]) have shown that the proportion of cubic stacking in their structures increases with pressure and atomic size of M. For small divalent cations such as in $CsMgF_3$ only two stacking variants have been found as a function of pressure, one corresponding to the trigonal $BaRuO_3$ structure type (30–40 kbar) and the other to the 6H variant of the hexagonal perovskite structure type (>40 kbar). These findings suggest that the presently reported hydride $CsMgH_3$ could possibly have a second high-pressure polymorph.

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