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$Sr_6Mg_7H_{26}$, a new saline high-pressure hydride with $Ba_6Zn_7F_{26}$-type structure

B. Bertheville[a], H. Kohlmann[b], D. Sheptyakov[c], K. Yvon[a,*]

[a]Laboratoire de Cristallographie, Université de Genéve, 24 quai E. Ansermet, CH-1211 Genève 4, Switzerland
[b]High Pressure Science and Engineering Center, Department of Physics, University of Nevada, Las Vegas, NV, USA
[c]Laboratory for Neutron Scattering, ETH Zürich and PSI, CH-5232 Villigen PSI, Switzerland

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Abstract

$Sr_6Mg_7H_{26}$ and its deuteride have been synthesized at high pressure (25 kbar) and temperature (900 K) from mixtures of the corresponding binary hydrides (deuterides). Structure refinements on X-ray and neutron powder diffraction data show a monoclinic $Ba_6Zn_7F_{26}$ type structure (space group $I2/m$, $a=14.254(2)$ Å, $b=5.6711(4)$ Å, $c=11.575(1)$ Å, $\beta=90.59(1)°$, deuteride, $T=293$ K). The four magnesium atoms have nearly octahedral deuterium coordinations with average bond distances Mg–D = 1.97, 1.97, 1.96 and 1.85 Å. The three strontium sites have 10- and 11-fold deuterium coordination with average bond distances Sr–D = 2.66 (CN = 10), 2.71 (CN = 11) and 2.62 Å (CN = 10). The latter are longer by ~0.07 Å, on the average, than the corresponding Eu–D distances in the europium analogue, thus underlining the structural analogy between Sr- and Eu-based metal hydrides.

Keywords: Hydrogen storage materials; Crystal structure; Neutron diffraction; High pressure

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1. Introduction

A relatively large number of magnesium based ternary alkaline-earth hydrides have been reported in recent years (see Ref. [1] for a review). While many have favourable weight efficiencies most are thermally too stable for reversible hydrogen storage applications at room temperature. The first members of this family were synthesized by solid-state reactions under moderate hydrogen gas pressures (up to 100 bar). Later, high-pressure methods (multi-anvil cell producing quasi-hydrostatic pressures of up to 35 kbar) yielded further members such as cubic $Ca_{19}Mg_8H_{54}$ and trigonal Sr_2MgH_6, and closely related europium containing metal hydrides such as Eu_2MgH_6, $Eu_6Mg_7H_{26}$ and $Eu_2Mg_3H_{10}$. Given the similarity between the europium and strontium hydride chemistry it was of interest to re-investigate the Sr–Mg–H system for which a ternary hydride of composition $Sr_6Mg_7H_{26}$ had not been reported yet. In the following it will be shown that this compound can be stabilised by the application of very high pressure, thus representing the fourth ternary metal hydride known in the Sr–Mg–H system.

2. Experimental

2.1. Synthesis

Binary metal hydrides (deuterides) were synthesized from the elements (Sr: Aldrich, 99.9%, distilled pieces; Mg: Aldrich, 99.99%, powder) in an autoclave filled with hydrogen (deuterium) gas. The resulting powders were mixed at the molar ratio Mg/Sr = 2.5 (i.e. at an $MgH(D)_2$ excess compared to the stoichiometric composition Mg/Sr = 7/6) in an argon filled glove box and put into the high-pressure high-temperature multi-anvil cell (for details see Ref. [2]). The mixtures were heated to 900 K during 120 min under a quasi-hydrostatic pressure of 25 kbar and then quenched. The reaction products were of white colour and contained the new $Sr_6Mg_7H(D)_{26}$ phase together with other hydride (deuteride) phases. Binary powder mixtures having lower Mg contents (Mg/Sr = 2, 1.5, 1) led to

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*Corresponding author. Tel.: +41-22-702-6231; fax: +41-22-702-6864.
E-mail address: klaus.yvon@cryst.unige.ch (K. Yvon).

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reaction products that contained less or no $Sr_6Mg_7H(D)_{26}$ phase and more $Sr_2MgH(D)_6$ and $Sr_2Mg_3H(D)_{10}$ high pressure phases. In spite of several attempts the title compound could not be obtained as a single-phase product and a strong magnesium hydride (deuteride) excess was always necessary.

2.2. Structure analysis

The hydride and deuteride samples were first characterized by X-ray powder diffraction at room temperature on a Bragg–Brentano diffractometer (Philips PW1 820, Cu Kα radiation, sealed sample holder). Apart from the $Sr_6Mg_7H(D)_{26}$ phase the diffraction patterns showed the presence of two other ternary hydride (deuteride) phases, $Sr_2MgH(D)_6$ [3] and $Sr_2Mg_3H(D)_{10}$ [4] and of unreacted α-$MgH(D)_2$ and high-pressure γ-$MgH(D)_2$ [5]. The contribution of $Sr_6Mg_7H(D)_{26}$ was indexed on a monoclinic cell with refined cell parameters for the hydride of $a=14.295(9)$, $b=5.717(3)$, $c=11.574(6)$ Å, $\beta=90.55(4)°$. The diffraction intensities were consistent with a $Ba_6Zn_7F_{26}$ type structure (space group $I2/m$). The hydrogen positions were determined from neutron diffraction data collected on HRPT [6] at SINQ (PSI, Villigen, $\lambda=1.886$ Å, step size = 0.05° in 2θ, $T=293$ K, sample mass 1.35 g, cylindrical vanadium container having an inner diameter of 7 mm). Metal and deuterium atom positions were refined by FULLPROF [7], taking as starting parameters those recently reported for $Eu_6Mg_7D_{26}$ [8]. In view of the numerous phases present ($Sr_6Mg_7D_{26}$, $Sr_2Mg_3D_{10}$, Sr_2MgD_6, MgD_2, γ-MgD_2, SrD_2 and V-sample holder) the number of parameters to be refined was reduced by constraining some (profile, isotropic displacement parameters) to be equal for all phases and for atoms of the same kind. The following 54 parameters were allowed to vary: one zero position, seven scale factors, four cell parameters ($Sr_6Mg_7D_{26}$), 33 atomic positions ($Sr_6Mg_7D_{26}$), three thermal displacement and four peak shape and two asymmetry parameters. The observed, calculated and difference patterns are shown in Fig. 1, and refinement results and selected interatomic distances are summarised in Tables 1 and 2, respectively. Note that in spite of the relatively high Bragg residual ($R_B=12.5\%$) and the large estimated standard deviations (e.s.d.s) the profile fit is satisfactory ($R_P=3.5\%$) thus supporting the structure model.

2.3. Phase stability

The thermal stability of $Sr_6Mg_7H_{26}$ was investigated by heating multi-phase samples under hydrogen pressure in an autoclave. A phase analysis by X-ray diffraction performed after the experiment under ambient conditions suggests that the $Sr_6Mg_7H_{26}$ phase decomposes at 700 K and 30 bars hydrogen pressure into $SrMgH_4$ and SrH_2.

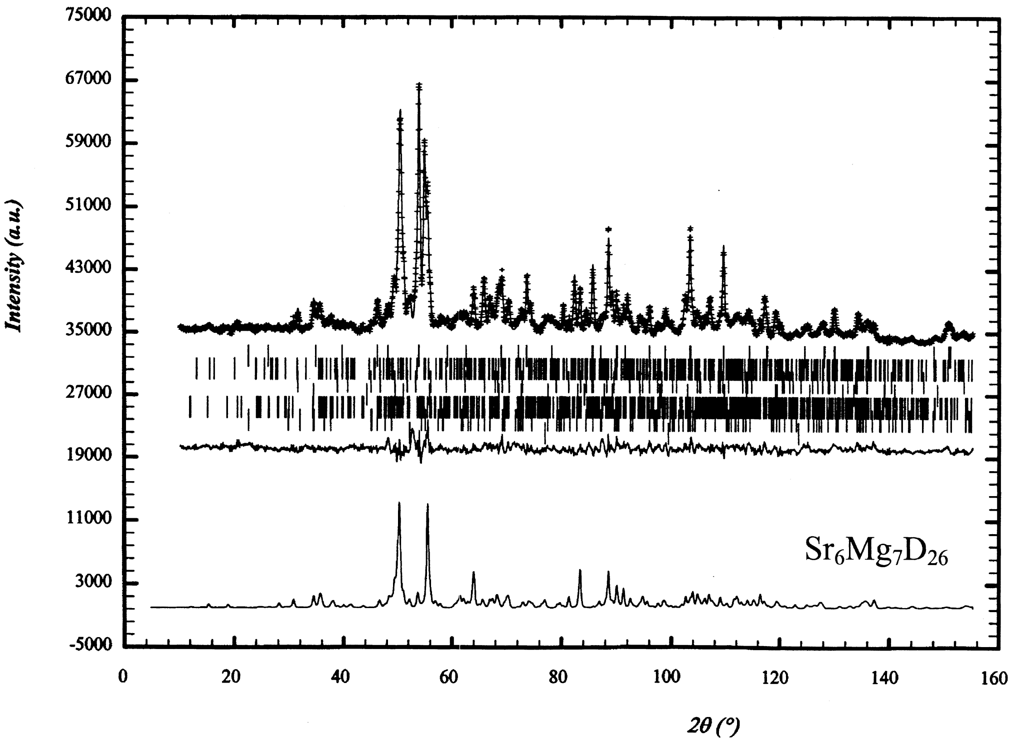

Fig. 1. Observed (+), calculated (solid lines) and difference (middle) neutron diffraction patterns for a $Sr_6Mg_7D_{26}$ containing sample ($T=293$ K, $\lambda=1.886$ Å). Bragg markers from top to bottom: Sr_2MgD_6, $Sr_2Mg_3D_{10}$, γ-MgD_2, MgD_2, $Sr_6Mg_7D_{26}$, SrD_2, V.

Table 1
Refinement results on neutron powder diffraction data for $Sr_6Mg_7D_{26}$

Atom	Site	x	y	z	B_{iso}(Å^2)
Sr1	4*i*	0.354(2)	0	0.267(2)	1.7(1)
Sr1′	4*i*	0.661(2)	0	0.254(3)	B_{iso}(Sr1)
Sr2	4*i*	0.855(2)	0	0.505(3)	B_{iso}(Sr1)
Mg1	4*i*	0.223(2)	0	0.015(4)	1.8(1)
Mg2	4*i*	0.998(3)	0	0.262(3)	B_{iso}(Mg1)
Mg3	4*g*	0	0.274(6)	0	B_{iso}(Mg1)
Mg4	2*c*	1/2	0	0	B_{iso}(Mg1)
D1	8*j*	0.241(2)	0.252(5)	0.124(2)	3.1(1)
D1′	8*j*	0.756(2)	0.233(5)	0.102(2)	B_{iso}(D1)
D2	8*j*	0.967(1)	0.263(5)	0.389(2)	B_{iso}(D1)
D3	8*j*	0.990(2)	0.281(4)	0.169(2)	B_{iso}(D1)
D4	4*i*	0.114(3)	0	0.284(3)	B_{iso}(D1)
D4′	4*i*	0.859(2)	0	0.280(3)	B_{iso}(D1)
D5	4*i*	0.594(2)	0	0.512(3)	B_{iso}(D1)
D6	4*i*	0.094(2)	0	0.003(3)	B_{iso}(D1)
D7	4*i*	0.382(2)	0	0.038(3)	B_{iso}(D1)

Space group: $I2/m$ (No. 12, non-standard setting); cell parameters: $a = 14.254(2)$ Å, $b = 5.6711(4)$ Å, $c = 11.575(1)$ Å, $\beta = 90.588(9)°$, $Z = 2$, e.s.d. values in parentheses. $R_B = 12.5\%$, $R_P = 3.5\%$, $R_{WP} = 4.4\%$, $S = 4.30$.

3. Results and discussion

$Sr_6Mg_7H_{26}$ crystallizes with the monoclinic $Ba_6Zn_7F_{26}$ type structure [9]. It is the fourth ternary metal hydride known in the Sr–Mg–H system (the others being $SrMgH_4$ [10], $Sr_2Mg_3H_{10}$ and Sr_2MgH_6) and the second that is stabilized by the application of high hydrostatic pressure (the other being Sr_2MgH_6). Its structure derives from the orthorhombic $Ba_6Mg_7H_{26}$ structure [11] by a small monoclinic lattice distortion ($\beta = 90.59°$) that is accompanied by drastic changes in the atomic environments, in particular with respect to the coordination numbers (CNs) and shapes of the coordination polyhedrons. As shown in Fig. 2 one of the barium sites (Ba1) having CN = 12 splits into two strontium sites (Sr1: CN = 10, Sr1′: CN = 11) having CN = 10 and 11, respectively, whereas the other barium site (Ba2) having CN = 12 transforms into a strontium site (Sr2) having CN = 10. As a result the geometries of the hydrogen coordinations around the Sr^{2+} sites in $Sr_6Mg_7H_{26}$ are very different from the cuboctahedral geometries found for the Ba^{2+} sites in $Ba_6Mg_7H_{26}$. The decrease of the CNs in the strontium compound compared to the barium compound is consistent with the smaller atomic size of Sr^{2+} compared to Ba^{2+}. A decrease in CNs due to atomic size effects has also been observed in monoclinic $Sr_2Mg_3H_{10}$ in which two Sr^{2+} sites have CN = 12 compared to the Ba sites in $Ba_2Mg_3H_{10}$ that have CN = 12 and 13 [12], and in $SrMgH_4$ in which Sr^{2+} has CN = 9 compared to Ba^{2+} in $BaMgH_4$ that has CN = 13 [13]. As to the four magnesium sites in $Sr_6Mg_7D_{26}$ they have nearly octahedral deuterium coordinations with average bond distances of Mg–D = 1.97 Å (Mg1, Mg2), 1.96 Å (Mg3) and 1.85 Å (Mg4).

Table 2
Selected interatomic distances (Å) in $Sr_6Mg_7D_{26}$ (estimated standard deviations in parenthesis)

Sr1–2D1	2.34(3)	Mg1–D6	1.84(4)	D1–Mg1	1.92(4)
2D3	2.65(4)	2D1′	1.92(4)	Sr1	2.34(3)
D5	2.66(5)	2D1	1.92(4)	Sr2	2.56(4)
D7	2.68(4)	D7	2.29(5)	Sr1	2.70(3)
2D1	2.70(3)		*Average 1.97*		
2D4	2.93(1)	Mg2–D4	1.67(5)	D1′–Mg1	1.92(4)
	Average 2.66	2D3	1.93(3)	Sr2	2.51(4)
Sr1′–2D1′	2.54(4)	D4′	1.99(5)	Sr1′	2.54(4)
2D1′	2.60(4)	2D2	2.14(4)	Sr1′	2.60(4)
2D3	2.64(4)		*Average 1.97*		
2D2	2.80(4)	Mg3–2D5	1.86(3)	D2–Mg4	1.91(3)
D4′	2.84(5)	2D3	1.97(2)	Mg2	2.57(4)
2D4′	2.88(1)	2D6	2.05(3)	Sr2	2.57(4)
	Average 2.71		*Average 1.96*	Sr1′	2.80(4)
Sr2–D4	2.48(5)				
2D1′	2.51(4)	Mg4–2D7	1.74(3)		
2D1	2.56(4)	4D2	1.91(3)	D3–Mg2	1.93(3)
2D2	2.57(4)		*Average 1.85*	Mg3	1.97(2)
D4′	2.61(5)	D4–Mg2	1.67(5)	Sr1′	2.64(4)
2D7	2.89(1)	Sr2	2.48(5)	Sr1	2.65(4)
	Average 2.62	2Sr1	2.93(1)		
				D4′–Mg2	1.99(5)
D5–2Mg3	1.86(3)	D6–Mg1	1.84(4)	Sr2	2.61(5)
Sr1	2.66(5)	2Mg3	2.05(3)	Sr1′	2.84(5)
				2Sr1′	2.88(1)
		D7–Mg4	1.74(3)		
		Mg1	2.29(5)		
		Sr1	2.68(4)		
		2Sr2	2.89(1)		

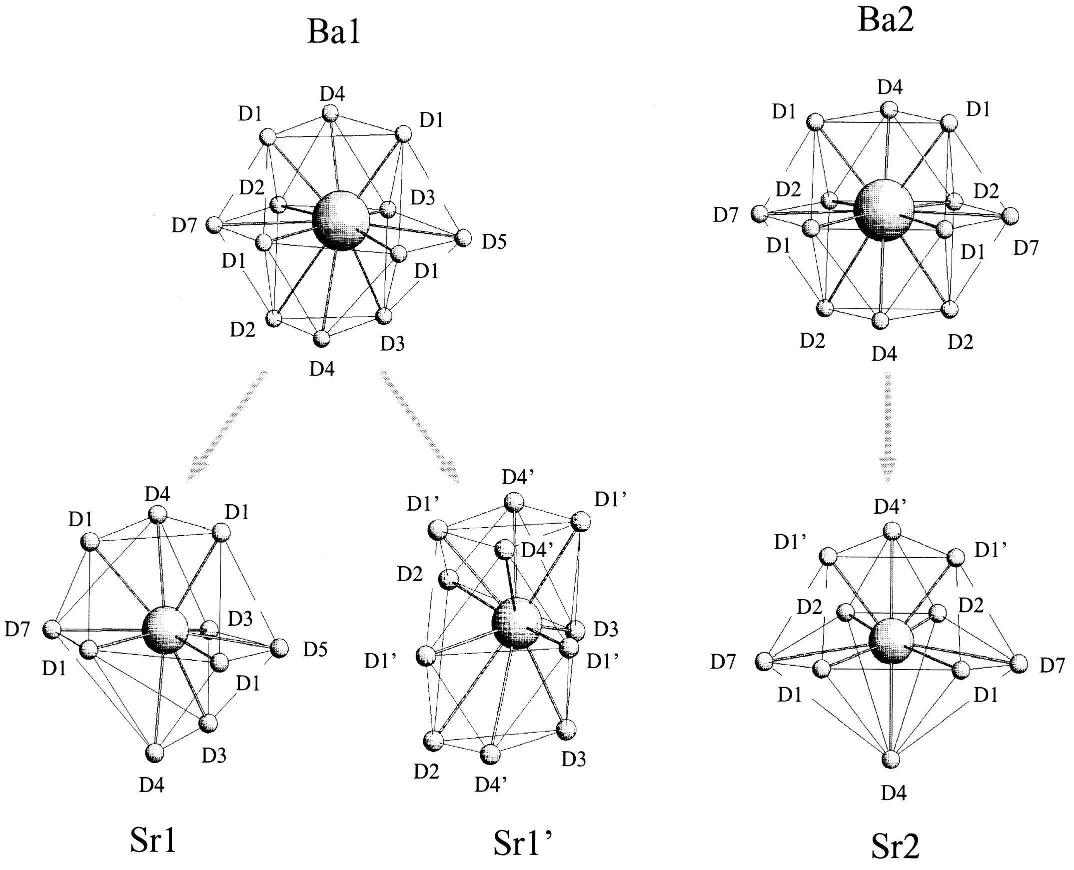

Fig. 2. Deuterium coordination polyhedra around the barium sites in orthorhombic $Ba_6Mg_7D_{26}$ [11] (top) and around the strontium sites in monoclinic $Sr_6Mg_7D_{26}$ (bottom); site symmetries *mm2* (Ba2), *m* (Ba1, Sr1, Sr1′, Sr2).

As shown in Table 3 all known magnesium and strontium based ternary metal hydrides including the present $Sr_6Mg_7H_{26}$ have europium analogues. Their structures are strictly isotypic except that the strontium compounds have slightly longer Sr–D bonds and bigger cell volume than the Eu compounds. The Sr–D distances in $Sr_6Mg_7D_{26}$, for example, are longer by ~0.07 Å, on the average, than the corresponding Eu–D distances in $Eu_6Mg_7D_{26}$. This difference is larger than expected from tabulated effective ionic radii for oxides and fluorides (Sr^{2+}: 1.36 Å; Eu^{2+}: 1.35 Å for CN = 10 [14]) and suggests that different sets of radii should be used for hydrides. On the other hand, the Mg–D distances in the strontium compounds tend to be shorter than in the europium compounds. Similar structural trends also exist for calcium and ytterbium based ternary metal hydrides, such as $Yb_{19}Mg_8H_{54}$ [15] and $Yb_4Mg_3H_{14}$ [16],

Table 3
Structure data and hydrogen storage efficiencies of isotypic ternary strontium- and europium–magnesium hydrides

Ternary hydride	Space group (structure type)	V_{cell} ($Å^3$)	Average d (Mg–D)[a] (Å)	Average d (Sr/Eu–D)[a] (Å)	ΔV[b] (%)	Hydrogen density	
						$g\ H_2\ l^{-1}$	wt%
Sr_2MgH_6[c]	*P*-3*m*1	111.7	2.03	2.65	−7.9	91.3	2.9
Eu_2MgH_6[c]	(K_2GeF_6)	108.1	1.97	2.64	−7.3	92.9	1.8
$SrMgH_4$	*Cmc*2_1	302.7	1.95	2.57	−0.5	88.5	3.5
$EuMgH_4$	($BaZnF_4$)	293.6	1.96	2.53	−0.4	91.2	2.2
$Sr_6Mg_7H_{26}$[c]	*I*2/*m*	945.8	1.94	2.66	−2.9	92.0	3.6
$Eu_6Mg_7H_{26}$[c]	($Ba_6Zn_7F_{26}$)	921.5	2.00	2.59	−2.6	94.5	2.4
$Sr_2Mg_3H_{10}$	*C*2/*m*	703.8	1.94	2.74	−3.8	95.1	3.9
$Eu_2Mg_3H_{10}$[c]	($Ba_2Ni_3F_{10}$)	690.8	1.99	2.68	−3.1	96.9	2.6

[a] For deuterides.

[b] Relative volume contraction compared to weighted sums of volumes of corresponding binary hydrides.

[c] Obtained only under very high pressure (~25 kbar).

that are isostructural with $Ca_{19}Mg_8H_{54}$ and $Ca_4Mg_3H_{14}$ [17], respectively. All together, these features underline the strong similarity between the hydride chemistry of the alkaline earths and that of the divalent rare earth elements. As to the hydrogen storage efficiencies those of the strontium compounds (89–97 g H_2 l^{-1}, 2.9–3.9 wt%) appear to be in a useful range only for high temperature applications. Finally, all strontium and europium hydrides, in particular those stabilised by very high-pressure, show more-or-less important volume contractions compared to the weighted sums of volumes of the corresponding binary hydrides (see ΔV values in Table 3). These differences presumably originate from packing effects.

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