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Strontium magnesium tetrahydride ($SrMgH_4$): a new ternary alkaline earth hydride

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Abstract

Strontium magnesium tetrahydride ($SrMgH_4$) and its deuteride ($SrMgD_4$) were prepared from Sr–Mg alloy at 765 K under a hydrogen (deuterium) pressure of 95 bar and characterized by X-ray and neutron powder diffraction. The compound crystallizes with the $BaZnF_4$ structure type, with the space group $Cmc2_1$ and with the following lattice parameters at 295 K: $a=3.9661(3)$ Å, $b=13.685(1)$ Å, $c=5.5755(6)$ Å (deuteride) and $Z=4$. It contains four symmetry-independent deuterium sites having tetrahedral (D(1), D(2) [3Sr, Mg], D(4) [2Sr, 2Mg]) and T-shaped (D(3) [Sr, 2Mg]) metal coordinations. The metal–deuterium bond distances range from 1.87 to 2.06 Å (Mg–D) and from 2.43 to 2.82 Å (Sr–D).

1. Introduction

Recently we have reported the synthesis and structural characterization of the first ternary alkaline earth hydride found in the Ca–Mg–H system, namely hexagonal $Ca_4Mg_3H_{14}$ [1]. In this paper we report the second ternary alkaline earth hydride found in the Sr–Mg–H system, namely orthorhombic $SrMgH_4$.

2. Experimental details

2.1. Synthesis

Binary SrMg alloys were prepared by induction melting of 1:1.05 mixtures of the elements (strontium (Cerac; −4 mesh; purity, 99.5%) and magnesium (Cerac; $\frac{1}{8}$ in; purity, 99.99%). The two-phase ($SrMg_2+Sr$) samples were powdered under argon and placed in a high temperature, high pressure autoclave. After evacuating to 10^{-5} bar pressure and flushing with argon, the autoclave was charged with hydrogen, heated to a temperature of 760(7) K at a hydrogen pressure of 96(4) bar for 8 days, cooled to room temperature

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and opened in an argon-filled glove-box. The deuteride was prepared at a temperature of 768(8) K and a deuterium pressure of 92(8) bar for 13 days. The final products were light grey in colour and sensitive to air.

2.2. *X-ray diffraction*

The hydride and deuteride samples were characterized by X-ray powder diffraction using a Guinier film camera (Cu $K\alpha_1$ radiation; sealed capillaries; internal standard: silicon; $a = 5.4308$ Å) and a low temperature Guinier diffractometer [2]. The patterns showed a new ternary hydride phase and small quantities of binary SrH_2SrD_2, MgO and SrO impurity phases. The ternary hydride phase was indexed by TREOR [3] on an orthorhombic cell ($a = 3.965(1)$ Å, $b = 13.700(2)$ Å and $c = 5.573(1)$ Å). The parameter ratios, systematic extinctions (possible space groups, *Cmcm* (No. 63), *C*2*cm* (≡*Ama*2 (No. 40)) and *Cmc*2$_1$ (No. 36) [4]) and intensity calculations suggested a CrB-type metal atom substructure with space group *Cmcm*. A Rietveld refinement using DBW3.2S [5] with strontium in 4*c* at 0, 0.14, $\frac{1}{4}$ and magnesium in 4*c* at 0, 0.42, $\frac{1}{4}$ converged, but the neutron data suggested that the true

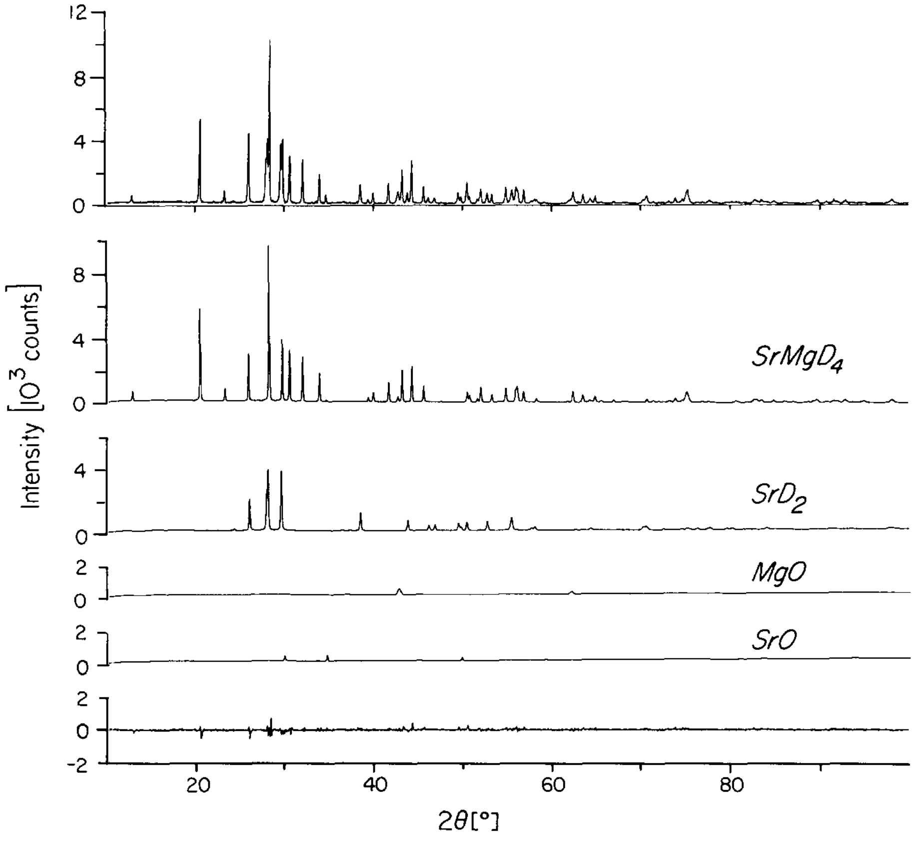

Fig. 1. Observed (top), calculated (middle) and difference (bottom) X-ray patterns of $SrMgD_4$ containing SrD_2, MgO and SrO impurity phases (Cu $K\alpha_1$ radiation).

TABLE 1

Refinement results on neutron diffraction data for $SrMgD_4$ ($T = 295$ K; estimated standard deviations are given in parentheses)

Atom	x	y	z	U_{iso} ($\times 10^2$ Å^2)
Sr	0	0.1527(4)	0.25	1.11(8)
Mg	0	0.4126(5)	0.211(1)	0.4(1)
D(1)	0	0.3343(5)	0.490(2)	3.96(9)
D(2)	0	0.3021(6)	0.015(2)	$U_{D(1)}$
D(3)	0	0.0734(7)	0.668(2)	$U_{D(1)}$
D(4)	0	0.5336(6)	0.367(2)	$U_{D(1)}$

Space group, $Cmc2_1$ (No. 36), all atoms in 4a. Cell parameters, $a = 3.9661(3)$ Å, $b = 13.685(1)$ Å, $c = 5.5755(6)$ Å. $R_B = 8.1\%$, $R_P = 2.4\%$, $R_{wp} = 3.1\%$, $R_{exp} = 1.0\%$ for 100 reflections. Form of the temperature factor, $T = \exp[-8\pi^2 U_{iso}(\sin^2\theta/\lambda^2)]$.

TABLE 2

Interatomic distances shorter than 3 Å for $SrMgD_4$ (estimated standard deviations are given in parentheses)

	Distance (Å)		Distance (Å)
Sr–D(2)	2.43(1)	D(2)–Mg	1.87(1)
2D(1)	2.463(6)	D(4)	2.40(1)
2D(2)	2.549(7)	Sr	2.43(1)
D(3)	2.572(9)	2Sr	2.549(7)
2D(4)	2.648(7)	D(1)	2.69(2)
D(1)	2.823(9)	2D(1)	2.727(7)
		2D(3)	2.751(9)
Mg–D(4)	1.87(1)	D(1)	2.96(2)
D(2)	1.87(1)		
D(1)	1.89(1)	D(3)–2Mg	2.007(2)
2D(3)	2.007(2)	Sr	2.572(9)
D(4)	2.06(1)	2D(4)	2.657(8)
		2D(4)	2.702(9)
D(1)–Mg	1.89(1)	2D(2)	2.751(9)
2Sr	2.463(6)	2D(1)	2.96(1)
D(2)	2.69(2)		
2D(2)	2.727(7)	D(4)–Mg	1.87(1)
D(4)	2.77(1)	Mg	2.06(1)
D(4)	2.81(1)	D(2)	2.40(1)
Sr	2.823(9)	2Sr	2.648(7)
2D(3)	2.96(1)	2D(3)	2.657(8)
D(2)	2.96(2)	2D(3)	2.702(9)
		D(1)	2.77(1)
		D(1)	2.81(1)
		2D(4)	2.94(1)

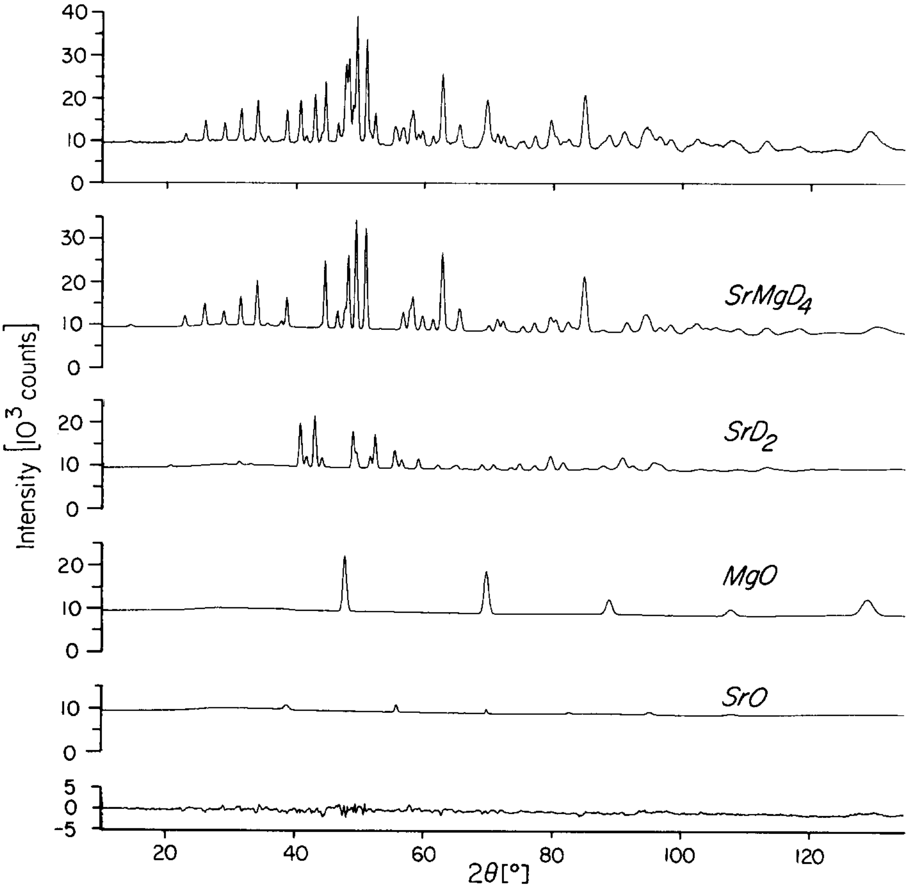

Fig. 2. Observed (top), calculated (middle) and difference (bottom) neutron patterns of $SrMgD_4$ containing SrD_2, MgO and SrO impurity phases ($\lambda = 1.7008$ Å).

space group was $Cmc2_1$ (see below). A refinement of the deuteride in the latter group converged at $R_B = 7.4\%$ and $R_F = 6.3\%$ (for patterns see Fig. 1). The low temperature pattern taken at $T = 10$ K ($a = 3.9696(1)$ Å, $b = 13.6462(5)$ Å and $c = 5.5773(2)$ Å (note that, at 295 K, $a = 3.9751(1)$ Å, $b = 13.7186(4)$ Å and $c = 5.5879(1)$ Å) showed no evidence for a structural phase transition.

2.3. *Neutron diffraction*

The hydrogen positions in the structure were established on a deuterated sample by neutron powder diffraction on the double-axis multicounter powder diffractometer [6] at the SAPHIR reactor at PSI Villigen (sample mass, 4.5 g; cylindrical vanadium container of 8 mm inner diameter, $T = 295$ K; Ge(311) monochromator; $\lambda = 1.7008$ Å; high intensity mode; $2\theta = 3.0$–$134.8°$; $\Delta(2\theta) = 0.1°$; $(\sin \theta/\lambda)_{max} = 0.543$ Å^{-1}; total counting time, 16 h). The transmission factor was measured ($\mu R = 0.151$), and the data were corrected accordingly. Profile refinements were performed using DBW3.2S [5] modified for simultaneous treatment of several phases. The structures of four phases were refined: the ternary deuteride $SrMgD_4$ with four symmetry-independent deuterium sites in space group $Cmc2_1$, binary SrD_2 ($PbCl_2$-type structure), MgO and SrO. The following 36 parameters were allowed to vary: four scale factors, three peak width parameters, the θ zero position, eight cell parameters ($SrMgD_4$, three; SrD_2, three; MgO, one; SrO, one) and 20 atomic parameters ($SrMgD_4$, 11 positional, three isotropic displacement parameters). The occupancy factors of the four deuterium sites did not differ significantly from 100% and were fixed at unity during the final refinement cycles. The results are summarized in Table 1. The bond distances and a list of D–D contact distances are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 2. Note that the contribution of MgO in the neutron pattern is much higher than that in the X-ray pattern which was taken on the same sample. The reason for this difference is unknown to us.

3. Results and discussion

Despite its similar composition, the structure of $SrMgD_4$ differs significantly from that of $Ca_4Mg_3D_{14}$ [1]. Strontium in $SrMgD_4$ is surrounded by nine close deuterium neighbours (Sr–Mg bond distances, less than 3 Å), forming a distorted trigonal prism of which one rectangular face is capped by one, and another face by two deuterium atoms, and by two distant deuterium neighbours (Sr–Mg bond distances, greater than 3 Å) that cap the third rectangular prism face. Calcium in $Ca_4Mg_3D_{14}$ has a tricapped trigonal prismatic deuterium configuration. Magnesium in $SrMgD_4$ is surrounded by six close deuterium neighbours, forming a distorted octahedral configuration similar to that in binary MgD_2. In $Ca_4Mg_3D_{14}$, magnesium is surrounded by seven deuterium atoms, forming a pentagonal bipyramid. These structural differences are presumably due to the size differences between the metal cations Ca^{2+} and Sr^{2+}.

Deuterium in $SrMgD_4$ has either tetrahedral (D(1), D(2) [3Sr, Mgl, D(4) [2Sr, 2Mg]) or T-shaped (D(3) [Sr, 2Mg]) metal coordination. The metal–deuterium bond distances (Sr–D, 2.43–2.82 Å; Mg–D, 1.87–2.06 Å) and shortest D–D contact distances (2.40 Å) are consistent with those observed in the binary deuterides SrD_2 (Sr–D, 2.45–2.84 Å, D–D, 2.92 Å (values obtained during this work)) and MgD_2 (Mg–D, 1.95 Å; D–D = 2.47 Å).

The interconnection of the trigonal prismatic SrD_6 units and octahedral MgD_6 units is shown in Fig. 3. Parallel to [100] the SrD_6 prisms are connected to columns via triangular faces and the MgD_6 octahedra are connected to columns via *trans* vertices. Perpendicular to [100] the MgD_6 octahedra are interconnected via *cis* vertices, and the SrD_6 prisms are interconnected via corners bicapping one prism face. Each SrD_6 prism is linked to three MgD_6 octahedra, and vice versa, involving either common edges or common vertices.

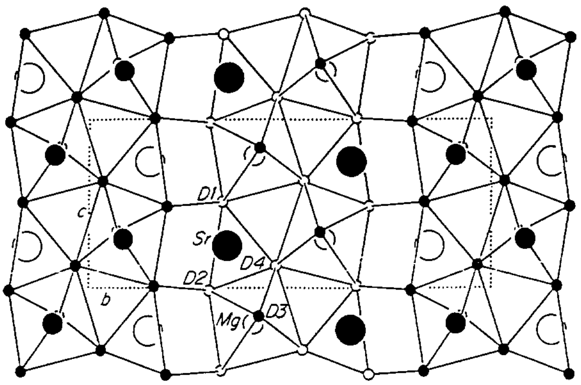

Fig. 3. Projection of orthorhombic $SrMgD_4$ along [100]: large circles, strontium; medium circles, magnesium; small circles, deuterium; open circles, atoms at $x = 0$; full circles: atoms at $x = \frac{1}{2}$; full lines, D–D contacts.

The deuterium atoms (D(3)) linking the MgD_6 octahedra along [001] are capping one of the SrD_6 prism faces.

$SrMgD_4$, which crystallizes with the $BaZnF_4$ structure type [7], is structurally related to the 'CrB-type' interstitial deuterides (hydrides) $LaNiD_{3.7}$ [8], $ZrNiH_3$ [9] and $CoZrD_3$ [10] in the sense that the non-centrosymmetric structure of the former is a distorted variant of the centrosymmetric structure of the latter. However, the bonding in these two types of compounds is very different because $SrMgD_4$ is presumably ionic whereas the interstitial hydrides are presumably metallic. The shortest metal–metal distances in $SrMgD_4$ are also significantly longer (Sr–Mg, 3.37 Å) than those in the interstitial hydrides (La–Ni, 3.20 Å; Zr–Ni, 2.82 Å; Zr–Co, 2.72 Å).

Measurements of the decomposition isotherms of $SrMgD_4$ are in progress to determine its thermal stability.

Acknowledgments

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