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Letter

The Ba analogue of $Sr_2Mg_3H_{10}$

F. Gingl[a], K. Yvon[a], M. Zolliker[b]

[a]*Laboratoire de Cristallographie, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland*

[b]*Laboratorium für Neutronenstreuung, Eidgenössische Technische Hochschule Zürich & Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

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Abstract

$Ba_2Mg_3H_{10}$ and its deuteride were synthesized from $BaMg_{1.7}$ alloy and characterized by X-ray and neutron powder diffraction. They crystallize with the monoclinic $Ba_2Ni_3F_{10}$ structure type in space group $C2/m$ ($a=18.014(2)$ Å, $b=5.876(1)$ Å, $c=7.879(1)$ Å, $\beta=111.93(1)°$, $V=773.7(1)$ Å^3 (hydride); $a=17.950(7)$ Å, $b=5.856(2)$ Å, $c=7.869(3)$ Å, $\beta=111.88(3)°$, $V=767.6(5)$ Å^3 (deuteride) and are essentially isostructural to the recently reported $Sr_2Mg_3H_{10}$, with slight differences in the coordination of the Ba atoms. The metal-deuterium bond distances range from 2.55 Å to 3.20 Å (Ba–D) and from 1.90 Å to 2.18 Å (Mg–D). The shortest D–D distance is 2.57 Å.

Keywords: Hydrides; Crystal structure; Powder diffraction

1. Introduction

The first ternary alkaline earth hydride, $Ca_4Mg_3H_{14}$, was characterized two years ago [1]. Since then other members of this group, such as $SrMgH_4$ [2], Ba_2MgH_6 [3] and $Sr_2Mg_3H_{10}$ [4], have been synthesized. All of them contain magnesium as a constituent and can be considered as saline compounds. While the Ca compound is the only representative for its structure type, isostructural pairs do exist for the ternary Sr and Ba compounds, such as $SrMgH_4$ [2] and $BaMgH_4$ [5]. In this letter, we present the synthesis and crystal structure of the Ba analogue of $Sr_2Mg_3H_{10}$ [4].

2. Experimental details

$BaMg_{1.7}$ alloys were prepared by arc melting mixtures of the elements (Ba: ALFA, 99%, Mg: CERAC, 1/8″, 99.99%). The ingots were powdered under argon and hydrogenated (deuterated) in a high-temperature high-pressure autoclave for 6 days at 700 K and 85 bar hydrogen (deuterium) pressure. The final products were light grey and sensitive to air.

The hydride and deuteride samples were characterized by X-ray powder diffraction at room temperature (Bragg-Brentano diffractometer, CuKα radiation, Si as internal standard). The patterns were indexed to a monoclinic C-centered cell ($a=18.014(2)$ Å, $b=5.876(1)$ Å, $c=7.879(1)$ Å, $\beta=111.93(1)°$, $V=773.7(1)$ Å^3 (hydride); $a=17.950(7)$ Å, $b=5.856(2)$ Å, $c=7.869(3)$ Å, $\beta=111.88(3)°$, $V=767.6(5)$ Å^3 (deuteride)). A refinement of the metal atom substructure of the deuteride based on the positional parameters of $Sr_2Mg_3D_{10}$ by using the program DBWS-9006PC [6] converged to $R_B=10.8\%$, $R_{wp}=10.4\%$, $S=2.33$

The hydrogen positions were determined from neutron powder diffraction data of the deuterated sample as measured on the DMC diffractometer [7] at the reactor SAPHIR, PSI Villigen (Ge (311) monochromator, $\lambda=1.6984$ Å, 2θ range 3.0–134.8°, step size $\Delta 2\theta=0.1°$, $(\sin\theta/\lambda)_{max}=0.544$ Å^{-1}, $T=293$ K). The sample (7 g) was enclosed in a cylindrical vanadium container of 9 mm inner diameter and measured in high-resolution mode. The transmission factor was measured ($\mu R=0.142$), and the data were corrected accordingly. For the structure refinement, the D atom coordinates of $Sr_2Mg_3D_{10}$ [4] were taken as starting parameters. The structures of three phases were refined, monoclinic $Ba_2Mg_3D_{10}$, monoclinic $Ba_6Mg_7D_{26}$ [5] and tetragonal MgD_2 [8]. The following 44 parameters were allowed to vary: three scale factors, the θ zero position, three peak shape parameters, 10 cell parameters ($Ba_2Mg_3D_{10}$, four; $Ba_6Mg_7D_{26}$, four; MgD_2, two), three thermal displacement parameters and 24 positional parameters for $Ba_2Mg_3D_{10}$. Scattering lengths were

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taken from [9]. Results are summarized in Table 1, and interatomic distances are given in Table 2. The observed, calculated and difference neutron powder diffraction patterns are shown in Fig. 1.

Table 1
Refinement results on neutron powder diffraction data for $Ba_2Mg_3D_{10}$ (T=295 K; estimated standard deviations in parentheses)

Atom	Site	x	y	z	U_{iso} ($\times 10^{-2}$ Å^2)
Ba1	4*i*	0.283(2)	0	0.673(3)	0.3(3)
Ba2	4*i*	0.385(2)	0	0.282(3)	U_{Ba1}
Mg1	4*i*	0.070(2)	0	0.451(3)	1.2(2)
Mg2	4*i*	0.175(1)	0	0.009(3)	U_{Mg1}
Mg3	4*g*	0	0.266(4)	0	U_{Mg1}
D1	8*j*	0.108(1)	0.259(3)	0.016(2)	2.2(1)
D2	8*j*	0.149(1)	0.232(4)	0.480(2)	U_{D1}
D3	4*i*	0.024(2)	0	0.181(3)	U_{D1}
D4	4*i*	0.137(1)	0	0.746(3)	U_{D1}
D5	4*i*	0.228(1)	0	0.273(3)	U_{D1}
D6	4*i*	0.530(2)	0	0.194(3)	U_{D1}
D7	4*h*	0	0.224(5)	1/2	U_{D1}
D8	4*e*	1/4	1/4	0	U_{D1}

Space group *C2/m* (No. 12).
Cell parameters a=17.950(7) Å, b=5.856(2), c=7.869(3) Å, β=111.88(3)°, V=767.6(5) Å^3, Z=4.
R_B=8.7%, R_P=4.1%, R_{wp}=5.6%, S=3.24 for 597 reflections.
Form of the temperature factor: $T=\exp[-8\pi^2 U_{iso}(\sin^2\theta/\lambda^2)]$.

Table 2
Selected interatomic distances shorter than 3.5 Å for $Ba_2Mg_3D_{10}$ (estimated standard deviations in parentheses)

Ba1	– 2 D2	2.55(4)	D1	– Mg3	1.90(2)
	2 D2	2.69(3)		Mg2	1.95(2)
	2 D1	2.87(2)		Ba2	2.78(3)
	D4	2.88(4)		Ba1	2.87(2)
	D5	2.93(3)	D2	– Mg1	1.92(3)
	2 D5	2.98(1)		Ba1	2.55(4)
	D6	3.12(5)		Ba2	2.68(3)
	2 D8	3.20(3)		Ba1	2.69(3)
Ba2	– 2 D7	2.68(3)	D3	– Mg1	1.97(3)
	2 D2	2.68(3)		2 Mg3	2.05(2)
	2 D1	2.78(3)			
	D5	2.79(4)	D4	– Mg2	1.92(3)
	D6	2.93(5)		Mg1	2.18(3)
	2 D4	2.95(1)		Ba1	2.88(4)
	2 D8	2.99(2)		2 Ba2	2.95(1)
Mg1	– 2 D2	1.92(3)	D5	– Mg2	1.94(3)
	2 D7	1.95(3)		Ba2	2.79(4)
	D3	1.97(3)		Ba1	2.93(3)
	D4	2.18(3)		2 Ba1	2.98(1)
Mg2	– D4	1.92(3)	D6	– 2 Mg3	1.97(2)
	D5	1.94(3)		Ba2	2.93(5)
	2 D1	1.95(2)		Ba1	3.12(5)
	2 D8	2.01(1)	D7	– 2 Mg1	1.95(3)
Mg3	– 2 D1	1.90(2)		2 Ba2	2.68(3)
	2 D6	1.97(2)	D8	– 2 Mg2	2.01(1)
	2 D3	2.05(2)		2 Ba2	2.99(2)
				2 Ba1	3.20(3)

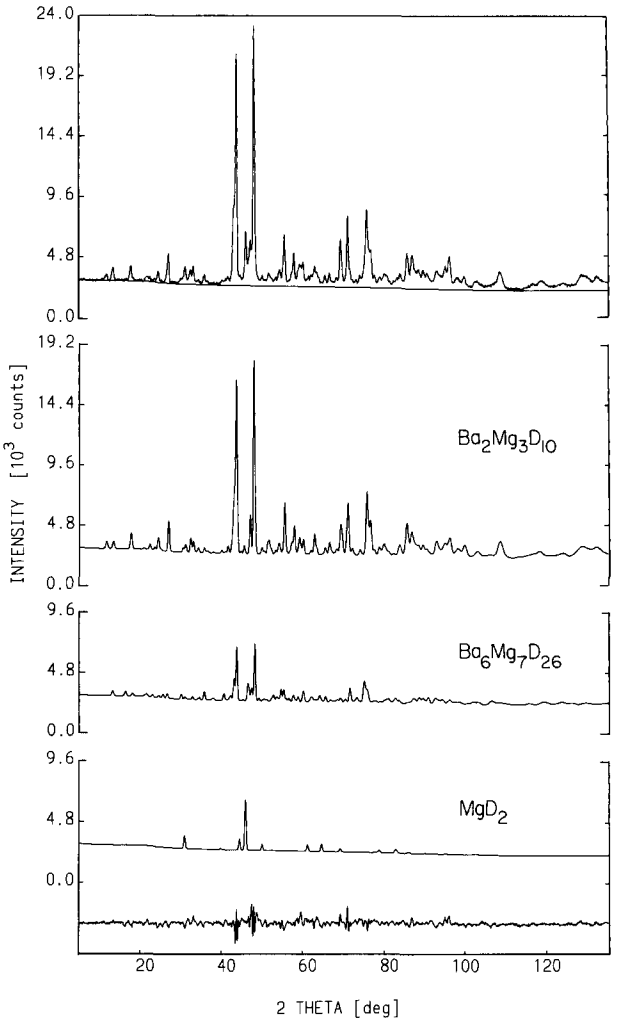

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron powder diffraction patterns of $Ba_2Mg_3D_{10}$, containing $Ba_6Mg_7D_{26}$ and MgD_2 impurity phases (λ=1.6984 Å).

3. Results and discussion

$Ba_2Mg_3D_{10}$ crystallizes with the monoclinic $Ba_2Ni_3F_{10}$ structure type [10]. It is essentially isostructural to recently reported $Sr_2Mg_3D_{10}$ [4] and contains 3 Mg and 2 Ba sites (for a structure drawing see Fig. 2 in [4]). While the deuterium environments of the small Mg atoms are very similar in both deuterides (sixfold octahedral), the coordination spheres of the larger alkaline earths differ (Fig. 2). In the Sr compound both Sr sites are twelvefold coordinated (Sr2, cuboctahedral; Sr1, twinned cuboctahedral), and the Sr–D distances show a clear gap (Sr1, 12 distances in the range 2.49–2.96 Å; 13th at 3.31 Å (D6); Sr2, 12 distances in the range 2.51–2.89 Å; 13th at 3.75 Å (D6)). In the Ba compound, both Ba sites show a clear gap, but only one is twelvefold coordinated (Ba2, 12 distances in the range 2.68–2.99 Å, 13th at 3.83 Å (D6)) while the other has 13 nearest deuterium neighbors (Ba1, 13 distances in the range 2.55–3.20 Å, 14th at 4.35 Å (D3)). In the other reported

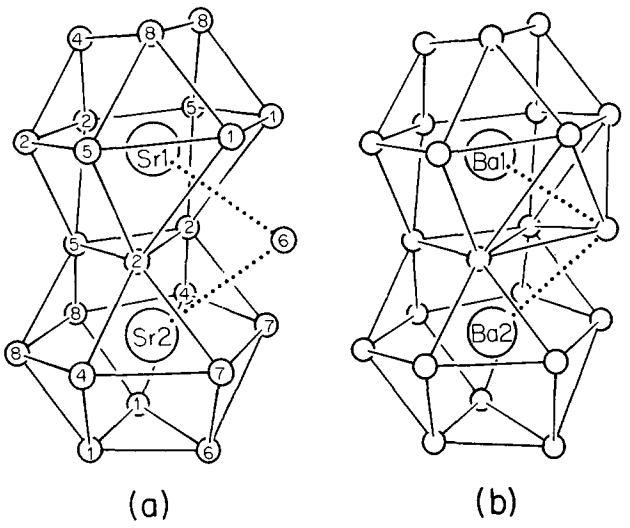

Fig. 2. Deuterium coordination spheres of Sr and Ba in $Sr_2Mg_3D_{10}$ (a) and $Ba_2Mg_3D_{10}$ (b); numbers in small circles refer to deuterium sites.

ternary compound of that system, Ba_2MgD_6 [3], there is only one Ba site, with twelvefold twinned cuboctahedral deuterium coordination, while the Mg site has octahedral deuterium coordination. This relative flexibility of the coordination around Sr and Ba compared with the more rigid environment of Mg is consistent with trends observed in hydrogen-alkaline earth bonding characteristics. The ten shortest Ba–D and Mg–D bond distances in $Ba_2Mg_3D_{10}$ (Ba, 2.55–2.99 Å, Mg, 1.90–2.18 Å) do not differ significantly from those in Ba_2MgD_6 (Ba–D, 2.73–2.86 Å, Mg–D, 1.97 Å) and in the binary deuterides BaD_2 (2.57–2.98 Å) [11] and MgD_2 (1.95 Å) [8]. As expected from matrix effects, the Mg–D distances in $Ba_2Mg_3D_{10}$ are longer than those in the Sr analogue (1.81–2.14 Å). Likewise, the shortest D–D distances in $Ba_2Mg_3D_{10}$ are 2.57 Å, as compared with 2.49 Å in the Sr analogue. The conditions of synthesis indicate that both compounds are thermally more stable than MgH_2.

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