ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 17–20

Journal of
ALLOYS
AND COMPOUNDS

Orthorhombic $Ba_6Mg_7H_{26}$: a new fluoride-related ternary alkaline earth hydride

F. Gingl[a,]*, A. Hewat[b], K. Yvon[a]

[a]*Université de Genève, Laboratoire de Cristallographie, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland*
[b]*Institut Laue Langevin, Avenue des Martyrs, B.P. 156, F-38042 Grenoble Cedex 9, France*

Abstract

$Ba_6Mg_7H_{26}$ and its deuteride were synthesized by sintering 6:7 mixtures of BaH_2 (BaD_2) and Mg powder at 730 K and 100 bar hydrogen (deuterium) pressure for two weeks and characterized by X-ray and neutron powder diffraction on a multiphase sample. They crystallize with a new structure type in space group *Immm* (No. 71), cell parameters at 295 K, hydride: a=5.8258(3) Å, b=11.9791(6) Å, c=14.905(1) Å, V=1040.2(1) Å^3; deuteride: a=5.8005(6) Å, b=11.925(1) Å, c=14.836(2) Å, V=1026.2(1) Å^3; Z=2. The structure contains two barium and four magnesium sites having cuboctahedral (Ba) and octahedral (Mg) deuterium coordinations. The metal–deuterium distances are in the range 2.61–3.14 Å (Ba–D) and 1.90–2.28 Å (Mg–D). The shortest D–D distance is 2.62 Å. The ternary fluoride $Ba_6Zn_7F_{26}$ can be considered as a monoclinic distortion variant of $Ba_6Mg_7D_{26}$.

Keywords: Barium magnesium hydride; Alkaline earth hydride; Neutron diffraction; Crystal structure

1. Introduction

Up to now, five ternary alkaline earth hydrides have been reported: one in the Ca–Mg–H system, $Ca_4Mg_3H_{14}$ [1], two in the Sr–Mg–H system, $SrMgH_4$ [2] and $Sr_2Mg_3H_{10}$ [3] and two in the Ba–Mg–H system, trigonal Ba_2MgH_6 [4] crystallizing with K_2GeF_6-type structure and monoclinic $Ba_2Mg_3H_{10}$ [5], which is isotypic with $Ba_2Ni_3F_{10}$ [6]. We have now identified a third barium magnesium hydride, namely $Ba_6Mg_7H_{26}$. Its structure has orthorhombic symmetry and is closely related to the monoclinic structure of the fluoride $Ba_6Zn_7F_{26}$ [7].

2. Experimental details

2.1. Synthesis

Mixtures of BaH_2 (BaD_2) and Mg powder (6:7) were heated in an autoclave for two weeks at a temperature of up to 730 K and a hydrogen (deuterium) pressure of 100 bar. The temperature was slowly increased and the final temperature was reached only after two days. The reaction products were white and sensitive to air. The thermal stability was examined by heating to 700 K at 1 K min^{-1}. No decomposition was observed.

2.2. X-ray diffraction

The powders were characterized by X-ray diffraction (Bragg–Brentano diffractometer Philips PW 1820, CuK_α or CoK_α, and Guinier diffractometer Huber G645; $CuK_{\alpha 1}$, internal standard: Si). The patterns were indexed to a body-centered orthorhombic cell (refined parameters, hydride: a=5.8258(3) Å, b=11.9791(6) Å, c=14.905(1) Å; deuteride: a=5.8005(6) Å, b=11.925(1) Å, c=14.836(2) Å). The metal–atom substructure was solved by considering its close analogy to that of the fluoride $Ba_6Zn_7F_{26}$, which was described as monoclinic (space group $C2/m$, a=19.46 Å, b=5.956 Å, c=12.243 Å, β=128.88°) with pseudo-orthorhombic symmetry [7]. For the orthorhombic structure model of the hydride (space group *Immm*, as confirmed later by neutron data), Rietveld refinements converged at R_B=8.2%, R_F=5.4%, R_P=3.6%, R_{WP}=4.9%, S=1.93, taking into account the presence of two impurity phases (Ba_2MgH_6/Ba_2MgD_6 and $BaMgH_4$/$BaMgD_4$). The MgO impurity observed in the neutron sample was not detected by X-rays.

---

*Corresponding author

0925-8388/97/$17.00
PII S0925-8388(96)03005-8

2.3. Neutron diffraction

The hydrogen positions were determined from neutron powder diffraction data of a deuterated sample as measured on the D2B diffractometer at the Institut Laue Langevin (high-resolution mode, Ge(335) monochromator, λ=1.594 Å, $2\theta_{max}$=160°, step size $\Delta 2\theta$=0.05°, T=295 K). The sample (6.5 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and measured in high-resolution mode for 13 h. Structure refinements (program DBWS-9006PC [8]) were performed by using the fluorine positions of $Ba_6Zn_7F_{26}$ as starting parameters for the deuterium sites. The model was refined for both orthorhombic symmetry (*Immm*; 13 independent atoms, 18 positional parameters) and monoclinic symmetry ($C2/m$; 16 independent atoms, 33 positional parameters). The agreement indices ($C2/m$: R_B=4.4%, R_F=3.4%, R_P=2.9%, R_{WP}=3.6%, S=1.29; *Immm*: R_B=5.3%, R_F=3.8%, R_P=3.0%, R_{WP}=3.8%, S=1.35) did not differ significantly and the refinements of the monoclinic model converged at the orthorhombic atom arrangement containing the two additional mirror planes; deviations were less than 0.1 Å. Therefore, the deuteride was considered to be orthorhombic within experimental resolution. Four phases were included in the final refinements: orthorhombic $Ba_6Mg_7D_{26}$, trigonal Ba_2MgD_6 [4], orthorhombic $BaMgD_4$ [9] and cubic MgO (NaCl type). The following 48 parameters were allowed to vary: four scale factors, one zero correction, three peak shape, nine cell parameters, eighteen positional and thirteen isotropic displacement parameters. Scattering lengths were taken from Ref. [10]. The refinement results are summarized in Table 1, the observed, calculated and difference neutron powder diffraction patterns are shown in Fig. 1. A list of selected interatomic distances is given in Table 2.

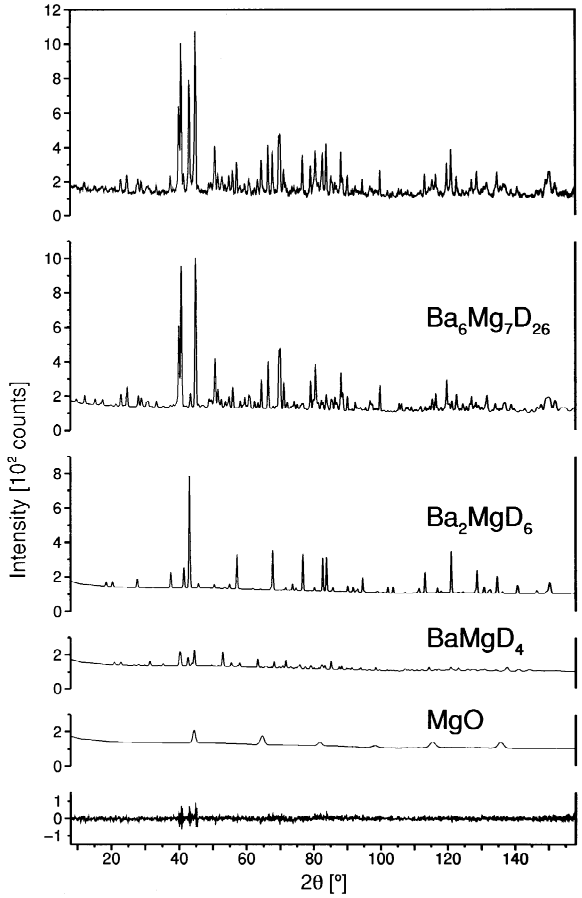

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron powder diffraction patterns of $Ba_6Mg_7D_{26}$, containing Ba_2MgD_6, $BaMgD_4$ and MgO as impurities (λ=1.594 Å).

Table 1
Refinement results on neutron powder diffraction data (D2B, high resolution) for $Ba_6Mg_7D_{26}$(T=295 K; estimated standard deviations in parentheses)

Atom	Site	x	y	z	U_{iso} (Å^2)
Ba1	8*l*	0	0.2577(3)	0.3520(3)	0.0072(9)
Ba2	4*j*	1/2	0	0.3554(5)	0.003(1)
Mg1	4*i*	0	0	0.2182(4)	0.013(1)
Mg2	4*g*	0	0.2588(5)	0	0.011(1)
Mg3	4*e*	0.253(1)	0	0	0.011(1)
Mg4	2*c*	1/2	1/2	0	0.012(2)
D1	16*o*	0.2340(6)	0.1133(2)	0.2449(2)	0.0225(6)
D2	8*n*	0.248(1)	0.3852(4)	0	0.033(1)
D3	8*n*	0.2640(9)	0.1625(3)	0	0.0232(9)
D4	8*l*	0	0.2746(4)	0.1275(3)	0.0239(9)
D5	4*j*	1/2	0	0.0903(4)	0.025(2)
D6	4*i*	0	0	0.0882(5)	0.034(2)
D7	4*i*	0	0	0.3719(6)	0.039(2)

Space group *Immm* (No. 71).
Cell parameters (X-rays) a=5.8005(6) Å, b=11.925(1) Å, c=14.836(2) Å, V=1026.2(1) Å^3, Z=2.
R_B=5.3%, R_F=3.8%, R_P=3.0%, R_{WP}=3.8%, S=1.35 for 610 reflections.
Form of the temperature factor: $T=\exp[-8\pi^2 U_{iso}(\sin\theta/\lambda)^2]$.

3. Results and discussion

$Ba_6Mg_7D_{26}$ shows the characteristics of an ionic compound. Its structure contains six cation sites (two Ba^{2+}, four Mg^{2+}) and seven anion (D^-) sites. The cation sites have octahedral (Mg1–Mg4) and twelve-fold cuboctahedral (Ba1, Ba2) anion coordinations. The deuterium octahedra centered by magnesium are more-or-less regular, except for one (Mg1), which is strongly elongated along a corner (see below). Those centered by Mg3 are linked by opposite edges to rutile-type chains running along *a*. These chains are connected by corner-sharing Mg2- and Mg4-centered octahedra to slabs parallel to the *ab* plane (Fig. 2). The slabs are linked by Mg1-centered octahedra along *c* to a three-dimensional network containing the Ba^{2+} ions (Fig. 3). The anion sites have various cation coordinations: octahedral coordination is found for D2 and D7 (4 Ba, 2 Mg), square-pyramidal coordination for D4 (4 Ba, 1 Mg), tetrahedral coordination for D1 (3 Ba, 1 Mg), D3 and D5

Table 2
Selected interatomic distances (Å) for $Ba_6Mg_7D_{26}$ (estimated standard deviations in parentheses)

Ba1	2	D1	2.610(4)	D2		Mg4	2.003(5)
	2	D1	2.708(5)			Mg2	2.084(7)
	2	D3	2.757(5)			D3	2.657(6)
	2	D4	2.942(1)		2	D4	2.718(6)
		D5	3.014(4)			D2	2.738(7)
		D7	3.087(4)		2	D7	2.761(7)
	2	D2	3.140(5)			D2	2.877(8)
		D4	3.337(6)		2	Ba2	2.923(7)
						D2	2.923(8)
Ba2	4	D1	2.626(6)		2	Ba1	3.140(5)
	2	D4	2.700(5)				
	2	D7	2.911(1)	D3		Mg2	1.914(6)
	4	D2	2.923(7)			Mg3	1.939(4)
						D2	2.657(6)
Mg1		D6	1.93(1)		2	D5	2.725(5)
	4	D1	1.956(3)			D3	2.738(7)
		D7	2.28(1)		2	Ba1	2.757(5)
					2	D4	2.777(5)
Mg2	2	D4	1.901(5)		2	D6	2.795(5)
	2	D3	1.914(6)			D3	3.063(7)
	2	D2	2.084(7)				
				D4		Mg2	1.901(5)
Mg3	2	D3	1.939(4)			Ba2	2.700(5)
	2	D5	1.962(6)		2	D2	2.718(6)
	2	D6	1.966(7)		2	D3	2.777(5)
					2	D1	2.784(5)
Mg4	2	D7	1.901(9)		2	D1	2.929(5)
	4	D2	2.003(5)		2	Ba1	2.942(1)
						D6	3.326(5)
D1		Mg1	1.956(3)			Ba1	3.337(6)
		Ba1	2.610(4)				
		Ba2	2.626(6)	D5	2	Mg3	1.962(6)
		D7	2.687(7)			D5	2.679(8)
		D1	2.702(3)		4	D3	2.725(5)
		Ba1	2.708(5)		2	D6	2.900(1)
		D1	2.715(5)		2	Ba1	3.014(4)
		D4	2.784(5)		4	D1	3.077(5)
		D4	2.929(5)				
		D6	3.012(7)	D6		Mg1	1.93(1)
		D5	3.077(5)		2	Mg3	1.966(7)
		D1	3.086(5)			D6	2.62(1)
		D1	3.269(3)		4	D3	2.795(5)
					2	D5	2.900(1)
					4	D1	3.012(7)
					2	D4	3.326(5)
				D7		Mg4	1.901(9)
						Mg1	2.28(1)
					4	D1	2.687(7)
					4	D2	2.761(7)
					2	Ba2	2.911(1)
					2	Ba1	3.087(4)

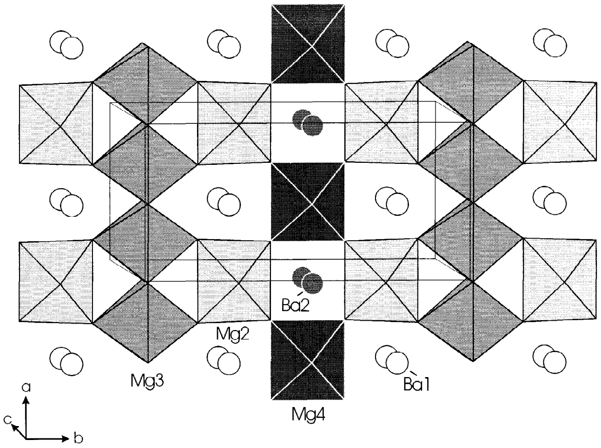

Fig. 2. Slab of Mg-centered octahedra in the *ab* plane.

(2 Ba, 2 Mg) and triangular coordination for D6 (3 Mg). Except for one long Mg–D bond (Mg1–D7=2.28 Å), the metal–deuterium distances (Mg–D: 1.90–2.00 Å; Ba–D: 2.61–3.14 Å) compare well with those in the binary deuterides MgD_2 (1.95 Å [11]) and BaD_2 (2.57–2.98 Å [12]) and the ternary deuterides Ba_2MgD_6 (Mg–D: 1.97 Å; Ba–D: 2.73–2.86 Å [4]) and $Ba_2Mg_3D_{10}$ (Mg–D=1.90–2.18 Å; Ba–D=2.55–3.20 Å [5]). The shortest D–D distance is 2.62 Å.

Fig. 4 shows the Ba^{2+} and D^- environment of Mg1 and Mg4. The deuterium octahedra around these two Mg sites are linked via D7 along *c*. The unusually long distance (Mg1–D7=2.28 Å) presumably results from the unbalanced electrostatic situation at the Mg1 site: there are six cation neighbors at distances from 3.54–3.65 Å, four Ba^{2+}

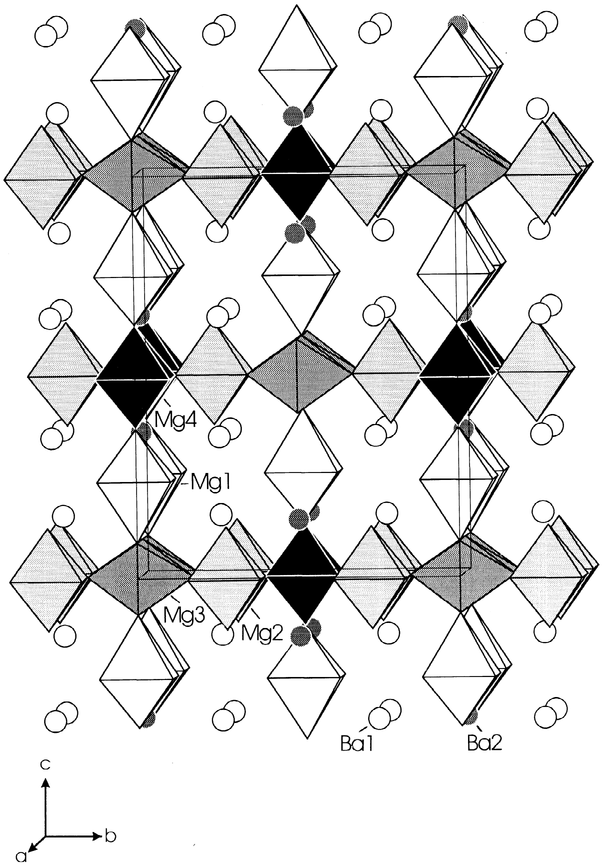

Fig. 3. Structure of $Ba_6Mg_7D_{26}$ projected approximately along [100].

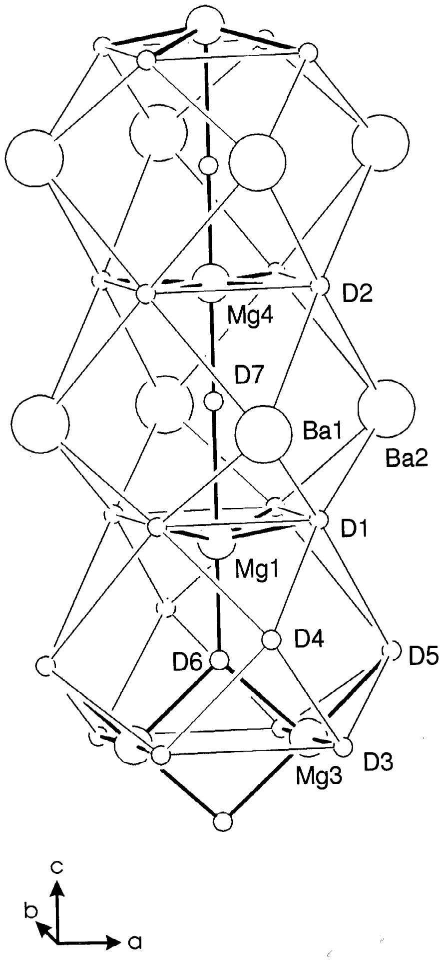

Fig. 4. Structure detail of $Ba_6Mg_7D_{26}$ showing the environment of Mg1 and Mg4. The Mg4 site symmetry is *mmm*.

ions above, but only two Mg^{2+} ions below. Mg1 is therefore shifted away from the square of Ba^{2+} ions. As a consequence, the Mg1–D7 bond is weakened and D7 is shifted away by 0.28 Å from the center of Ba^{2+} ions towards Mg4 which occupies the center of a Ba^{2+} cube; the Mg4–D7 bonds are very short (1.90 Å), while the Mg4–D2 bonds are in the usual range (2.00 Å).

The structure of $Ba_6Mg_7D_{26}$ can also be described in terms of a distorted close packing of Ba^{2+} and D^- ions with Mg^{2+} ions in octahedral holes. The coordination spheres of the D^- ions can be derived from cuboctahedra; the D^- ions are surrounded by 11 (D3), 12 (D1, D2, D4, D7) or 13 (D5, D6) Ba^{2+} or D^- ions. A similar description also applies to Ba_2MgD_6 [4] and $Ba_2Mg_3D_{10}$ [5].

$Ba_6Zn_7F_{26}$ (space group $C2/m$) can be considered as a monoclinic distortion variant of orthorhombic $Ba_6Mg_7D_{26}$. Its structure derives from the hydride structure by a rotation of the anion octahedra about the monoclinic *b* axis, thus leading to a loss of two mirror planes. The deviation from orthorhombic symmetry in the fluoride structure is relatively small since the atomic shifts are only about 0.06 Å (Ba), 0.18 Å (Zn) and 0.33 Å (F). The Zn2-centered fluorine octahedron shows the same distortion as the corresponding Mg1-centered deuterium octahedron; the Mg1–D7 bond analogue in the fluoride (Zn2–F9) is much longer than the other five Zn–F bonds (2.28 Å vs. 1.99–2.03 Å).

The hydrogen storage capacity of $Ba_6Mg_7H_{26}$ is 2.6 wt.%, corresponding to a hydrogen density of 81.7 $g\,l^{-1}$. Under 1 bar hydrogen, the compound is thermally stable up to 700 K.

Acknowledgments

We thank Dr. J. Rodriguez-Carvajal for collecting preliminary neutron diffraction data on D1A at the reactor Orphee (Saclay, France), Mr. J.-L. Lorenzoni for technical assistance and Mrs. B. Künzler for help with producing the photographs. This work was supported by the Swiss Federal Office of Energy and the Swiss National Science Foundation.

References

[1] F. Gingl, F. Bonhomme, K. Yvon and P. Fischer, *J. Alloys Comp.*, *185* (1992) 273.
[2] F. Gingl, K. Yvon and P. Fischer, *J. Alloys Comp.*, *187* (1992) 105.
[3] F. Gingl, K. Yvon and P. Fischer, *J. Alloys Comp.*, *206* (1994) 73.
[4] K. Kadir and D. Noréus, *Z. Phys. Chem.*, *179* (1993) 243.
[5] F. Gingl, K. Yvon and M. Zolliker, *J. Alloys Comp.*, *216* (1994) L1.
[6] M. Leblanc, G. Ferey and R. de Pape, *J. Solid State Chem.*, *33* (1980) 317.
[7] J. Renaudin, M. Samouël, M. Leblanc, A. de Kozak and G. Ferey, *J. Solid State Chem.*, *59* (1985) 103.
[8] D.B. Wiles and R.A. Young, *J. Appl. Cryst.*, *14* (1981) 149; see also A. Sakthivel and R.A. Young, *Programs DBWS-9006 and DBWS-9006PC*, School of Physics, Georgia Institute of Technology, Atlanta, GA, 1990.
[9] F. Gingl and K. Yvon, to be published.
[10] V.F. Sears, *Neutron News*, *3* (1992) 26.
[11] W.H. Zachariasen, C.E. Holley and J.F. Stamper Jr., *Acta Crystallogr.*, *16* (1963) 352.
[12] W. Bronger, S. Chi-Chien and P. Müller, *Z. Anorg. Allg. Chem.*, *545* (1987) 69.