Barium oxoaluminate hydride

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The crystal structure of $Ba_3(AlO_4)H$ is isotypic with Ba_3SiS_5 and contains AlO_4^{5-} and H^- anions. The hydride and oxide anions are coordinated by six Ba and five Ba/one Al atoms in an octahedral geometry. The hydrogen content was examined by MAS–NMR experiments of the deuterated compound.

Comment

$Ba_3(AlO_4)H$ crystallizes in the orthorhombic space group *Pnma* with the Ba_3SiS_5 structure type (Schmitz, 1981). The crystal structure is composed of AlO_4^{5-} and H^- anions separated by the charge compensating Ba^{2+} cations. The Al atoms in $Ba_3(AlO_4)H$ are thus coordinated by four O ligands in a distorted tetrahedral environment, with Al—O distances ranging from 1.750 (3) to 1.780 (5) Å and O—Al—O angles ranging from 107.4 (1) to 118.0 (2)°. These values are comparable to those observed in the oxoaluminate $BaLa(AlO_4)$ (Kovba *et al.*, 1985; d_{Al-O} = 1.75–1.77 Å). All the

oxygen ligands in the structure of the title compound are coordinated by five Ba and one Al cation in a distorted octahedral geometry (Fig. 1). The hydride ions, whose existence and character was determined by solid-state MAS–NMR spectroscopy (see below), are located in the centres of distorted octahedra of Ba cations with Ba—H distances ranging from 2.80 (7) to 2.98 (8) Å (Fig. 2). These distances are comparable to those observed in BaH_2 (Bronger *et al.*, 1987; Snyder *et al.*, 1994), where the two crystallographically independent hydride ions are coordinated by four and five Ba^{2+} cations, respectively. The $[HBa_6]$ octahedra are connected *via* common corners to form a three-dimensional network $[HBa_{6/2}]$ corresponding to the $[TiO_{6/2}]$ partial structure of the perovskite structure type (Fig. 3). Accordingly, $Ba_3(AlO_4)H$ can be derived from the perovskite structure by group–subgroup relation employing the antitype analogy $Ca(TiO_3)$–$AlO_4(HBa_3)$: starting with the perovskite type (space group $Pm3m$, a = b = c), the first step is a *t*3 transformation to the tetragonal subgroup $P4/mmm$. Further trans-

Figure 2
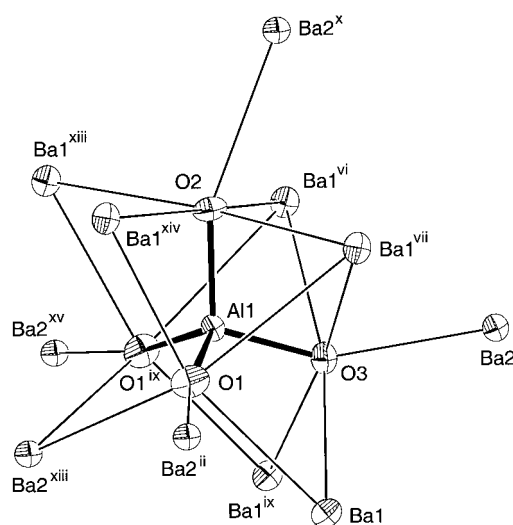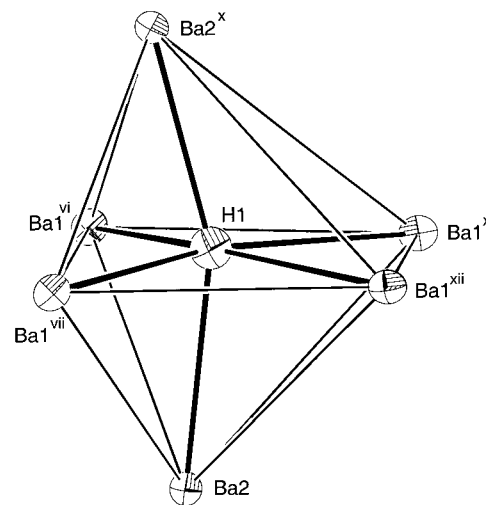*ORTEP* (Johnson, 1968) view of the $[HBa_6]$ octahedra (75% probability ellipsoids).

Figure 1
ORTEP (Johnson, 1968) view of the $[AlO_4]^{5-}$ anion together with the Ba atoms coordinating the O ligands (75% probability ellipsoids). Symmetry codes as in Table 1, with the addition of (x) $x - \frac{1}{2}, y - \frac{1}{2}, \frac{3}{2} - z$; (xi) $x, \frac{1}{2} - y, 1 + z$; (xii) $x, y, 1 + z$; (xiii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (xiv) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (xv) $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$.
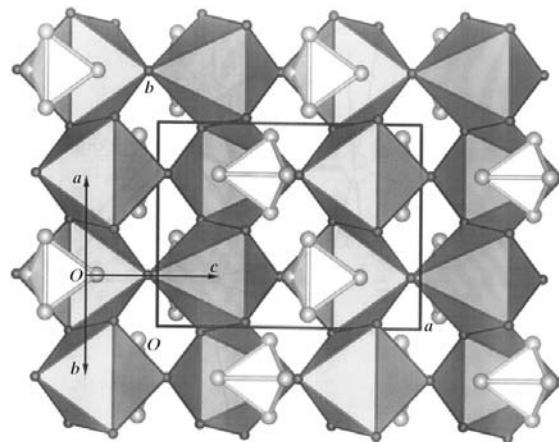

Figure 3
View of the unit cell (projection down [001]) of the crystal structure of $Ba_3(AlO_4)H$ (dark grey octahedra: $[HBa_6]$; light grey tetrahedra: $[AlO_4]$; vector triple: unit cell of the perovskite aristotype).

formation according to $a' = a + b$, $b' = a - b$ and $c' = c$ ($t2$) yields the space group $Cmmm$. Doubling of the c axis ($k2$ transformation) leads to the subgroup $Icmm = Cmcm$. A final $k2$ transformation with an origin shift ($x + \frac{1}{4}$, $y - \frac{1}{4}$, $z - \frac{1}{4}$) results in the space group $Pbnm = Pnma$ of the title compound. The coordination numbers of the Ba^{2+} cations by oxide and hydride ions are eight (Ba1) and nine (Ba2), respectively.

Experimental

Single crystals of $Ba_3(AlO_4)H$ are formed by reaction of a mixture of BaH_2 and corundum with a molar ratio of 6:1. BaH_2 (3.0 g, 21.53 mmol) and corundum (0.3658 g, 3.66 mmol) were heated in corundum crucibles under an argon atmosphere in steel autoclaves up to 1070 K within 8 h, held at this temperature for 6 h and cooled to room temperature at a rate of 40 K h^{-1}. The X-ray powder patterns of the samples can be perfectly indexed on the basis of the reported single-crystal data of $Ba_3(AlO_4)H$. The preparation of the corresponding deuteride was carried out substituting BaD_2. ^{2}H NMR experiments were performed on a Bruker Avance DSX 300 spectrometer operating at a deuterium resonance frequency of 46.07 MHz. A Bruker doubly tuned MAS probe for 4 mm outer diameter rotors was used. The powdered samples of $Ba_3(AlO_4)D$ and BaD_2 were sealed in KelF inserts, which in turn were tightly fitting into zirconia rotors with KelF caps. The rotation frequency was 15 kHz. Spectra were acquired with single 90° pulses at a dwell time of 50 µs. Four scans were taken at a recycle delay of 1 h. The 90° pulse width was 3.74 µs. The title compound contains only one crystallographically independent D^- ion, which gives rise to a peak at a chemical shift of 6.1 p.p.m. with respect to hexamethylbenzene-d_{18}. BaD_2 with two crystallographically independent D^--atom positions shows two lines in the spectrum, which at 8.3 and 9.1 p.p.m. appear in the same range as the signal of $Ba_3(AlO_4)D$.

Crystal data

$Ba_3(AlO_4)H$	Mo $K\alpha$ radiation
$M_r = 504.01$	Cell parameters from 2363
Orthorhombic, $Pnma$	reflections
$a = 10.4889\ (8)$ Å	$\theta = 6.331\text{–}56.533°$
$b = 8.1503\ (9)$ Å	$\mu = 18.932$ mm^{-1}
$c = 7.2440\ (12)$ Å	$T = 293\ (2)$ K
$V = 619.27\ (13)$ Å^3	Irregular, clear light red
$Z = 4$	$0.17 \times 0.12 \times 0.10$ mm
$D_x = 5.406$ Mg m^{-3}	

Data collection

Bruker AXS CCD diffractometer	752 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: multi-scan	$\theta_{max} = 28.31°$
($SADABS$; Sheldrick, 1996)	$h = -13 \rightarrow 13$
$T_{min} = 0.070$, $T_{max} = 0.151$	$k = -6 \rightarrow 10$
3661 measured reflections	$l = -9 \rightarrow 8$
810 independent reflections	

Table 1
Selected geometric parameters (Å).

Ba1—O2^i	2.744 (3)	Ba2—O1^{vii}	2.694 (3)
Ba1—O3	2.766 (3)	Ba2—H1^{viii}	2.80 (7)
Ba1—H1^{ii}	2.82 (5)	Ba2—O2^{viii}	2.828 (5)
Ba1—O2^{ii}	2.829 (3)	Ba2—O1^i	2.844 (3)
Ba1—O1	2.854 (3)	Ba2—O1^{iii}	2.844 (3)
Ba1—O1^{iii}	2.913 (3)	Ba2—H1	2.98 (8)
Ba1—H1^{iv}	2.97 (7)	Al1—O1^{ix}	1.750 (3)
Ba1—O3^{ii}	2.998 (3)	Al1—O1	1.750 (3)
Ba1—O1^v	3.191 (3)	Al1—O3	1.774 (5)
Ba2—O3	2.635 (4)	Al1—O2	1.780 (5)
Ba2—O1^{vi}	2.694 (3)		

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (iv) $x, y, z - 1$; (v) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (vii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$; (ix) $x, \frac{1}{2} - y, z$.

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.023$	$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2]$
$wR(F^2) = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.129$	$(\Delta/\sigma)_{max} = 0.025$
810 reflections	$\Delta\rho_{max} = 1.05$ e Å^{-3}
46 parameters	$\Delta\rho_{min} = -2.26$ e Å^{-3}

Data collection: $SMART$ (Bruker, 1999); cell refinement: $SAINT$ (Bruker, 1999); data reduction: $SAINT$; program(s) used to solve structure: $SHELXS$97 (Sheldrick, 1997); program(s) used to refine structure: $SHELXL$97 (Sheldrick, 1997); molecular graphics: $ORTEP$ (Johnson, 1968) and $DRAWxtl$ (Finger & Kroeker, 1999); software used to prepare material for publication: $SHELXL$97.

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