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Lithium Aluminium Borate, $LiAl_7B_4O_{17}$

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In $LiAl_7B_4O_{17}$ the aluminium ions are found in octahedral and trigonal bipyramidal sites, while the boron atoms are tricoordinated to oxygen atoms in planar triangular coordination. The AlO_6 octahedra form chains, by edge sharing, running along *c*. These chains are interconnected by assemblies of four AlO_5 trigonal bipyramids, with one common oxygen, and by B–O bonds. Lithium is found in the channels not occupied by AlO_5 groups. Crystals were grown from a $PbO–B_2O_3–Al_2O_3–Li_2O$ melt by cooling from 1575 to 775 K at a rate of 2 K h^{-1}. The title compound crystallizes in the tetragonal space group *I*4/*m* with unit cell parameters $a=10.5454(7)$ and $c=5.6246(4)$ Å, $Z=2$.

$LiAl_7B_4O_{17}$ was obtained by a by-product when $LiAl_5O_8$ was synthesized from the PbO/B_2O_3 flux. A better understanding of relationships in this system required a structure determination of this previously unknown compound. The same compound was concurrently also encountered during preparative work in a study comprising a search of novel Li^+ ion conductors in the $Li_2O–Al_2O_3–B_2O_3$ system.

Aluminium borate with a similar stoichiometry ($2Al_2O_3 \cdot B_2O_3$) is used as a catalyst for reduction of various organic compounds.[1] As 'whiskers' it has properties comparable to silicon carbide and finds applications as reinforcement materials in plastics and metal alloys.[2–5] The title compound is probably isostructural to $Cu_2Al_6B_4O_{17}$,[6] which is a catalyst used for dehydrocyclization of organic compounds.[7–10] The unit cell parameters of $a=10.594$ and $c=5.687$ Å for the copper compound as well as an identical space group strongly supports this conjecture. However, its crystal structure has not been determined.

Experimental

Crystals of $LiAl_7B_4O_{17}$ were grown from an equimolar $PbO–B_2O_3$ flux. Equal amounts of Al_2O_3 and Li_2CO_3 were ground together with PbO and B_2O_3, transferred to a platinum crucible and heated to 1575 K at a rate of 50 K h^{-1}. The melt was then left to soak for 8 h, after which the temperature was decreased by 2 K h^{-1} to 775 K and then to room temperature through self cooling. A mixture of transparent octahedral crystals ($LiAl_5O_8$), with edges up to 6 mm in length, and needle-shaped clear crystals ($LiAl_7B_4O_{17}$) with lengths up to 4 mm were produced. The two types of crystals were easily separated owing to their different morphology. The density of the needle-shaped crystals were determined by flotation in a $CHCl_3/CHBr_3$ solution.

Crystal data pertinent to the intensity data collection and least-squares refinement are given in Table 1. Three intensity control reflections were measured every 3600 s of X-ray exposure time with a maximum random variation of ±2%. Owing to an unknown experimental error all reflections of the type *hk*0 were lost. Systematically absent reflections indicated a body-centred tetragonal lattice, and the intensity distribution gave the Laue group 4/*m*. Space group *I*4/*m* was therefore selected. The space group determination was also confirmed by X-ray diffraction photographs, taken with de Jong and precession techniques. Data were corrected for Lorentz, polarization and absorption effects (XTAL3.4).[11] Aluminium and oxygen positions were determined by direct methods (SIR92)[12] in space group *I*4/*m*. The remaining oxygen, boron and lithium positions were found in subsequent Δρ-maps (DIRDIF).[13] The structure was refined by full-matrix least-squares (SHELXL-93)[14] minimizing $\Sigma w(|F_o|^2-|F_c|^2)^2$. Electron density difference maps showed that one of the aluminium positions was not fully occupied. The occupancy parameter for Al2 was therefore refined, and it converged to 75(1)%. In subsequent least-squares the value of the occupancy parameter for Al2 was fixed to 3/4. Reflex 004 was excluded from the refinement due to extinction. Δρ-maps showed residual electron density in the channels of the structure as two peaks with densities >1.0 e $Å^{-1}$. These positions were assumed to be two lithium sites. The occupancy

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Table 1. Crystal data and refinement parameters for $LiAl_7B_4O_{17}$.

Formula	$LiAl_7B_4O_{17}$
M_r	532.05
Crystal system	Tetragonal
Space group	$I4/m$ (No. 87)
a/Å	10.5454(7)
c/Å	5.6246(4)
V/Å^3	625.5(1)
Z	2
D_x/g cm^{-3}	2.84(2)
D_m/g cm^{-3}	2.82
μ/cm^{-1}	6.86
Crystal size/mm^3	$0.25 \times 0.04 \times 0.04$
No. of faces	6, {100} and {001}
Absorption correction	Numerical integration, grid $8 \times 4 \times 4$
Diffractometer	Enraf–Nonius CAD-4
Radiation/Å	0.71069 (Mo $K\alpha$)
Scan type	$\omega/2\theta$ scan
Scan width/°	$\Delta\omega = 0.97 + 0.37 \tan\theta$
Maximum scan time/s	60
θ-range for data collection/°	$2 < \theta < 35$
θ-range for unit cell dimensions/°	$31 < \theta < 44$ (21 reflections)
Transmission factor range	0.84–0.86
Number of reflections	
Measured	1355
Independent	621
Observed, $I > 2\sigma(I)$	520
R_{int}	0.018
hkl range	h=0–17; k=0–17; l=1–9
Refinement on	F^2
Least-squares weight	$w = [\sigma^2(F) + (0.04P)^2 + 2.26P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F, I > 2\sigma(I)]$	0.039
$R_w(F^2)$	0.117
S	1.05
Number of reflections in refinement	620
Number of parameters	49
$(\Delta/\sigma)_{max}$	<0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.67, −0.62
Extinction correction[14]	0.0005(56)

parameter for Li was constrained to give a total charge of two for these sites. This model resulted in a decrease of R_w from 0.19 to 0.12 (F^2, all data). Anisotropic displacement parameters were used for all atoms except for lithium, which was assigned a fixed isotropic displacement parameter of U=0.01 Å. Atomic scattering factors and anomalous dispersion factors were taken from Ref. 15.

Single crystals of $LiAl_2B_4O_{17}$ were also obtained by cooling a melted mixture of $Li_4B_4O_7$ and the double amount of Al_2O_3 in a platinum crucible. The sample was heated to 1325 K, held for 1 h, cooled to 1175 K at a rate of 600 K h^{-1}, then cooled to 975 K h^{-1} at a rate of 10 K h^{-1} and finally cooled to room temperature by removal from the furnace. A second data set was collected using a crystal prepared by this method. Least-squares refinements yielded an Al–B–O framework identical to that found for the crystal obtained from the PbO–B_2O_3 flux. Only minor residual electron density was, however, observed in the channels, and the Li atom positions could not be reliably assessed. These results indicate that the Li^+ ions can occupy several positions in the channels. The difference in the Li atom distribution in the crystals prepared by the two methods might be connected to the different temperature profiles employed in the syntheses. Lists of observed and calculated structure factors and anisotropic displacement parameters are available from one of the authors (G.S.) as well as data and results from the second data set.

Table 2. Observed and calculated 2θ values for the Guinier–Hägg diffraction pattern of $LiAl_7B_4O_{17}$ up to the 20th observed line: $\Delta 2\theta = 2\theta_{obs} - 2\theta_{calc}$. λ = 1.540598 Å. Cell figures-of-merit: M_{20} = 89, F_{20} = 85 (0.0091, 26).[21]

hkl	$2\theta_{obs}$/°	$\Delta 2\theta$/°	d_{obs}/Å	$10^2 I/I_0$
110	11.904	0.016	7.43	17
200	16.840	−0.002	5.26	100
101	17.908	0.016	4.949	20
220	23.921	0.015	3.717	1
211	24.674	0.006	3.605	12
310	26.790	0.012	3.325	2
301	30.028	0.007	2.974	3
002	31.886	0.037	2.804	1
400	34.073	0.010	2.629	37
321	34.634	0.015	2.588	1
202	36.247	0.007	2.4763	8
420	38.225	−0.005	2.3526	1
411	38.737	0.003	2.3227	1
222	40.225	0.013	2.2401	5
312	42.084	0.004	2.1454	36
510	43.849	0.002	2.0630	17
501	46.037	0.006	1.9699	10
103	49.421	0.002	1.8427	6
530	50.568	0.018	1.8035	17
422	50.568	−0.014	1.8035	
600	52.127	0.003	1.7532	3

Powder samples of $LiAl_7B_4O_{17}$ were prepared by heat treating intimately ground and pelleted mixtures of p.a. quality $Li_4B_4O_7$, Al_2O_3 and B_2O_3. The pellets were held at 800 °C for 5 days and then rapidly cooled. Stoichiometric mixtures, $Li_4B_4O_7$–$7Al_2O_3$–$2B_2O_3$, yielded samples that contained minor amounts of Al_2O_3. An X-ray pure sample were obtained from a mixture with composition $1.05Li_4B_4O_7$–$7Al_2O_3$–B_2O_3. The cell dimensions a = 10.5197(4), c = 5.6151(4) Å, V = 621.4 Å^3 were obtained from Guinier–Hägg data, using Si as an internal standard. The indexed powder pattern, for the first 20 observed lines, is given in Table 2.

Description of the structure

Final atomic coordinates and equivalent displacement parameters are given in Table 3 and selected geometrical parameters in Table 4. Displacement ellipsoid plots of the Al coordination are shown in Fig. 1 and two polyhedral drawings of the structure in Fig. 2.

Elongated octahedra about Al1 are formed by axial O1, O1^{i} and equatorial O3, O3^{ii}, O4 and O4^{ii} atoms (Fig. 1); symmetry codes are given in Table 4. These

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).[a]

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	Occupancy
Al1	1/4	1/4	1/4	0.0069(2)	1
Al2	0.17675(11)	0.02428(10)	0	0.0142(3)	3/4
B	0.2397(3)	0.4975(2)	0	0.0112(4)	1
Li1	0.3983(7)	−0.0087(7)	0	0.01	0.370(4)
Li2	0.2838(21)	0.0101(21)	0	0.01	0.130(4)
O1	0.2423(2)	0.43174(14)	0.2122(2)	0.0192(4)	1
O2	0	0	0	0.0311(11)	1
O3	0.1433(2)	0.2110(2)	0	0.0087(3)	1
O4	0.3728(2)	0.2429(2)	0	0.0088(3)	1

[a] $U_{eq} = 8/3\pi^2[U_{11}(aa^*) + U_{22}(bb^*) + U_{33}(cc^*)]$.

Table 4. Selected bond distances (in Å) and angles (in °) with e.s.d's in parentheses.

AlO_6 octahedron			
Al1–O1^{i} (×2)	1.9300(15)	O1–Al1–O3^{ii}	83.59(8)
Al1–O3^{ii} (×2)	1.8473(14)	O1–Al1–O4^{ii}	90.78(8)
Al1–O4^{ii} (×2)	1.9131(14)	O3–Al1–O4^{ii}	81.03(7)
		O1–Al1–O1^{i}	180
AlO_5 trigonal bipyramid			
Al2–O1^{iii} (×2)	1.8879(15)	O1^{i}–Al2–O2	118.78(7)
Al2–O2	1.8814(12)	O1^{iv}–Al2–O3^{i}	98.64(7)
Al2–O3^{iv}	1.8037(24)	O2^{iv}–Al2–O3^{iv}	93.73(8)
Al2–O3	2.0004(24)	O3^{iii}–Al2–O3^{iv}	178.61(12)
		O1–Al2–O1^{i}	118.06(10)
BO_3 triangle			
B–O1	1.381(2)	O1–B–O4^{vi}	120.11(10)
B–O4^{vi}	1.368(4)	O1–B–O1^{v}	119.65(7)
Lithium			
Li1–O1^{iii} (×2)	2.344(6)	Li2–O1^{iii} (×2)	1.753(9)
Li1–O3^{iv}	2.432(8)	Li2–O3^{iv}	1.791(22)
Li1–O4	2.667(8)	Li2–O3	2.585(22)
Li1–O1^{iv,vii}	2.760(7)	Li2–O4	2.628(22)
		Li2–O2	2.995(22)

Symmetry operations used. i: $1/2-x$, $1/2-y$, $1/2-z$; ii: $1/2-x$, $1/2-y$, $1/2+z$; iii: $1/2-x$, $1/2-y$, $-1/2+z$; iv: y, $-x$, z; v: x, y, $-z$; vi: y, $-x+1$, z; vii: x, $-y$, $-z$.

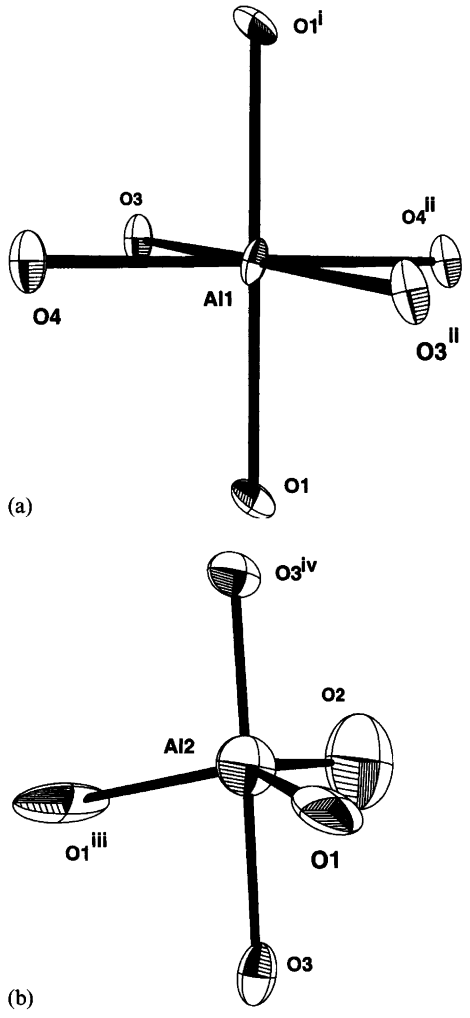

Fig. 1. The coordination around Al1 and Al2. Atoms are displayed as displacement ellipsoids at a probability level of 70%. Symmetry codes are in Table 4.

octahedra form zig-zag chains along *c*, ($x = 1/4$, $y = 1/4$) by sharing the O3–O4 and O3^{ii}–O4^{ii} edges (Fig. 2). The dihedral angle between the equatorial planes in two adjacent octahedra is 20.35(5)°. The chains of octahedra are crosslinked in two ways. First by the boron atoms (Fig. 2), since each boron is bounded to two O1 atoms in one chain and one O4 atom in another. The second type of connection is produced by the Al2 and O2 atoms. The O2 atoms, in position 2(a) with symmetry 4/*m*, occupy the centre of each second channel formed between the chains of octahedra. Each O2 is surrounded by four Al2 positions, position 8(h), with occupancy 3/4 (see Experimental section), resulting in a polyhedral unit of four edge-sharing trigonal bipyramids (Fig. 2), formed by the O1 and O3 atoms of the octahedral chains and the common oxygen atom O2. Since the occupancy of Al2 is only 3/4 one of the four Al2 positions in the polyhedral unit is empty. Each trigonal bipyramid has an equatorial plane formed by the O2 atom and O1 and O1^{iii} atoms from the same octahedral chain, while the axial O3 and O3^{i} atoms are from two different chains.

The two O3–O4 edges of the octahedral unit, 2.443(3) Å, are shorter than the other ten edges in this polyhedron, these are in the range 2.699(2)–2.8591(6) Å. Thus the octahedron is distorted with three different

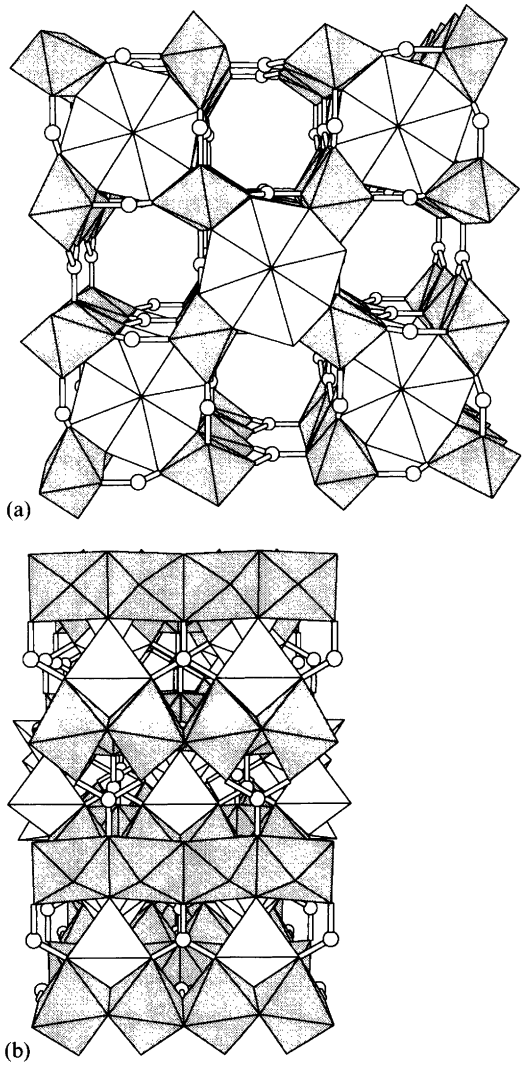

Fig. 2. Polyhedral drawing of $LiAl_7B_4O_{17}$ viewed along **c** in (a) and along **b** in (b). The octahedra rows are shown in grey and the B atoms as circles. The polyhedral units of four edge-sharing trigonal bipyramids are shown in white with the shared oxygen O2 in the centre. Note that one of the four bipyramids in each polyhedral unit is empty.

Al–O bond lengths and a range of O–Al–O angles. The trigonal bipyramid is more regular, with equal Al–O bond lengths and O–Al–O bond angles near 120° in the equatorial plane. Al2 is 0.230(13) Å out of the equatorial plane, with a difference in bond lengths of 0.197(3) Å between the two axial Al–O bonds.

Refinement of the occupancy factor for Al2 showed that every fourth Al2 atom is missing. This is in accordance with the electrostatic bond strength model, where a four fully occupied Al2 sites would result in a formal charge of −2.4 for O2. The disturbance caused by the partially occupied Al2 sites is also reflected in the enlarged displacement ellipsoid for O2 (Fig. 1b).

The BO_3 group is close to ideal with B–O bond lengths in the range 1.368(3)–1.381(2) Å and with B displaced 0.029(7) Å from the plane through the three oxygen atoms. This is in agreement with values found in $B(OH)_3$.[16] The lithium atoms are located in the channels not occupied by the polyhedral unit of four trigonal bipyramids. The diameter of these channels is ca. 3.5 Å. Their positions are rather approximate due to the small X-ray scattering power of Li. The Li positions are only partially occupied (Table 3), which is in agreement with geometrical considerations. The Li–O distances are reasonable, ranging from 1.753(9)–2.995(22) and 2.244(6)–2.760(7) Å, for the two lithium atoms, respectively.

Discussion

The most prominent features of the title compound are the chains of edge-sharing octahedra in one dimension. This arrangement is also found in sillimanite (Al_2SiO_5),[17] andalusite (Al_2SiO_5),[18] mullite ($Al_2O_3 \cdot SiO_2$)[19] and in $9Al_2O_3 \cdot 2B_2O_3$.[20] Polyhedral drawings of these structures are shown in Fig. 3, and some relevant crystallographic data are listed in Table 5. If only the chains of octahedra are considered, the unit cells can be transformed to an approximately tetragonal unit cell similar to all structures. The octahedral chains are, however, quite different in the title compound compared to the other. In andalusite, sillimanite and mullite the equatorial planes of the octahedra in the chains are parallel. This can be described by the two O3–O4–O3 angles, in the equatorial plane, along the octahedral chains. These angles are 179.0(2), 171.8(2) and 180.0(1)° for andalusite, sillimanite and mullite, respectively. In the title compound the corresponding angles are 159.1(6)°, which gives the chains a wave-like appearance (Fig. 2b). The mixed oxide $9Al_2O_3 \cdot 2B_2O_3$ represents an intermediate between the two types described above, with angles of 155.4(2) and 179.9(2)° on each side of the chain. As can be seen from Fig. 3 there are differences between the structures but they also represent a set of structures where the coordination number of Al gradually goes from four and six to five and six. In sillimanite and mullite aluminium (and silicon) are four and six coordinated. In the mixed oxide $9Al_2O_3 \cdot 2B_2O_3$ and in andalusite aluminium (and silicon in andalusite), are four-, five- and six-coordinated while in the title compound aluminium are only five and six coordinated. Similarities and differences between andalusite, mullite, sillimanite and $9Al_2O_3 \cdot 2B_2O_3$ have been discussed by Garsche and co-workers.[20] In the title compound the octahedral chains are connected by boron in two dimensions (Fig. 2), while in $9Al_2O_3 \cdot 2B_2O_3$ the boron connections are one-dimensional only (Fig. 3).

The lithium atoms in the channels of the title compound are not easy to remove. Attempts of ion exchange of Li^+ for Na^+ or K^+ have been unsuccessful. This might be due to the boron atoms which are strongly bound to the framework in the structure, thus preventing the ions in the channels from moving freely. Another reason is that channels are running in one direction only, thus preventing the 'free' movement necessary for ion exchange. Ion conductivity measurements have not been made.

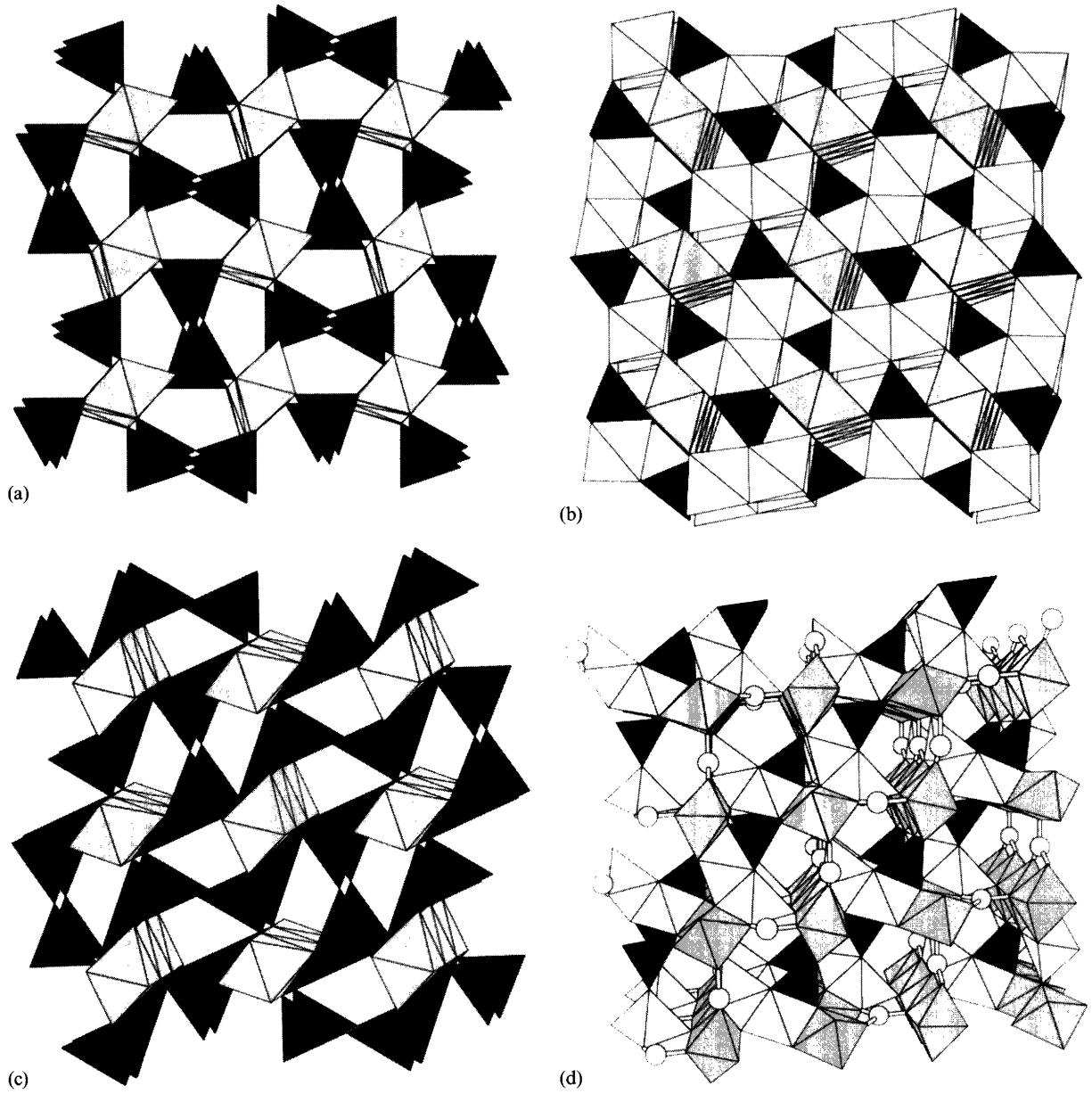

Fig. 3. Perspective views of (a) sillimanite (Al_2SiO_5),[17] (b) andalusite (Al_2SiO_5),[18] (c) mullite ($Al_2O_3 \cdot SiO_2$)[19] and (d) $9Al_2O_3 \cdot 2B_2O_3$.[20] The octahedra rows are shown in light grey. Tetrahedra are shown in dark grey and AlO_5 polyhedra in white. In sillimanite the tetrahedra are occupied by silicon and aluminium, which is shown by a difference in colour.

Table 5. Selected structural parameters for mullite,[17] sillimanite,[22] andalusite,[18] $9Al_2O_3 \cdot 2B_2O_3$[19] (A_9B_2 below) and the title compound.

Compound:	Mullite	Sillimanite	Andalusite	A_9B_2	Title
M_r	168.61	162.05	162.05	1056.9	532.05
Space group	*Pbam*	*Pbnm*	*Pnnm*	$Cmc2_1$	*I4/m*
a/Å	7.584(3)	7.584(3)	7.4856(6)	7.7942(2)	10.5454(7)
b/Å	7.693(3)	7.6738(3)	7.8985(2)	15.0110(2)	10.5454(7)
c/Å	2.890(1)	5.7698(8)	5.559(2)	5.6689(1)	5.6246(4)
V/Å^3	168.6(2)	332.3(1)	342.5(1)	654.8(1)	625.5(1)
D_x/g cm^{-3}	3.12	3.24	3.14	2.68	2.84

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