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The Structure of Sodium Borate $Na_3[B_5O_9].H_2O$

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Abstract

$3Na_2O.5B_2O_3.2H_2O$ is a new phase synthesized at 523 K under hydrothermal conditions. Crystal data are: crystal-chemical formula $Na_3[B_5O_9].H_2O$, M_r = 285·03, a = 11·2373 (2), b = 6·0441 (1), c = 11·1336 (2) Å, $Pca2_1$, Z = 4, V = 756·2 Å^3, D_x = 2·504 Mg m^{-3}, μ(Mo $K\alpha$) = 0·397 mm^{-1}, $F(000)$ = 560. Direct methods were used to solve the structure which was later refined by least-squares calculations to an R of 0·030 for 1060 observed reflexions. The basic structural unit is the polyanion $[B_5O_9]^{3-}$, composed of three tetrahedra and two triangles. These pentaborate groups are polymerized to form an open B—O framework, with three series of channels parallel to **a**, **b** and **c**. The water molecule and the Na atoms, whose corner-sharing polyhedra build in their turn an Na—O framework, are located in the channels.

Introduction

The present paper deals with the crystal structure of the compound $Na_3[B_5O_9].H_2O$, corresponding to the $Na_2O:B_2O_3:H_2O$ molar proportions 3:5:2 (hereafter 3:5:2). It is a new phase obtained during the study of the sodium hydroxide–boron trioxide–water system under hydrothermal conditions, at 523 K. The structural study was performed in order to confirm the chemical composition determined by analytical methods and also to contribute to the crystal-chemical knowledge of sodium borates.

According to the structural results 3:5:2 can be placed, in the crystal-chemical classification of Tennyson (1963), among the tectoborates. However, in the scheme of crystal-chemical classification proposed by Christ & Clark (1977) the present phase should be regarded as a pentaborate $5:2\Delta + 3T$.

Experimental

Crystals of the compound 3:5:2 were obtained from a mixture of B_2O_3 and NaOH held in a hydrothermal environment at 523 ± 5 K in a pressure vessel for 48 h. Crystals often have short prismatic habit with an $\{h0l\}$ prism well developed.

Crystal data are given in the *Abstract*. Lattice constants were determined from 25 high-angle reflexions measured on a single-crystal diffractometer at 291 K. The diffraction symmetry is *mmm*; the systematic extinctions are consistent with the space group *Pbcm* or the corresponding noncentrosymmetric $Pca2_1$. The structure solution indicates the latter.

Intensities were measured with a Philips PW 1100 four-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy), with Mo $K\alpha$ radiation. A total of 1157 reflexions were measured in the range $2 < \theta < 30°$; 1060 were judged to be observed according to the criterion $F_o \geq 5\sigma(F_o)$. Intensities were corrected for Lorentz–polarization effects and for absorption, the latter being carried out on the basis of the semi-empirical method proposed by North, Phillips & Mathews (1968).

The structure was solved by direct methods using the *MULTAN* program (Main, Woolfson, Lessinger, Germain & Declercq, 1974). All 200 reflexions with $E \geq 1{\cdot}33$ were included in the phase-determining process. Non-hydrogen atoms were located on F_o Fourier maps while H atoms were positioned by means of a ΔF Fourier synthesis. The refinement was carried out by full-matrix least squares, using first isotropic and then anisotropic (except H atoms) thermal parameters, to give a final $R = 0{\cdot}030$ for the observed reflexions (R = 0·036 for all data). A weight $w = 1/\sigma^2(F_o)$, with σ derived from counting statistics, was given to all observed reflexions. Scattering-factor curves for all atoms were taken from *International Tables for X-ray Crystallography* (1974). Positional parameters and equivalent isotropic thermal parameters are given in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters and an *ab* projection of the B–O framework have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38037 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

The *B*'s of the non-hydrogen atoms are the equivalent ones, after Hamilton (1959).

	x	*y*	*z*	*B* (Å²)
Na(1)	0·3614 (1)	0·0794 (2)	0·2500	1·53
Na(2)	0·5647 (1)	0·5250 (2)	0·2561 (2)	1·79
Na(3)	0·2430 (1)	0·3486 (2)	0·5061 (3)	1·49
B(1)	0·7473 (4)	0·1355 (4)	0·5125 (5)	0·58
B(2)	0·9584 (3)	0·2774 (5)	0·5088 (4)	0·67
B(3)	0·6045 (3)	0·0394 (5)	0·3482 (3)	0·64
B(4)	0·9118 (3)	−0·0645 (5)	0·6278 (3)	0·61
B(5)	0·5399 (3)	0·3264 (5)	0·4975 (4)	0·47
O(1)	0·7096 (2)	−0·0015 (4)	0·4074 (2)	0·66
O(2)	0·7878 (2)	−0·0034 (4)	0·6093 (2)	0·60
O(3)	0·6517 (2)	0·2761 (4)	0·5563 (3)	0·74
O(4)	0·8447 (2)	0·2842 (4)	0·4654 (3)	0·87
O(5)	1·0414 (2)	0·4295 (3)	0·4707 (2)	0·63
O(6)	0·9928 (2)	0·1193 (3)	0·5895 (2)	0·66
O(7)	0·5671 (1)	−0·0997 (3)	0·2587 (3)	0·63
O(8)	0·5322 (2)	0·2133 (3)	0·3776 (2)	0·60
O(9)	0·4377 (1)	0·2769 (3)	0·5700 (2)	0·57
O(10)	0·3006 (2)	0·4974 (4)	0·2534 (4)	1·96
H(1)	0·321 (4)	0·578 (7)	0·182 (5)	3·3 (9)
H(2)	0·314 (4)	0·585 (7)	0·311 (4)	3·1 (9)

Discussion

The present structure consists of an open three-dimensional borate framework with channels parallel to **a**, **b** and **c**, where Na atoms and the water molecule are located.

The basic unit of the three-dimensional network is the pentaborate polyanion $[B_5O_{12}]^{9-}$, with point symmetry 1. It is formed by two triangles and three tetrahedra and consists of two similar six-membered alternating B–O rings, in approximately perpendicular planes.

The same pentaborate polyanion of the 3:5:2 compound has been found in other structures. In ulexite, $NaCa[B_5O_6(OH)_6].5H_2O$ (Clark & Appleman, 1964; Ghose, Wan & Clark, 1978), it exists in the isolated and fully hydrated form. In garrelsite, $NaBa_3[Si_2B_7O_{16}(OH)_4]$ (Ghose, Wan & Ulbrich, 1976), the $[B_5O_{12}]^{9-}$ groups are linked together, through Si tetrahedra and additional B tetrahedra, to form silicoborate sheets. In probertite, $NaCa[B_5O_7(OH)_4].3H_2O$ (Rumanova, Kurbanov & Belov, 1966; Menchetti, Sabelli & Trosti-Ferroni, 1982), the polyanion is polymerized in chains by sharing a tetrahedral corner with a triangular corner of the adjacent polyanion. In $Na_3[B_5O_8(OH)_2].H_2O$ (Menchetti & Sabelli, 1977), and in heidornite, $Na_2Ca_3Cl[B_5O_8(OH)_2](SO_4)_2$ (Burzlaff, 1967), the polymerization results in a two-dimensional network. Finally, in hilgardite, $Ca_2[B_5O_9]Cl.H_2O$ (Ghose & Wan, 1979), the polyanions are connected to each other to form a three-dimensional framework.

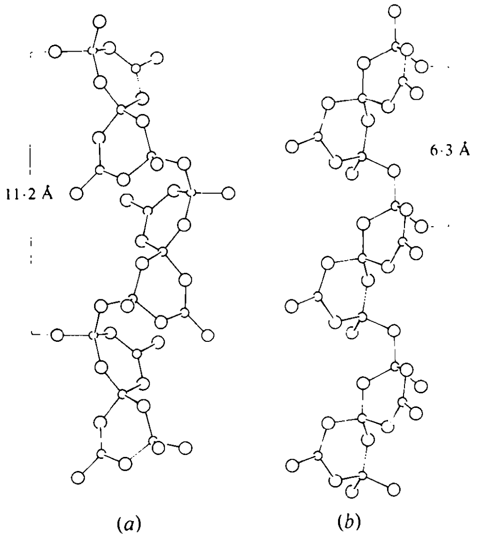

Fig. 1. B–O chains in (*a*) 3:5:2 and (*b*) hilgardite.

In 3:5:2, the pentaborate polyanions form chains parallel to **a** by sharing two tetrahedral corners. As shown in Fig. 1, the repeat unit of the chain comprises two interlinked pentaborate polyanions: this accounts for the ~11·2 Å *a* axis, almost twice the length of the polyanion. A similar chain, but with a halved repeat unit, is present in hilgardite. However, the *c* dimension of hilgardite (6·3 Å) is longer than *a*/2 in 3:5:2, since hilgardite chains are more stretched. Connexions between adjacent chains in 3:5:2 take place in the **b** and **c** directions (see Figs. 2 and 3) by means of O atoms which are common corners of a triangle and a tetrahedron. Each chain is connected to four adjacent chains, and an open borate framework with the asymmetric unit $[B_5O_9]^{3-}$ is formed in this way. Fig. 3 shows a peculiar aspect of this framework, viewed in the **a** direction. In the channel, created by four interlinked chains, are located the Na(2) atoms and the water molecule. Channels parallel to **b** (see Fig. 2) and **c** are irregularly shaped.

Tables 2 and 3 report interatomic distances and angles. The average tetrahedral B–O distances within the B(1), B(4) and B(5) tetrahedra are 1·475, 1·478 and 1·473 Å respectively, with an overall mean value of 1·475 Å. However, within each tetrahedron, the two bond distances between the B and O atoms also belonging to triangles are significantly longer than the other two; the overall mean values are 1·500 and 1·450 Å respectively. On the other hand, B–O triangular distances are rather homogeneous (1·367–1·377 Å). In fact, all the O atoms linked to a triangular B have a similar environment in that they belong also to a borate tetrahedron and to Na polyhedra. The average B–B separations are 2·529 and 2·539 Å in rings 1 and 2, respectively. These values are greater than those found in other borates with the same polyanion; for instance, the value found in $Na_3[B_5O_8(OH)_2].H_2O$ (Menchetti & Sabelli, 1977) is 2·50 Å for both rings, while in hilgardite the values are 2·474 and 2·448 Å, respectively. The two B—O rings are almost perpendicular to each other. Information on the mean planes

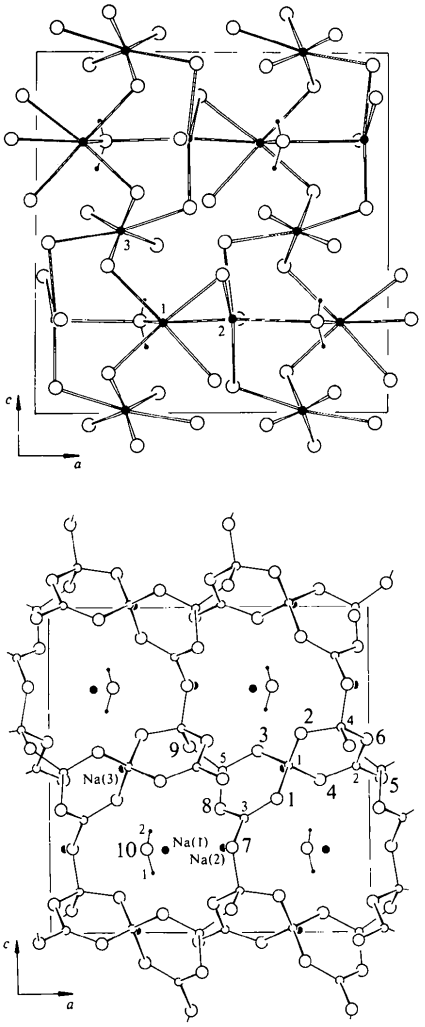

Fig. 2. Projections along the *b* axis of the Na—O framework (top) and of the B—O framework (bottom), with Na(1) and water in the channels parallel to **b**. Numbering refers to B atoms (small circles), O atoms (large circles), Na atoms (filled circles) and H atoms (dots).

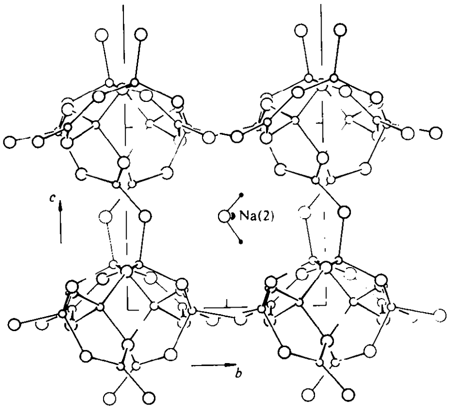

Fig. 3. A *bc* projection of the B—O framework showing Na(2) and water in the channels parallel to **a**.

Table 2. Na—O, B—O *bond distances*, B—B *distances and* O—O *edges of boron coordination polyhedra* (Å)

Na(1)—O(7)	2·554 (2)	B(3) triangle	
Na(1)—O(8)	2·521 (2)	B(3)—O(1)	1·375 (4)
Na(1)—O(10)	2·618 (3)	B(3)—O(7)	1·370 (4)
Na(1)—O(2$^{\mathrm{iv}}$)	2·340 (2)	B(3)—O(8)	1·368 (4)
Na(1)—O(6$^{\mathrm{vi}}$)	2·436 (2)	Mean	1·371
Na(1)—O(1$^{\mathrm{x}}$)	2·491 (2)	O(1)—O(7)	2·378 (3)
Mean	2·493	O(1)—O(8)	2·402 (3)
		O(7)—O(8)	2·342 (3)
Na(2)—O(9$^{\mathrm{vii}}$)	2·393 (3)	Mean	2·374
Na(2)—O(8)	2·348 (3)		
Na(2)—O(7$^{\mathrm{ii}}$)	2·269 (2)	B(4) tetrahedron	
Na(2)—O(5$^{\mathrm{ix}}$)	2·419 (3)	B(4)—O(2)	1·456 (4)
Na(2)—O(10$^{\mathrm{iii}}$)	2·655 (3)	B(4)—O(6)	1·498 (4)
Mean	2·417	B(4)—O(7$^{\mathrm{v}}$)	1·492 (5)
		B(4)—O(9$^{\mathrm{viii}}$)	1·465 (4)
Na(3)—O(9)	2·341 (2)	Mean	1·478
Na(3)—O(5$^{\mathrm{i}}$)	2·351 (3)	O(2)—O(6)	2·430 (3)
Na(3)—O(3$^{\mathrm{ix}}$)	2·551 (3)	O(2)—O(7$^{\mathrm{v}}$)	2·401 (3)
Na(3)—O(4$^{\mathrm{ix}}$)	2·537 (3)	O(2)—O(9$^{\mathrm{viii}}$)	2·400 (3)
Na(3)—O(1$^{\mathrm{x}}$)	2·398 (3)	O(6)—O(7$^{\mathrm{v}}$)	2·398 (4)
Na(3)—O(2$^{\mathrm{x}}$)	2·434 (3)	O(6)—O(9$^{\mathrm{viii}}$)	2·482 (3)
Mean	2·435	O(7$^{\mathrm{v}}$)—O(9$^{\mathrm{viii}}$)	2·358 (4)
		Mean	2·412
B(1) tetrahedron			
B(1)—O(1)	1·495 (5)	B(5) tetrahedron	
B(1)—O(2)	1·440 (5)	B(5)—O(3)	1·449 (4)
B(1)—O(3)	1·454 (5)	B(5)—O(8)	1·502 (5)
B(1)—O(4)	1·510 (5)	B(5)—O(9)	1·435 (4)
Mean	1·475	B(5)—O(5$^{\mathrm{ix}}$)	1·505 (4)
		Mean	1·473
O(1)—O(2)	2·413 (3)		
O(1)—O(3)	2·447 (4)	O(3) O(8)	2·430 (4)
O(1)—O(4)	2·388 (3)	O(3)—O(9)	2·410 (3)
O(2)—O(3)	2·354 (3)	O(3)—O(5$^{\mathrm{ix}}$)	2·368 (3)
O(2)—O(4)	2·449 (4)	O(8)—O(9)	2·421 (3)
O(3)—O(4)	2·394 (4)	O(8)—O(5$^{\mathrm{ix}}$)	2·396 (3)
Mean	2·407	O(9)—O(5$^{\mathrm{ix}}$)	2·393 (3)
		Mean	2·403
B(2) triangle			
B(2)—O(4)	1·367 (4)	Ring 1	
B(2)—O(5)	1·377 (4)	B(1)—B(2)	2·523 (5)
B(2)—O(6)	1·367 (4)	B(1)—B(4)	2·555 (6)
Mean	1·370	B(2)—B(4)	2·510 (5)
		Mean	2·529
O(4)—O(5)	2·379 (3)		
O(4)—O(6)	2·381 (4)		
O(5)—O(6)	2·358 (3)	Ring 2	
Mean	2·373	B(1)—B(3)	2·502 (6)
		B(1)—B(5)	2·606 (5)
		B(3)—B(5)	2·510 (5)
		Mean	2·539

Symmetry code

None x, y, z
(i) $-1 + x, y, z$
(ii) $x, 1 + y, z$
(iii) $-\frac{1}{2} + x, 1 - y, z$
(iv) $1 - x, -y, -\frac{1}{2} + z$
(v) $\frac{1}{2} - x, y, \frac{1}{2} + z$
(vi) $\frac{1}{2} - x, y, -\frac{1}{2} + z$
(vii) $1 - x, 1 - y, -\frac{1}{2} + z$
(viii) $\frac{1}{2} + x, -y, z$
(ix) $-\frac{1}{2} + x, 1 - y, z$
(x) $-\frac{1}{2} + x, -y, z$

and the values of dihedral angles in the polyanion are given in Table 4.

The three independent Na atoms are irregularly coordinated by O atoms which, except for O(10), also belong to the borate framework. Both Na(1) and Na(3) are linked to six O atoms, while Na(2) links five O atoms only. The coordination polyhedron around Na(3) is interesting in that it resembles a bisphenoid with two additional corners. The bisphenoid consists of four O atoms belonging to two B(1) tetrahedra of two adjacent unit cells (see Fig. 2). The Na—O distances range from 2·269 to 2·655 Å, with an overall mean value of 2·450 Å; the next-nearest O atoms are at 2·938 (5) and 2·973 (3) Å from Na(3) and Na(2) respectively. The above values are, on the whole, in agreement with those found in the literature, where irregular coordination polyhedra around Na atoms are often described (see, for instance, Menchetti & Sabelli, 1979). Na polyhedra are connected to each other by corner sharing to form a three-dimensional network interconnected with the borate one. The open character of the structure, deriving only from the particular arrangement of the borate framework, does not appear so evident if one takes into account the whole structural building. In fact, in accordance with the compact packing of the structure, the density of 3:5:2 is 2·50 Mg m^{-3}. This value is higher than those found in other hydrated sodium borates; *e.g.* 2·34 and 2·28 Mg m^{-3} in the compounds 3:3:2 and 1:2:1, respectively (Corazza, Menchetti, Sabelli & Stoppioni, 1977).

As previously described, the two independent H atoms were located from a difference Fourier synthesis and then refined. In Table 5 the distances and the angles involving the water molecule are reported. All the values are in good agreement with those generally found in X-ray crystal structure determinations. The donor–acceptor distances are fairly short; therefore, the related H bonds are to be considered rather strong.

The electrostatic valence balance, computed according to Brown & Shannon (1973), is given in Table 6. The balance is fully satisfactory for all the O atoms, except for O(7), which appears to be overbonded, and for O(10) belonging to the water molecule, which is underbonded. A noticeable improvement in the balance takes place when 'long' Na—O distances (with values close to 3·0 Å) are taken into account.

Table 3. O—B—O *and* B—O—B *angles* (°)

O(1)—B(1)—O(2)	110·6 (2)	O(2)—B(4)—O(6)	110·7 (2)
O(1)—B(1)—O(3)	112·1 (3)	O(2)—B(4)—O(7^{v})	109·1 (2)
O(1)—B(1)—O(4)	105·3 (4)	O(2)—B(4)—O(9^{viii})	110·5 (2)
O(2)—B(1)—O(3)	108·9 (4)	O(6)—B(4)—O(7^{v})	106·7 (2)
O(2)—B(1)—O(4)	112·2 (3)	O(6)—B(4)—O(9^{viii})	113·8 (2)
O(3)—B(1)—O(4)	107·7 (2)	O(7^{v})—B(4)—O(9^{viii})	105·8 (2)
O(4)—B(2)—O(5)	120·3 (3)	O(3)—B(5)—O(8)	110·9 (3)
O(4)—B(2)—O(6)	121·2 (3)	O(3)—B(5)—O(9)	113·3 (3)
O(5)—B(2)—O(6)	118·5 (3)	O(3)—B(5)—O(5^{ix})	106·6 (2)
		O(8)—B(5)—O(9)	111·0 (2)
O(1)—B(3)—O(7)	120·1 (3)	O(8)—B(5)—O(5^{ix})	105·7 (3)
O(1)—B(3)—O(8)	122·2 (3)	O(9)—B(5)—O(5^{ix})	108·9 (2)
O(7)—B(3)—O(8)	117·6 (3)		
Ring 1		Ring 2	
B(1)—O(4)—B(2)	122·5 (3)	B(1)—O(1)—B(3)	121·3 (3)
B(2)—O(6)—B(4)	122·2 (2)	B(3)—O(8)—B(5)	121·9 (2)
B(4)—O(2)—B(1)	123·8 (3)	B(5)—O(3)—B(1)	127·7 (3)

Table 4. *Displacements of other atoms* ($\sigma \simeq 0·01$ Å) *from the planes of the ring* O *atoms, and dihedral angles* ($\sigma \simeq 0·2°$) *in the polyanion*

	Ring 1		Ring 2	
Ring O atoms	O(2),O(4),O(6)		O(1),O(3),O(8)	
Associated atoms	B(1)	−0·09 Å	B(1)	0·22 Å
	B(2)	0·10	B(3)	−0·13
	B(4)	−0·34	B(5)	−0·14
	O(5)	0·30	O(7)	−0·45
	O(7^{v})	0·49	O(9)	−1·35
	O(9^{viii})	−1·73	O(5^{ix})	1·04
Angle between rings (°)	86·7			
O atoms of triangle	O(4),O(5),O(6)		O(1),O(7),O(8)	
B atom of triangle	B(2) 0·005 Å		B(3) −0·013 Å	
Triangle–ring angle (°)	8·6		12·8	

Table 5. *Water-molecule geometry*

O(10)—O(3^{vii})	2·641 (5) Å	O(3^{vii})—O(10)—O(4^{ix})	115·3 (1)°
O(10)—O(4^{ix})	2·749 (5)	H(1)—O(10)—H(2)	105 (4)
O(10)—H(1)	0·96 (5)	O(10)—H(1)···O(3^{vii})	177 (4)
O(10)—H(2)	0·85 (4)	O(10)—H(2)···O(4^{ix})	165 (4)
H(1)···O(3^{vii})	1·68 (5)		
H(2)···O(4^{ix})	1·92 (4)		

Table 6. *Electrostatic valence balance*

	Na(1)	Na(2)	Na(3)	B(1)	B(2)	B(3)	B(4)	B(5)	H(1)	H(2)	Sum
O(1)	0·16		0·18	0·71		0·99					2·04
O(2)	0·23		0·16	0·82			0·79				2·00
O(3)			0·13	0·79				0·80	0·23		1·95
O(4)			0·13	0·68	1·01					0·20	2·02
O(5)		0·19	0·20		0·98			0·69			2·06
O(6)	0·19				1·01		0·71				1·91
O(7)	0·14	0·27				1·00	0·72				2·13
O(8)	0·15	0·22				1·01		0·69			2·07
O(9)		0·20	0·20				0·78	0·82			2·00
O(10)	0·13	0·12							0·77	0·80	1·82

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Structure Determination of the Fluorite-Related Superstructure Phases $Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$

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Abstract

$Er_{10}W_2O_{21}$ and $Y_{10}W_2O_{21}$ are orthorhombic, space group *Pbcn*, $Z = 4$: for the former, $a = 15{\cdot}8221\ (11)$, $b = 10{\cdot}4814\ (9)$, $c = 10{\cdot}5407\ (8)$ Å, $D_x = 9{\cdot}029$ Mg m^{-3}, and for the latter, $a = 15{\cdot}8761\ (13)$, $b = 10{\cdot}5232\ (8)$, $c = 10{\cdot}5778\ (10)$ Å, $D_x = 5{\cdot}986$ Mg m^{-3}; $T = 298$ K. The structures were determined and refined from integrated powder X-ray diffraction data supplemented by single-crystal electron diffraction results. [$R = 0{\cdot}037\ (0{\cdot}051)$ for 159 (158) observations for the Y(Er) compounds.] The phases are isostructural, and have unit cells derived from a 3 × 2 × 2 array of fluorite-type subcells: cations and formal anion vacancies are ordered so that the W cations are all in sixfold coordination by O, whilst four-fifths of the Er or Y cations are sevenfold and the remainder sixfold coordinated. Corner-linked pairs of WO_6 octahedra form isolated groups in the structure.

Introduction

Some success has already been achieved in identifying the structural principles relating certain homologous series of *anion-excess*, fluorite-related superstructures. Vernier structures (Hyde, Bagshaw, Andersson & O'Keeffe, 1974) of the series M_nX_{2n+1} have been studied in various systems (Galy & Roth, 1973; Jung & Juza, 1973; Bevan & Mann, 1975; Bärnighausen, 1976; Lüke & Eick, 1976; Bärnighausen & Haschke, 1978; Papiernik, Mercurio & Frit, 1980), and quite recently the principle underlying the series M_nX_{2n+5} of the CaF_2–LnF_3 (Ln = rare earth, Y) systems has been discovered (Bevan, Greis & Strähle, 1980). However, there has been little success with *anion-deficient*, fluorite-related superstructures because, despite the existence of many such phases, detailed structural information is sparse. Some structures, determined from single-crystal X-ray studies, have been reported

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