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Modular Interpretation of Oxyborate Structures

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Abstract

Oxyborate structures are considered as being built of two types of order–disorder (OD) layers which serve as building modules, which explain the formation of different structural modifications, both homogeneous maximum degree of order (MDO) and inhomogeneous (periodic and aperiodic), lattice and diffraction features. Stacking faults are a direct consequence of the OD nature of the building modules.

Introduction

By interpreting high-resolution electron microscope (HREM) images, Bovin, O'Keefe & O'Keefe (1981) have considered the structural variations of oxyborates M_3BO_5 ($M = \text{Mg, Mn, Fe, Ni, Sb, Sn, Ti, Al}$) to occur as a result of slip and twinning mechanisms. Inspection of the structural schemes published shows that another interpretation based on symmetry considerations (Dornberger-Schiff, 1964; Zvyagin & Belokoneva, 1984) is possible. This provides not only an understanding of the reasons for structural variations, but also a simple means for their description and for the derivation of lattice and diffraction characteristics. The case of oxyborates may serve as a model for the general application of the modular approach (Zvyagin, 1993).

Building modules of oxyborates and their stacking

Oxyborate structures are built up of octahedra-like polyhedra whose distortions are defined by the framework which they form and by its dimensions. In a side projection these octahedra look like rhombi composed of two isosceles triangles [Fig. 1(a)], so that the opposite basal faces are displaced by half of their height instead of one third, as in regular octahedra.

Such octahedra are linked to form chains through shared edges. The chains are associated into two types of layers parallel to slip and twin planes. In layers of

type 1, chains of two opposite orientations alternate with rows of B atoms [Fig. 1(b)]. In layers of type 2, triple-chain ribbons alternate with single chains of oppositely oriented octahedra, the ribbons and chains being linked together through common apices [Fig. 1(c)]. Both types of layers have common two-dimensional lattices, one repeat distance, a_o , defined as five octahedral bases high, and the other, b_o , as the basal edge length normal to a_o .

The alternating layers 1 and 2 share common edges so that the octahedral faces of one layer cover the inter-octahedral vacant tetrahedra of the other layer, and the B atoms are coordinated by three O atoms of the octahedral apices forming B triangles (Fig. 2). The possible layer-stacking alternatives are completely defined by the layer symmetries $P2_1/m2/m(2/a)$ and $P12/m\bar{1}$, respectively (the brackets refer to the direction of missing periodicity). Any preceding layer can be transformed into an equivalent position available for a succeeding layer of the same type by symmetry λ -operations, transforming the intermediate layer of the other type into itself (Dornberger-Schiff, 1982;

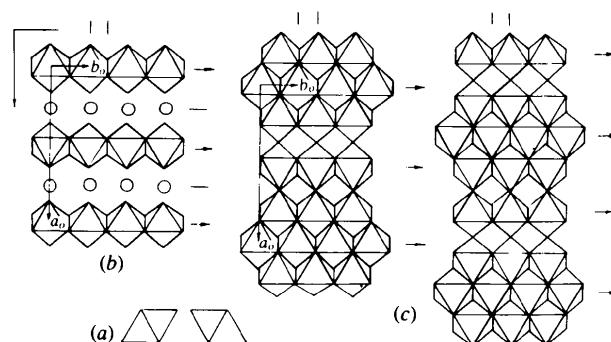


Fig. 1. Building units of oxyborate structures: (a) building octahedra having opposite orientations in side projection; (b) building layers of type 1 (H); (c) building layers of type 2 presented in two opposite orientations (N and И). Layers H, И and N are viewed along the normals to the layers.

Dornberger-Schiff & Grell, 1982). These λ -operations, acting as ρ -operations that relate consecutive layers of the same type, are twofold rotations around diad axes parallel to b_0 in both types of layer, and a glide operation a across a plane parallel to the layers for layer 1. Operation 2 retains the orientation of the layers, whereas operation a reverses the orientation of layer 2 relative to the axis a_0 . Thus, layer 1 adjoins layer 2 unambiguously and there are two alternative stackings for type 2 layers, differing in their orientation along the a_0 axis. This is the reason why different layer sequences exhibit structural modifications and why layer-stacking faults occur. In accordance with the λ - and ρ -operations defining the positions and orientations of the adjacent layers, adjacent layer pairs are symmetrically equivalent. Therefore, these layers are OD layers, and their sequences form OD structures (Dornberger-Schiff, 1964). These layers and their pairs may be considered as particular cases of building modules (BM) whose

combinations differ in number of module types, their proportions, alternation order, periodicity and stacking restrictions, and represent the diversity of modular structures including polysomes, hybrids and polytypes (Zvyagin, 1993).

Descriptive symbols of BM and their sequences

According to their symmetries, layers 1 and 2 may be denoted by 'non-polar' letters H, N and \mathbb{N} , respectively (Zvyagin & Belokoneva, 1984; Zvyagin & Romanoff, 1991). The same layers were distinguished by Takeuchi, Haga, Kato & Miara (1978) and designated with letters A, B and C relating to N, \mathbb{N} and H, respectively. Consecutive adjacent layers form layer pairs which, being polar and symmetrically equivalent, may be denoted by the letters NH = b, HN = q, \mathbb{N} H = d, H \mathbb{N} = p. Layer pairs b and q, and d and p are related by twofold rotations around axes parallel to b_0 , pairs b and d, and p and q are related by reflections in planes normal to a_0 , whereas glide operations a across planes parallel to the layers which transform \mathbb{N} into N and N into \mathbb{N} relate pairs b and p, and d and q. Any sequence of layers considered, by convention, upwards from below is described by a sequence of letters from left to right. The letters H, N, \mathbb{N} define the layer sequence unambiguously (letters H may be omitted as redundant and replaced by dots between letters N and \mathbb{N}). Any structure may be described by either letters b and d or p and q. For any structure described, e.g. by letters b and d or p and q, there is an equivalent structure which is described by interchanged letters, i.e. d and b or q and p, respectively, related by reflection in a plane normal to the a_0 axis or by 180° rotation around the a_0 axis. Numbers of consecutive equal letters N, \mathbb{N} , b, d, p or q compose short-hand numerical symbols like those of Zhdanov (1945) proposed for close packing, which are especially well suited for polytypes with long periods. Conventionally, one may put the numbers of \mathbb{N} -layers in the odd positions and the numbers of N-layers in the even positions of the symbols in order to obtain an unambiguous representation of layer sequences.

As shown by Fig. 2, B-containing channels are formed in adjacent layer pairs which project into isosceles triangles with sides equal to double the octahedral edge projections. In b and d pairs the triangles point down, while in p and q pairs they point upwards. In each layer pair the H layer is occupied by the trapezium halves of the triangles and the \mathbb{N} , N layers by the apical halves of the triangles, layers \mathbb{N} and N being distinguished by the relative displacements of the adjacent triangles. In sequences of layer pairs the triangles of each orientation are joined into chains, so that \mathbb{N} layers displace the triangle lying above adjacent to the one lying below and to the right, while the N layers displace it to the left. Any alternation sequence of layers \mathbb{N} and N results in zigzag chains of triangles. The

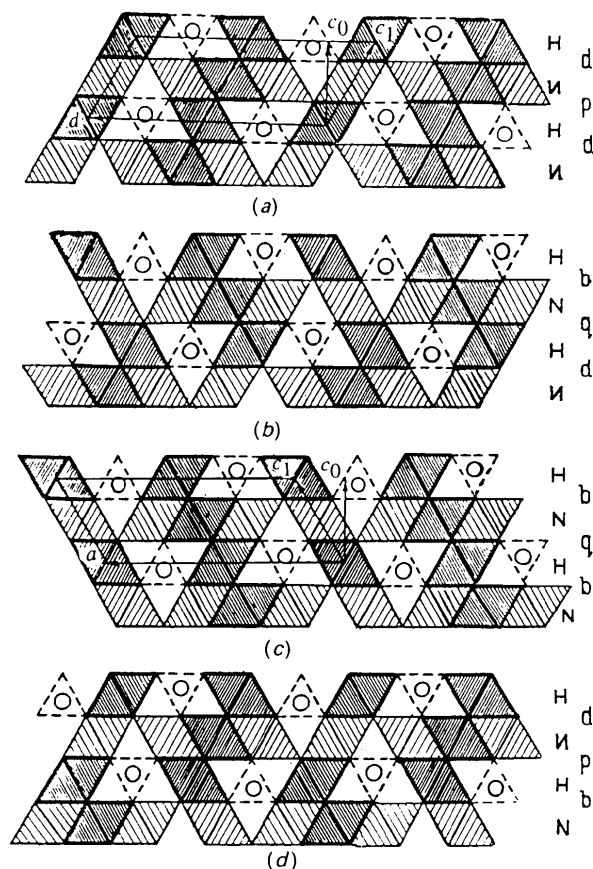


Fig. 2. Quadruples of building layers (a) $\mathbb{N}\mathbb{N}\mathbb{N}\mathbb{N}$, (b) $\mathbb{N}\mathbb{N}\mathbb{N}\mathbb{N}$, (c) $\mathbb{N}\mathbb{N}\mathbb{N}\mathbb{N}$ and (d) $\mathbb{N}\mathbb{N}\mathbb{N}\mathbb{N}$ forming triplets of layers pairs (a) dpd, (b) dqd, (c) bqb and (d) bqd projected along the b_0 axis. The symbols correspond to an upward sequence of layer types 2121. Layers \mathbb{N} and N can be easily distinguished by the slope of the diagonal edge of octahedra in the three-chain ribbons. The occupied octahedra are shadowed in order to outline triangular cross-sections of channels containing coordination triangles (dashed line) of B atoms (circles).

numbers of triangles in the links of these chains directly correspond to the numbers of short-hand numerical symbols (the two border triangles of a link are counted as one, belonging to adjacent links). Therefore, images of such triangle chains (Fig. 3) may serve as simplified structural schemes of oxyborates. These features may be directly recognized in the high-resolution electron microscope (HREM) images, where the triangle chains are seen as rows of light spots indicating the projected positions of the B atoms (Bovin *et al.*, 1981).

Apart from layer and layer-sequence symbols, the λ -operation symbols may be used to describe layer sequences (λ -operations 2 and a of layers H being sufficient), λ -operation 2 of layers \bar{H} and N is redundant and may be replaced by dots indicating the positions of the corresponding layers. Symbols 2 and a of the λ -operations acting in the H layers relate adjacent layers designated with the same or mirror-image letters (*e.g.* as for pairs bb, dd or bd). Therefore, they play the same role as letters h and c for close-packed structures, where h is attributed to a layer B in positions ABA or CBC, and c in combinations ABC or CBA.

Structural modifications and defects

The most natural reason for the existence of different sequences of \bar{H} and N layers interleaved with

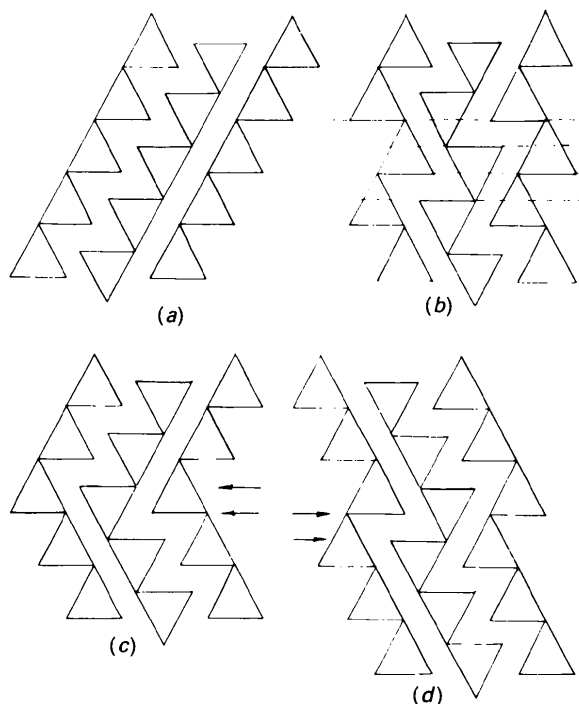


Fig. 3. Triangle chains characterizing the structures of (a) pinakiolite and (b) ludwigite, (c) a single twin and (d) single slip; the dashed lines mark the boundaries (in upward succession) between layers H and \bar{H} , \bar{H} and H, H and N, N and H, the arrows indicate possible positions of twin and slip planes.

intermediate H layers is the OD nature of the building layers. The symmetrical equivalence of adjacent layer pairs implies equivalent energies of interaction between parts of the structure that are close to one another and which dominate over the interaction of more distant structural parts (Dornberger-Schiff, 1964). Under such conditions, minor fluctuations in crystallization conditions and media composition may cause replacement of one stacking variant by another and violate a certain sequence order of layers.

As in other cases where only two alternative variants exist for the stacking of the succeeding BM (layer) relative to the preceding one (*e.g.* as in close packing, SiC and ZnC and in graphites) here there are only two homogeneous (simple) modifications having MDO (maximum degree of order) structures which present the smallest possible number (two in this case) of different kinds of layer triples (Dornberger-Schiff, 1982; Zvyagin, 1988; Durovic, 1992). For each of these, only one λ -operation (2 or a) acting in the H layers relates the layers \bar{H} and/or N adjacent to the H layers (Table 1). Structures, both periodic and aperiodic, in which different λ -operations relate layers adjacent to H layers, are inhomogeneous (complex) and may be considered as 'mixtures' of the homogeneous structures characterized by the relative numbers of λ -operations 2 and a acting in the H layers.

The structures of pinakiolite (P) and ludwigite (L) considered by Bovin *et al.* (1981) are thus homogeneous and simple, whereas the other periodic structures, those of orthopinakiolite (OP), takeuchiite (T) and hypothetical structure (HS1) (the scheme of which is shown by Bovin *et al.*, 1981, in their Fig. 8) are inhomogeneous and complex as 'mixtures' of P and L represented by ratios P/L . The recently studied chestermanite (Alfredsson, Bovin, Norrestam & Terasaki, 1991) is isostructural with OP. Raade, Mladeck, Din, Griddle & Stanley (1988) have identified one more member of the oxyborate modular system, blatterite (B). These structures are considered in Table 1 together with two additional hypothetical structures (HS2 and HS3) and are characterized by symbolic notations and P/L ratios.

Structures of a modular family should be considered in a common coordinate system having two axes inside the BM (a_0 and b_0) and the third (c_0) defined by the thickness of the repeated BM combination (layer pair b, d, p or q). In some disagreement with the usual axes designation (see *e.g.* Bovin *et al.*, 1981; Raade *et al.*, 1988), the oxyborate 'modular' axes are attributed to distances $a_0 \cong 12.5$, $b_0 \cong 3$ and $c_0 \cong 4.6$ Å, the doubling of b_0 caused by cation ordering in some oxyborates being disregarded.

According to Fig. 2, an \bar{H} layer displaces the overlying H layer, relative to the underlying H layer, to the right by $-a_0/5$, whereas an N layer causes a similar displacement to the left by $a_0/5$. Therefore, a periodic

Table 1. Building module sequences in oxyborate structures

Objects	BM symbols	BM-pair symbols	λ -operation symbols	Short symbols	m	n	P/L
Pinakioilite (<i>P</i>)	.И.И..	.dd.. or .pp..	.2.2..	[1,0]	-1	1	1:0
	.N.N..	.bb.. or .qq..		[0,1]	1	1	
Ludwigite (<i>L</i>)	.И.N..	.db.. or .pq..	.a.a..	[1,1]	0	2	0:1
Orthopinakioilite (OP)	.И.И.N.N..	.ddb. or .ppqq.	.2.a..	[2,2]	0	4	1:1
Takeuchiite (<i>T</i>)	.И.И.И.N.N.N..	.ddd. or .ppppq.	.2.2.a..	[3,3]	0	6	2:1
Blatterite (<i>B</i>)	.И.И.И.И.N.N.N.N..	.ddd. or .ppppq.	.2.2.2.a..	[4,4]	0	8	3:1
Hypothetical structure (HS1)	.И.N.N..	.db. or .pq.	.a.a.2..	[1,2]	1	3	1:2
	.И.И.N..	.db. or .pq.	.a.2.a..	[2,1]	-1	3	
Hypothetical structure (HS2)	.И.N.N.N..	.dbb. or .ppqq.	.a.a.2.2..	[1,3]	2	4	1:1
	.И.И.И.N..	.ddb. or .ppp.	.a.2.2.a..	[3,1]	-2	4	
Hypothetical structure (HS3)	.И.N.N.N.N..	.dbbb. or .ppqqq.	.a.a.2.2.2..	[1,4]	3(-2)	5	3:2
	.И.И.И.И.N..	.ddd. or .pppp.	.a.2.2.2.a..	[4,1]	-3(2)	5	
Slip	.И.И.N.И.И..	.dbbd. or .pppp.	.2.2.2.a.a.2.2.2..	[∞ ,1, ∞]			
Twining	.И.И.И.N.N.N..	.ddd. or .ppppq.	.2.2.2.a.2.2.2..	[∞ , ∞]			
Some aperiodical sequence part	.И.И.N.N.N.И.N.N.N.N..		.2.a.2.2.a.a.2.2.2..	[..2,3,1,4..]			~6:3

structure having a repeat of n layer pairs is described in a coordinate system $\mathbf{a} = \mathbf{a}_o$, $\mathbf{b} = \mathbf{b}_o$, $\mathbf{c} = m\mathbf{a}_o/5 + n\mathbf{c}_o$, so that the normal projection of the c axis measured in a units is $(c/a)\cos\beta = m/5$. The m values (0, ± 1 , ± 2 , ...) correspond to differences in sums of numbers in even and odd positions of the short-hand symbols and n is equal to their sum (Table 1). Angle β is defined by the relationship $\cos\beta = ma/5nc_o$. Depending on m/n , β may deviate significantly from 90° , but it is always possible to replace m by $m' = m + 5k$ (k is an integer number of a translations) which may have a smaller absolute value corresponding to an angle β' closer to 90° . In the case of pinakioilite $m = 1$, $n = 1$ and $\beta = 118.5^\circ$. The conversion to axes $\mathbf{a}' = \mathbf{a} + \mathbf{c}$, $\mathbf{c}' = \mathbf{c}$ (Fig. 4) gives $a' = 11.0 \text{ \AA}$, $\beta' = 94.0^\circ$. It is clear from Figs. 6 and 9 of Bovin *et al.* (1981) that single 'slip' and 'twining' operations are nothing but simple and quite natural for OD BM-sequence changes in the λ -operations (Table 1), which may simply occur with layer-by-layer crystal growth. According to the sequences of symbols (Table 1) and simplified images (Fig. 3) where only triangle chains are shown, two planes bordering an $\text{I}(N)$ layer or an H layer may be regarded as slip or twin plane, respectively. The choice of these planes is, thus, ambiguous. It is also difficult to imagine how a displacement or rotation of one crystal part against the other may occur in a framework structure, breaking all interatomic bonds along a 'slip' or 'twin' plane. Therefore, the corresponding mechanisms are not convincing and may have no direct relation to reality for oxyborates and many modular structures.

It is remarkable, however, that the existing oxyborate structures are illustrated either by linear triangle chains (P -like structures) or by zigzag chains with equal links, so that adjacent links are in twin relationships [symbols $(n/2, n/2)$, $n = 2, 4, 6, 8$]. HS1,2,3, having values $m = 1, 2, 3$, remain hypothetical perhaps because their chain links are different. It seems that combinations of layers representing a chain link play the role of enlarged modules, the thickness of which is fixed. These links may be in the same orientation and form P -like

structures, or be arranged with a regular alternation of two opposite orientations and from L -, OP -, T - and B -like structures. The HS stacking may be then manifested as occasional defects not repeated periodically over great areas.

According to Raade *et al.* (1988) 'the cation species must have a great influence on the period of the twin operations as suggested by Bovin *et al.* (1981)'. This means that peculiarities of composition and cation distribution define the enlarged module thickness. The

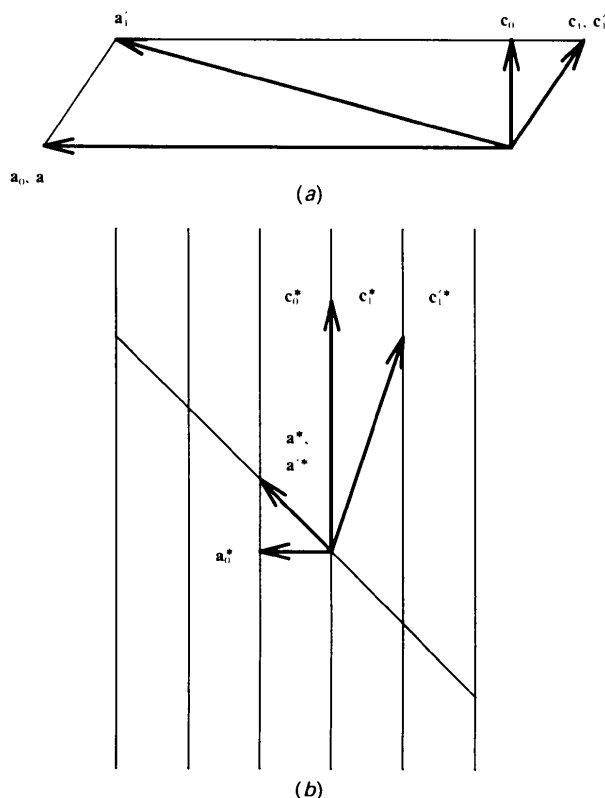


Fig. 4. Relationship between axes in the (a) direct and (b) reciprocal spaces.

two types of such module sequences: [1,0] or [1,0] and [1,1], respectively, may be considered as homogeneous arising from module-by-module crystal growth, whereas the HS defects proceed by some violation of the growth conditions.

Some general diffraction features of oxyborate structures

Common lattice features in direct space are accordingly represented in reciprocal space and, hence, in diffraction patterns. Most distinctly, such features are displayed in selected-area electron diffraction (SAED) patterns of single crystals. The set of coordinate axes in the reciprocal space is defined by the relationship between linear transformations of axes in both spaces as $\mathbf{a}^* = \mathbf{a}_0^* - (m/5n)\mathbf{c}_0^*$, $\mathbf{b}^* = \mathbf{b}_0^*$, $\mathbf{c}^* = \mathbf{c}_0^*/n$. According to these equations, any electron-diffraction patterns obtained from a single crystal in orientation with the b axis parallel to the incident beam images the reciprocal lattice plane $\mathbf{a}^*\mathbf{c}^*$. This pattern contains $h0l$ reflections distributed along rows having constant h and variable l indices. The separations between the rows are proportional to $1/a_0$, and the intervals between the reflections of the row are proportional to $1/(nc_0)$. The consecutive reflections $h00$ are displaced along their rows by $-mc^*/5 = -m/(5nc_0)$, in accordance with the relationship $a^*\cos\beta^* = -m/5$. At the choice of other axes a' giving β' -angles closer to 90° , the c'^* axis unites reflections of different rows. In the particular case of $m = -1$, $n = 1$, $\mathbf{a}'^* = \mathbf{a}^*$, $\mathbf{c}'^* = -\mathbf{a}^* + \mathbf{c}^*$ (Fig. 4). The transformation of indices being covariant with the transformation of axes in the direct space is accordingly $h' = h + 1$, $k' = k$, $l' = l$.

Concluding remarks

The application of the modular approach has provided a clear and simple understanding of the variations in oxyborate structures. At the same time, it has displayed

almost all the general features of the modular approach: choice of modules; formulation of the stacking rules; use of symbolic notations as a simple means for operation with structures; derivation of homogeneous structures and presentation of inhomogeneous structures as combinations of the homogeneous ones; treatment of all individual structures as members of a united system considered relative to common coordinate axes in the direct and reciprocal spaces and in diffraction patterns. In the view of the modular approach, the concepts of 'slip' and 'twinning' seem redundant for explaining the oxyborate structural variations.

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The Structures of α - and β - $\text{Bi}_2\text{Ti}_4\text{O}_{11}$

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Abstract

The phase transition and the crystal structures of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ have been investigated by X-ray diffrac-

tion. The compounds possess the following parameters: α - $\text{Bi}_2\text{Ti}_4\text{O}_{11}$: monoclinic, space group $C2/c$, $a = 14.5999$ (6), $b = 3.8063$ (2), $c = 14.9418$ (8) Å, $\beta = 93.129$ (4)°, $V = 829.1$ (1) Å³, $Z = 4$,