

Zircon, Anhydrite, Scheelite and Some Related Structures Containing Bisdisphenoids

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Abstract

A number of structure types, especially those of ABX_4 compounds with a large difference between the sizes of the A and B atoms, consist of AX_3 bisdisphenoids and BX_4 tetrahedra. They include some important mineral structures such as zircon ($ZrSiO_4$), anhydrite ($CaSO_4$) and scheelite ($CaWO_4$). It is shown that these structures are closely and simply related *via* crystallographic twin operations. A bisdisphenoid sharing an edge with a tetrahedron is easily deformed to a pair of edge-sharing octahedra or to a row of four edge-sharing tetrahedra. The former reveals a simple relation between ABX_4 structures and MX_2 ($=MMX_4$) octahedral structures. It also enables a parallel to be drawn between high-pressure transformations in the two series, ABX_4 and MX_2 . The latter enables relations with tetrahedral structure types to be perceived.

Introduction

Despite lucid description and discussion by structural inorganic chemists (Wells, 1970, 1975; Kepert, 1965, 1982) and geometers (Cundy & Rollett, 1961) it seems that the eight-coordination polyhedron known as a bisdisphenoid or dodecadeltahedron is still rather unfamiliar; this is strange because it is a not uncommon coordination figure and, as we shall see, is observed in some important mineral structure types. Known by a number of other names also, this polyhedron, shown in Fig. 1, has 12 triangular faces, 18 edges and, of course, 8 vertices. Wells (1970) has discussed its simple topological relations to the cube, square antiprism and bicapped trigonal prism. Like the cube it may be described as consisting of two interpenetrating, concentric tetrahedra (disphenoids). But, unlike the cube, these are irregular; one being elongated and the other compressed along the common $\bar{4}$ axis. These two tetrahedra are shown

in Fig. 2, which should be compared with Fig. 1(d) (in which the open and filled circles define elongated and compressed tetrahedra).

It is possible to have all vertices equidistant from the centre of the bisdisphenoid (Kepert, 1982) but, in most crystal structures in which it occurs, there are two sets each of four equivalent bond lengths (*i.e.* centre to vertex) corresponding to the two tetrahedra which interpenetrate. The two vertex types are differentiated in Fig. 1; the filled circles being somewhat closer to the centre than the open ones.

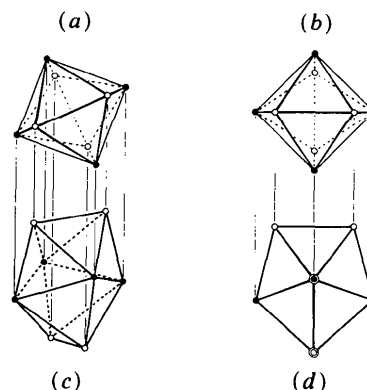


Fig. 1. Various 'skeletal' views of a bisdisphenoid: top: (a) and (b) in plan, projected down its $\bar{4}$ axis; bottom: (c) a perspective view, (d) in elevation. (Double circles denote superimposed atoms/vertices.)

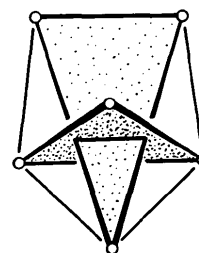


Fig. 2. A bisdisphenoid projected as in Fig. 1(d), but resolved into two interpenetrating (dotted) tetrahedra: one elongated, the other squat. They have a common $\bar{4}$ axis.

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Bisdisphenoid structures of stoichiometry AX_4 and ABX_4

β -ThCl₄

One of the simplest structures composed of bisdisphenoids (with *A* atoms at their centres and *X* atoms at their vertices), and a useful starting point for our descriptions, is that of β -ThCl₄ (Mucker, Smith, Johnson & Elson, 1969; Mason, Jha & Chiotti, 1974) and isostructural actinide tetrahalides. It is a straightforward array of ThCl₈ bisdisphenoids sharing edges in the two equivalent directions of its tetragonal ($I4_1/amd$, $Z=4$) unit cell ($c/a=0.881$), and is shown in two projections in Fig. 3. The two different Th–Cl bond lengths are 2.72 and 2.90 Å.

Zircon, ZrSiO₄

Examination of the right-hand part of Fig. 3 reveals the presence of empty (rather regular) tetrahedra between the rows of bisdisphenoids: they are edge-connected to bisdisphenoids in adjacent rows. If these tetrahedra are occupied by *B* atoms the AX_4 structure of the ThCl₄ type becomes the ABX_4 structure of the

ZrSiO₄ (zircon) type: also tetragonal ($I4_1/amd$, $Z=4$, with $c/a=0.905$). In this structure (Robinson, Gibbs & Ribbe, 1971), shown in Figs. 4 and 5, there are Zr atoms in the O₈ bisdisphenoids (bond lengths 2.43 and 2.75 Å) and Si atoms in the O₄ tetrahedra. These two sorts of polyhedra are edge-connected, and alternate in rods along *c*. Adjacent rods are, of course, united along *x* and *y* by the same edge-sharing between bisdisphenoids as occurs in ThCl₄.

Anhydrite, CaSO₄

Wyckoff (1965) describes the structure of anhydrite, CaSO₄, as a distortion of that of zircon. This is correct, but it misses a very real and elegant relationship. Anhydrite (Morikawa, Minato, Tomita & Iwai, 1975) contains rods of edge-connected CaO₈ bisdisphenoids and SO₄ tetrahedra, analogous to the rods of ZrO₈ + SiO₄ in zircon. In the *x* direction these rods are connected by edge-sharing between the bisdisphenoids, again as in zircon. But, in the *y* direction they are united *via* corner-sharing between bisdisphenoids, see Fig. 6; and in this it differs from zircon – compare Fig. 6 with Fig. 4. The symmetry is thus

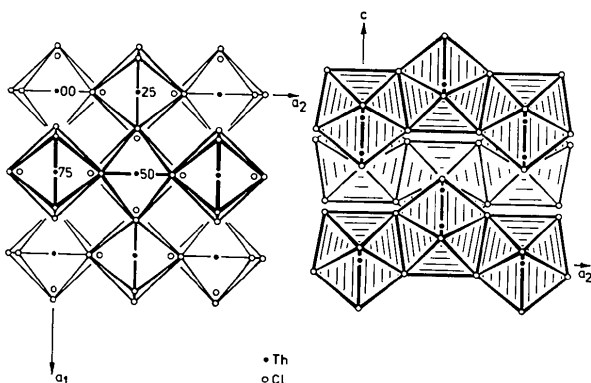


Fig. 3. The structure of ThCl₄ projected on (001) on the left and (100) on the right. In the former Th-atom heights are in units of $c/100$. Compare Figs. 1(b) and 1(d).

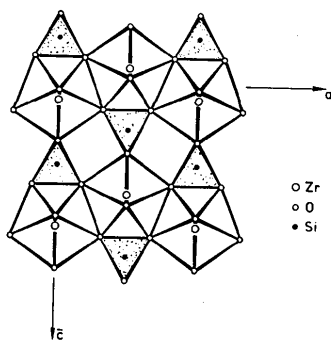


Fig. 4. A (100)=(010) layer of ZrO₈ bisdisphenoids and SiO₄ tetrahedra in the zircon structure: compare with the right-hand part of Fig. 3.

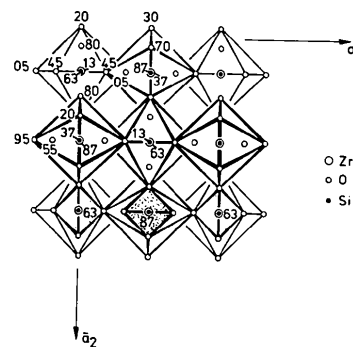


Fig. 5. The zircon, ZrSiO₄, structure projected on (001): atom heights in units of $c/100$. (For clarity only three SiO₄ tetrahedra are depicted.) Comparison with the left-hand part of Fig. 3 emphasizes the similarity. (Note that the origins differ by $\frac{1}{2}a + \frac{1}{8}c$.)

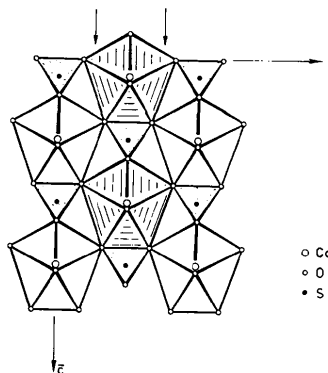


Fig. 6. A single layer (half a unit cell) of the CaSO₄ structure projected on (100).

reduced to orthorhombic; the space group is *Amma* and $a = 6.999$, $b = 6.992$, $c = 6.240 \text{ \AA}$ ($Z = 4$); Ca–O bond lengths are 2.34 and 2.56 \AA .

The full structure is shown in two projections, on (010) and (100) of *Amma*, in Fig. 7(a, b). A comparison of these or of Figs. 5 and 8 (*c*-axis projections) or, more simply, of Figs. 4 and 6 reveals the following. Both the zircon and anhydrite structures consist of the same type of rod (of alternating bisdisphenoids and tetrahedra) connected into identical sheets by edge-sharing between bisdisphenoids in adjacent rods (Figs. 4 and 7a). But the sheets are differently connected (and juxtaposed) in the two structures. The anhydrite structure may be described as mimetically twinned zircon, the twin (and composition) planes, marked by short arrows in Fig. 6, being (020) of *Amma*. In Fig. 6 it is clear that the central shaded layer of zircon type is oriented exactly as in the zircon drawing in Fig. 4, but that the outer layers have their

c axes reversed. The twinning operation is therefore a 180° rotation of these layers about **b** (anhydrite) \equiv **a** (zircon). [The same result is achieved by translating alternate (020) layers of zircon by $\mathbf{a}/2$.]

Silver perchlorate, AgClO_4

Since zircon is tetragonal the twinning operation on (020) to produce the CaSO_4 type may equally well, and with an identical result, be carried out on (200). If it is done on both (200) and (020) *simultaneously* a new tetrahedral structure will be generated in which both $\mathbf{a}/2$ and $\mathbf{b}/2$ layers will look like the anhydrite layers of Fig. 6. The same rods of $\text{AX}_3 + \text{BX}_4$ will now be connected *via* corner-sharing between bisdisphenoids in both **a** and **b** directions, and this is the structure of silver perchlorate (Berthold, Ludwig & Wartchow, 1979) shown projected on (001) in Fig. 9. In this case $Z = 2$ and $c/(\sqrt{2}a) = 0.959$. The two Ag–O bond lengths are 2.50 and 2.78 \AA .

With an additional small rotation of the bisdisphenoids about their $\bar{4}$ axes, a similar double twinning of ThCl_4 produces the Pd_4S ($= \text{Pd}_4\text{Se}$) structure (Gronvold & Røst, 1962), shown in Fig. 10 (which should be compared with Fig. 9). In this case too $Z = 2$, and now $c/(\sqrt{2}a) = 0.763$. [Similar small rotations relate the structures of potassium dihydrogenphosphate, KH_2PO_4 , and cahnite, $\text{Ca}_2\text{BAS}(\text{OH})_4\text{O}_4$, to that of zircon.]

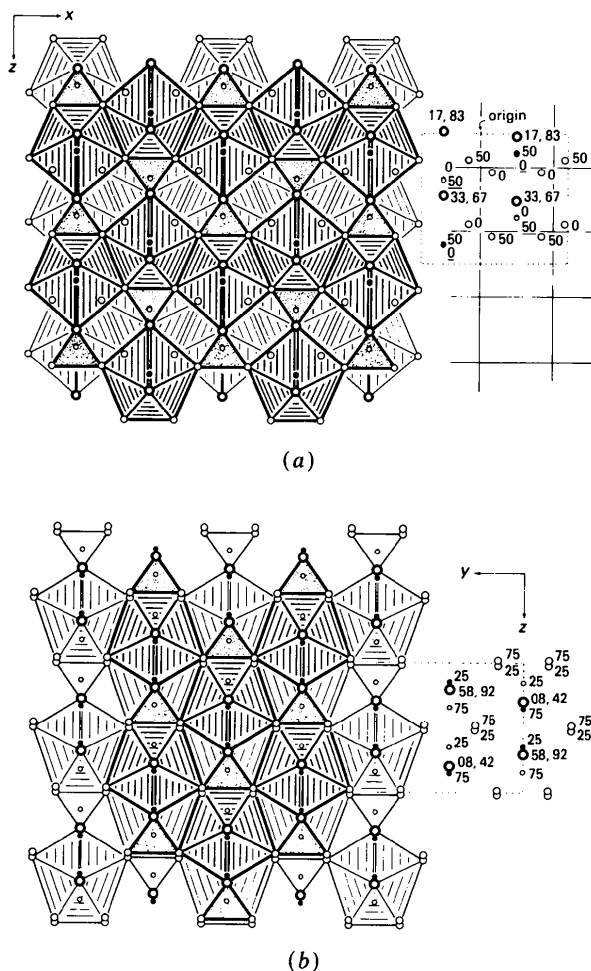


Fig. 7. The complete CaSO_4 structure projected on (a) (010), and (b) (100) of *Amma*. Large circles are O atoms, small circles are Ca (filled) and S (open). Atom heights are in units of 1/100 of the projection axis. [S-atom heights are underlined in (a).]

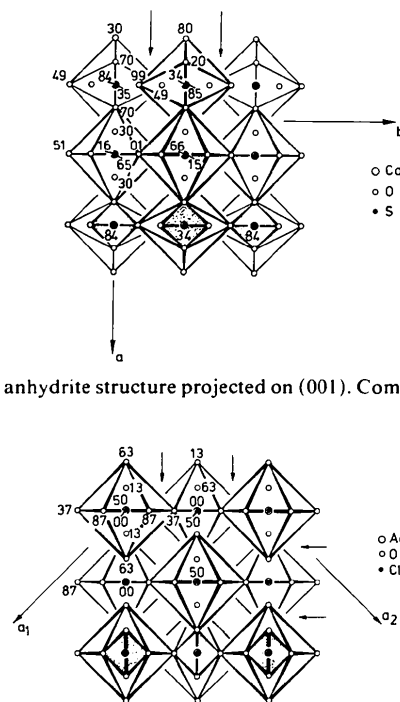


Fig. 8. The anhydrite structure projected on (001). Compare Fig. 5.

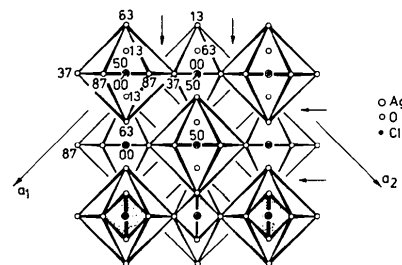


Fig. 9. The structure of AgClO_4 projected down its tetragonal axis. Compare Figs. 8 and 5.

To relate the ABX_4 structures of zircon, anhydrite and $AgClO_4$ to that of scheelite, $CaWO_4$ (which contains CaO_8 bisdisphenoids and WO_4 tetrahedra), it is simpler to adopt another viewpoint, and another description of the first three structures – which we now consider.

The topology of some rods of octahedra, bisdisphenoids and tetrahedra

Fig. 11 shows rods of (a) alternating, edge-shared bisdisphenoids and tetrahedra and (b) edge-shared octahedra and (c) edge-shared tetrahedra; the equivalent translation repeat unit being given in each case. Surprisingly small topological distortions convert each of these rods to the others; this is extremely important for detecting some close relationships between structure types which at first sight appear to be quite unrelated.

It is used in the following.

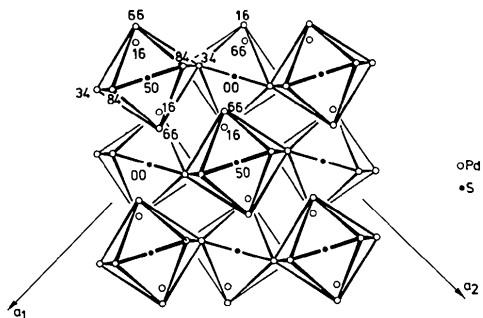


Fig. 10. The structure of Pd_4S projected along its tetragonal axis. Compare Fig. 9. Compared with $AgClO_4$ the tetrahedra are unoccupied, and the PdS_8 bisdisphenoids are tilted about their 4 axes.

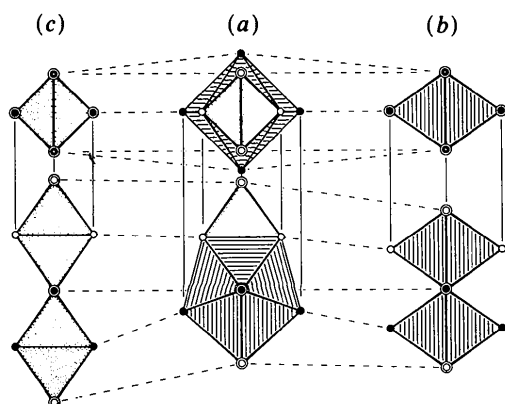


Fig. 11. Plan views (above) and elevations (below) of equivalent translation repeat units in rods of (a) alternating bisdisphenoids and tetrahedra joined by sharing edges (centre), (b) edge-sharing regular octahedra (right), (c) edge-sharing regular tetrahedra (left), showing that they are all topologically equivalent. Octahedra and bisdisphenoids are line-shaded; tetrahedra are dotted. Double and triple circles represent, respectively, two and three superimposed anions.

The ABX_4 bisdisphenoid structures regarded as arrays of AX_4 and BX_4 tetrahedra

We have already pointed out that, by definition, a bisdisphenoid consists of two interpenetrating tetrahedra, Fig. 2, and we have mentioned that the centre-vertex distances fall into two groups of four each; the filled circles of Fig. 1 are usually closer to the centre of the figure than the open circles. Hence, as we have also indicated earlier, the coordination of the A atom by X atoms is AX_{4+4} , rather than simply AX_8 . If the four more distant X atoms are ignored, and we concentrate on the 'squashed' AX_4 tetrahedron, then the rods of edge-connected AX_8 bisdisphenoids and BX_4 tetrahedra, characteristic of the $ZrSiO_4$, $CaSO_4$ and $AgClO_4$ structures and referred to above, can be redrawn as shown by the heavy lines and dotted tetrahedra in Fig. 12 – which should be compared with Figs. 2, 11(a) and 11(c).

Regarded in this way the $AgClO_4$ structure consists of unconnected, flat layers formed by alternating (large, squashed) AgO_4 and (small) ClO_4 tetrahedra

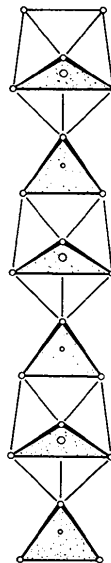


Fig. 12. The basic building element of the zircon, anhydrite and $AgClO_4$ structures. Thin lines represent bisdisphenoids (compare Fig. 11a) and thick lines represent tetrahedra (compare Figs. 2 and 11c).

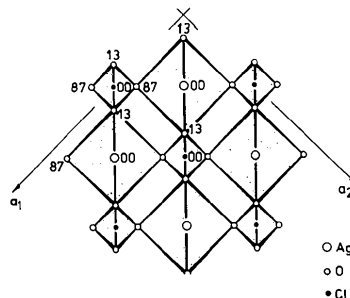


Fig. 13. One (001) layer of corner-connected tetrahedra (alternately AgO_4 and ClO_4) in the structure of $AgClO_4$.

sharing corners, Fig. 13. Such layers are stacked along [111] at intervals of $z/c = \frac{1}{2}$ (see Fig. 14). [Each layer is a superstructure (owing to Ag,Cl ordering) of the type of layer that exists in red, tetragonal HgI_2 (Jeffrey & Vlasse, 1967) – although they are differently stacked.] Note that in each layer all the cations have the same z parameter.

The analogous layers in $CaSO_4$ are corrugated in the x direction, owing to the different topological arrangement of the two types of tetrahedra (see Figs. 15 and 16). [They now resemble the $(ZnO_2)^{2-}$ part of the $SrZnO_2$ structure (von Schnering & Hoppe, 1960).]

In $ZrSiO_4$ the corresponding layers are corrugated in both the x and y directions, Fig. 17, leading to a

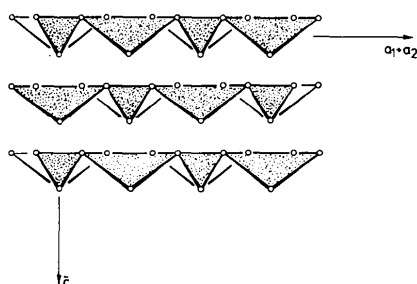


Fig. 14. The stacking of layers of tetrahedra (Fig. 13) along the c axis of $AgClO_4$: ClO_4 tetrahedra in one layer are immediately above and below AgO_4 tetrahedra in adjacent layers, and *vice versa*.

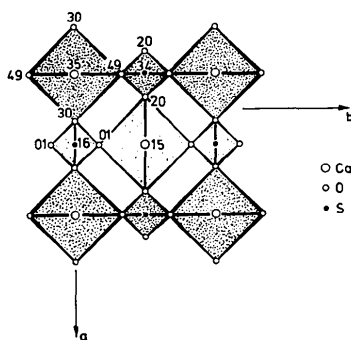


Fig. 15. One (001) layer of corner-connected tetrahedra (alternately CaO_4 and SO_4) in the anhydrite structure.

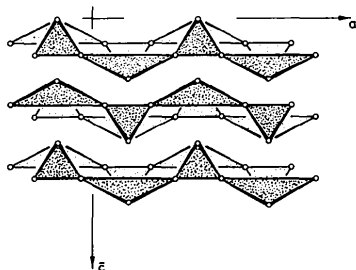


Fig. 16. The stacking of layers of tetrahedra (Fig. 15) along the c axis of $CaSO_4$. CaO_4 tetrahedra are immediately above and below SO_4 tetrahedra, and *vice versa*.

three-dimensional, corner-connected array of alternating ZrO_4 and SiO_4 tetrahedra (instead of isolated layers). There are, in fact, two such arrays – identical and interpenetrating. Each is a BPO_4 -like superstructure of the $C9$ ('ideal high-cristobalite') type: a completely expanded array of corner-connected tetrahedra (O'Keeffe & Hyde, 1976). It is therefore a superstructure of the *anti-Cu_2O* structure type (or even *anti-ice VII* or *VIII*).

We consider now the scheelite structure type (Kay, Frazer & Almodovar, 1964). In Fig. 18 this is shown in projection along c , and one of the four identical

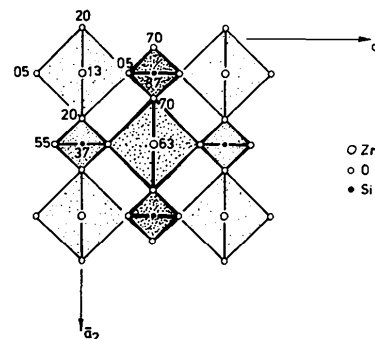


Fig. 17. One of the two identical interpenetrating three-dimensional frameworks of corner-connected tetrahedra in the zircon structure projected on (001). The 'stacking' follows the same pattern as in Figs. 14 and 16: ZrO_4 tetrahedra in one framework are immediately above and below SiO_4 tetrahedra in the other framework, and *vice versa*.

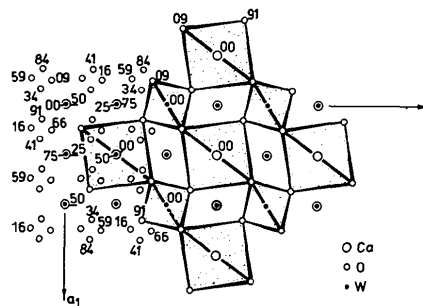


Fig. 18. The scheelite structure projected on (001), and regarded as a corner-connected array of CaO_4 and WO_4 tetrahedra. Only one of the four equivalent layers is drawn. (Compare Fig. 13.)

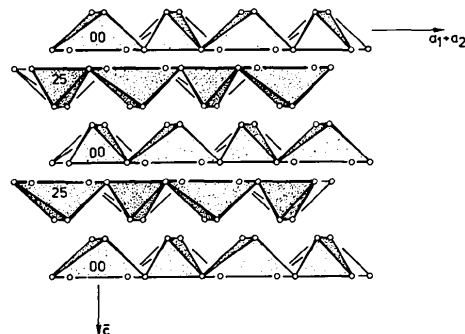


Fig. 19. The stacking of layers of tetrahedra (shown in Fig. 18) along c in the scheelite structure.

(001) layers of corner-connected CaO_4 and WO_4 tetrahedra is drawn. (The two Ca–O bond lengths in this bisdisphenoid structure are almost the same: 2.44 and 2.48 Å; Fig. 18 shows only the former.) It is obvious that this layer is a very slightly deformed version of that in AgClO_4 (Fig. 13), the deformation being a small tilt of the tetrahedra about c . But the stacking of the layers is different from that in AgClO_4 (compare Figs. 19 and 14). Alternate layers are stacked in the same way as adjacent layers in AgClO_4 ; and there are two such sets, interleaved and oppositely oriented [*i.e.* their $c(\text{AgClO}_4)$ axes are inverted]. Thus the scheelite type is the AgClO_4 type twinned on (002) (of AgClO_4) – which results in a doubling of the c axis. In CaWO_4 adjacent layers are related by glide reflection ($Z = 4$, and $c/2a = 1.085$, compared with $Z = 2$ and $c/a = 1.356$ for AgClO_4). (TiCl_2 is isostructural with scheelite; it is in fact $\text{Ti}^+\text{Ti}^{3+}\text{Cl}_4^-$, with Ti^+ in eight coordination and Ti^{3+} tetrahedrally coordinated.)

Hence, starting with the zircon structure type, twinning on (200) or (020) yields the anhydrite type; twinning on (200) and (020) produces the AgClO_4 type; and twinning on (200), (020) and (002) generates the scheelite type.

Relationships between ABX_4 structures with AX_8 bisdisphenoids and BX_4 tetrahedra and MX_2 structures with MX_6 octahedra*

Fig. 20 shows how a rod of edge-sharing octahedra can be transformed, by small shifts of the atoms, into a rod of alternating bisdisphenoids and tetrahedra of the sort that we have observed in the zircon, anhydrite and silver perchlorate structures. (The upper and lower parts of the figure show the two important projections. Compare the latter with Fig. 11*a* and *b*.) This process corresponds to the substitution of alternate octahedrally coordinated M atoms in the chain

* A different approach to this topic, from a completely different but complementary viewpoint, has recently been given elsewhere (O'Keefe & Hyde, 1984).

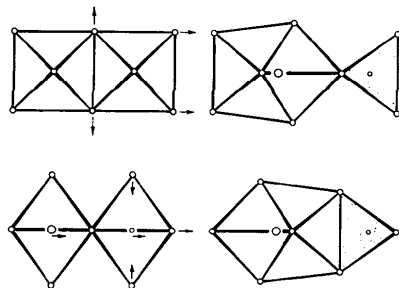


Fig. 20. The transformation of a pair (or part of a row) of edge-sharing octahedra (left) to a bisdisphenoid sharing an edge with a tetrahedron (right). The arrows indicate the directions in which anions are displaced. (Compare Fig. 11*a* and *b*.)

by A atoms that are somewhat large for octahedral coordination, and the intermediate M by B atoms which are somewhat small for an octahedron.

The tetragonal, rutile-type MX_2 structure consists of infinite rectilinear rods or chains of edge-sharing MX_6 octahedra parallel to c , united by corner-sharing to the octahedra in identical adjacent rods. If the above substitution of M by alternately bigger and smaller cations, B and S , is made, then one of the ABX_4 (now BSX_4) structures is readily obtained. The upper part of Fig. 21 shows that if all the cation shifts in each rod are in the *same* direction, then the resulting bisdisphenoids share edges and the zircon structure will result. The lower part of Fig. 21 shows that if the cation shifts in adjacent chains are always in *opposite* directions then the bisdisphenoids will share only corners, and the resulting structure will be that of AgClO_4 . The octahedral rods in this figure corre-

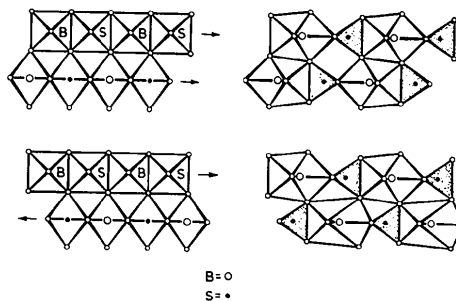


Fig. 21. The transformation of two (corner-connected) strings or rods of edge-sharing octahedra (a rutile element) to a zircon-type structure element (top) or an AgClO_4 -type element (below). The required small shifts of the cations B and S are in directions indicated by the arrows.

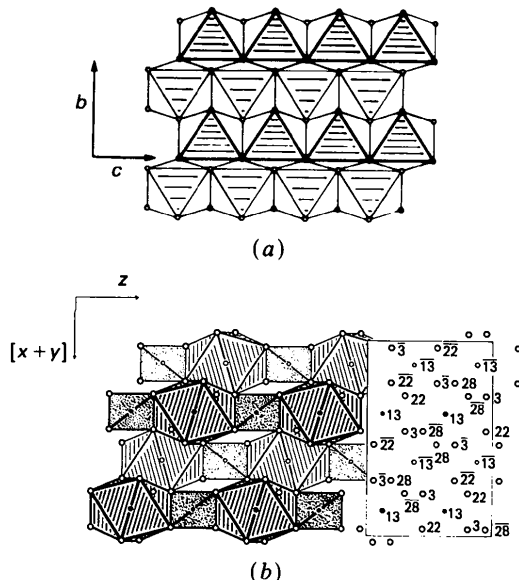


Fig. 22. Projection of (a) the rutile structure on (100) and (b) the zircon structure on ($1\bar{1}0$).

spond to part of a (110) layer of rutile type. If all the cation shifts are in one direction for the rods of one layer but in the opposite direction for the rods in the two adjacent layers the result will obviously be the anhydrite structure.

Clearly then a cooperative transformation *between* these three structure types may be readily achieved by appropriate cation shuffles parallel to *c* or $-c$. This is a plausible mechanism for the transformation between, for example, the low- and high-temperature forms of NaClO_4 , the former being anhydrite type and the latter (Berthold, Kruska & Wartchow, 1979) probably of the AgClO_4 type.

In this context, we may also recall that Vegard (1916) first reported that zircon had the rutile structure, although he subsequently corrected this (Vegard, 1926). The relation described above shows that this confusion is by no means as ludicrous as might at first appear – in spite of the statement that the resemblance between the dimensions of the two unit

cells is 'fortuitous, as there is no relation between the two structures' (Bragg & Claringbull, 1965). Fig. 22 compares the polyhedral descriptions of the structures: rutile on (100) and zircon on (1 $\bar{1}$ 0).

In the same vein, in Fig. 23 we have drawn the (real) scheelite structure as an MX_2 structure with octahedrally coordinated cations. In these terms it consists of (horizontal) zigzag rows of edge-sharing octahedra at two levels ($y/b = 0, \frac{1}{2}$), joined by corner-sharing. This is a (distorted) superstructure of the $\alpha\text{-PbO}_2$ structure type which is shown in Fig. 24. [Compare $c/a = 2.19$ for (tetragonal) scheelite with the corresponding values for (orthorhombic) $\alpha\text{-PbO}_2$: $2b/a = 2.41$, $2b/c = 2.17$, mean value = 2.29.]

In other words, scheelite is related to $\alpha\text{-PbO}_2$ in a way that is analogous to the relationship between zircon (or CaSO_4 or AgClO_4) and rutile. And so it is interesting to recall that the effect of high pressure on the rutile and zircon structures is to transform them to the $\alpha\text{-PbO}_2$ and scheelite types respectively. Furthermore, we have seen that scheelite may be described as twinned AgClO_4 type, and we note that $\alpha\text{-PbO}_2$ has also been described as twinned rutile (O'Keeffe & Hyde, 1980).

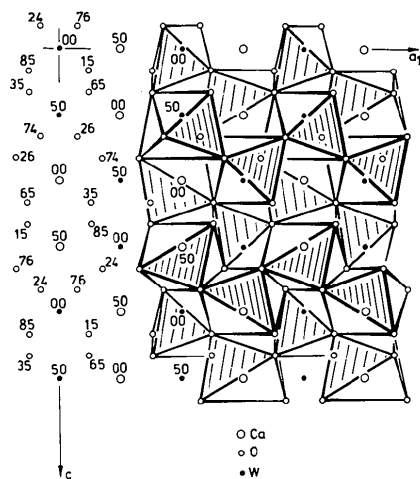


Fig. 23. A projection of the scheelite structure on to (010). The cation-centred coordination polyhedra are drawn as octahedra (by analogy with Fig. 11a and b).

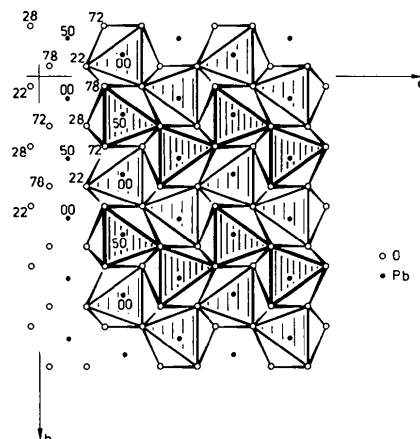


Fig. 24. The $\alpha\text{-PbO}_2$ structure projected on (100). The coordination of the cations is octahedral (compare Fig. 23).

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