Oxides with a tunnel structure characterized by a mixed framework of octahedra and tetrahedra

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Abstract. Oxides with a three-dimensional mixed framework built up from octahedra and tetrahedra are attractive owing to the possibility of forming large tunnels which can intersect as in the ionic conductors, or also to build anisotropic electronic conductors. The structural relationships between these oxides are analyzed here. Three classes of oxides are mainly studied here: mixed frameworks with tetrahedral silicate and germanate groups, oxides in which tetrahedral phosphates are involved and compounds involving silicophosphate groups. Other examples of mixed frameworks such as those involving GaO_4 tetrahedra and NbO_4 tetrahedra are also described.

Keywords. Mixed framework oxides; tunnel structure oxides; non-stoichiometric oxides.

1. Introduction

The properties of oxides characterized by a tunnel structure may be drastically influenced by the nature of their framework. For instance, the widest tunnels are observed for tetrahedral oxides: the zeolites are well known for their ion exchange properties and especially for their catalytic properties. On the other hand, octahedral oxides exhibit much smaller tunnels, but they offer the possibility of obtaining various physical properties; for instance the oxygen bronzes are known for their electron transport properties whereas bronzoids can be obtained which are ferroelectric or ionic conductors. In this respect, the synthesis of oxides with a mixed framework of octahedra and tetrahedra is attractive. Nevertheless, the number of these oxides is limited, owing to the weak ability of octahedra and tetrahedra to adapt to each other. The present review deals with the study of such frameworks. Mixed valence oxides resulting from the creation of anionic vacancies in an octahedral framework, such as oxygen-deficient perovskites will not be discussed here. Thus, the 'true' 'mixed frameworks' will be mainly built by association of SiO_4 , GeO_4 , PO_4 , NbO_4 , MoO_4 and GaO_4 tetrahedra with MO_6 octahedra, M being a transition element.

2. Mixed frameworks with tetrahedral 'silicate' and 'germanate' groups (Roedder 1951; Myashiro 1956; Robbins and Levin 1961; Gross *et al* 1965; Seifert and Schreyer 1967, 1969; Blasse and Bril 1970; Olsen and Bunch 1970; Shannon and Katz 1970; Choisnet *et al* 1972, 1976, 1977; Puscharovskii *et al* 1972; Evans *et al* 1973; Goreaud *et al* 1973; Groult *et al* 1976; Nguyen *et al* 1976, 1980; Chailleux *et al* 1978; Shannon *et al* 1978; Studer and Raveau 1978; Raveau 1979).

The great rigidity of the SiO_4 and GeO_4 tetrahedra makes for few oxides with a

tunnel structure built up from SiO_4 (or GeO_4) tetrahedra and MO_6 octahedra are known. Moreover most of the them are richer in the tetrahedral element than in the octahedral one. The oxides $A_{6-x}M_6\text{Si}_4\text{O}_{26}$ and $A_{6-x}M_6\text{Ge}_4\text{O}_{26}$ are the only ones which correspond to a ratio M/Si greater than one. Even for molar ratios M/Si ,

Figure 1. The siliconiobate and tantalate $A_3M_6\text{Si}_4\text{O}_{26}$ and $K_{6-2x}\text{Ba}_x\text{Ta}_6\text{Si}_4\text{O}_{26}$. (a) the octahedral units M_3O_{15} , (b) the triple files of octahedra and the Si_2O_7 groups, (c) projection of the structure on to the (001) plane.

smaller than one, few oxides with a tunnel structure are known; three examples will be described here: the benitoïtes $AMSi_3O_9$ and $AMGe_3O_9$, the milarites $A_xM_3M'Si_{12}O_{30}$ and the silicates $Na_5MSi_4O_{12}$.

The siliconiobates and tantalates $A_3M_6Si_4O_{26}$ ($A = Ba, Cr, M = Ta, Nb$) $K_{6-x}Ba_xTa_6Si_4O_{26}$ and the silicogermanates $K_6M_6Si_{4-x}Ge_xO_{26}$ ($M = Ta, Nb$) form an important family of tunnel structures. In these hexagonal oxides the $M_6Si_4O_{26}$ framework is built up from octahedral units ' M_3O_{15} ' (figure 1a) and disilicate groups sharing their corners. Along c the octahedral units ' M_3O_{15} ' share their corners, forming infinite triple files of octahedra (figure 1b) identical to those observed in the hexagonal tungsten bronze structure (HTB); laterally, in the (001) plane the octahedral files share their corners with Si_2O_7 (or Ge_2O_7) groups whose ternary axis is parallel to c (figure 1c). This host lattice forms pentagonal tunnels very similar to those observed for the tetragonal tungsten bronze and characterized by angles of 90° and 120° . In these tunnels the K^+ and Ba^{2+} ions are located at two different levels along c (figure 1b); the difference between these two sites is due to the presence in one of them of the bridging oxygen of the Si_2O_7 group at the same level; consequently two sorts of coordinations are observed for the A ions ($10+3$) and ($10+5$). The important deviation from stoichiometry on the A cations, with x values ranging from 0 to 3, is another common point with the TTB structure. The boroniobate and tantalate $KM_3B_2O_{12}$ ($M = Ta, Nb$) have got a very similar framework, in spite of their different formation. This latter structure is simply deduced from the $M_6Si_4O_{26}$ framework by replacing each disilicate group by two triangular BO_3 groups, which ensure the cohesion between the octahedral files. Thus the $M_6B_4O_{24}$ framework (figure 2) is very similar to the one of $K_6M_6Si_4O_{26}$. The great flexibility of such a structure is confirmed by its possible intergrowth with the hexagonal oxide $A_3M_8O_{21}$ ($A = Ba, Sr, K; M = Nb, Ta, Ti$). This latter oxide represented by the composition $Ba_3Nb_4Ti_4O_{21}$, has its octahedral framework formed of octahedral units M_6O_{24} resulting from the association of two ' M_3O_{15} ' units by the edges of their octahedra (figure 3). Along c the M_3O_{15} units share the corners of their octahedra forming infinite triple files of octahedra whereas in the (001) plane these files share their corners with octahedra whose ternary axis is parallel to c (figure 4). Consequently, the (001) planes of both frameworks exhibit a bidimensional accord. This similarity between the two structures allows the building up of a series of intergrowths $(A_{6-x}M_6Si_4O_{26})_n \cdot (A_3M_8O_{21})_m$ as shown on figure 5 which corresponds to $K_{10}Nb_{22}Ge_4O_{68}$ ($n = 1, m = 2$).

The numerous hexagonal silicates and germanates $AMSi_3O_9$ and $AMGe_3O_9$

Figure 2. The boroniobate $K_3Nb_3B_2O_{12}$: the triple files of octahedra and their connection with the BO_3 triangles.

Figure 3. The structural unit ' M_6O_{24} ' resulting from the association of two ' M_3O_{15} ' units.

Figure 4. Projection of the structure of the hexagonal oxides $K_3M_8O_{21}$ on to the (001) plane.

($A = K, Rb, Tl, Ba$; $M = Ta, Nb, Sn, Ti$) belonging to the benitoïte family result from the ability of MO_6 octahedra to adopt a tetrahedral framework. Their framework is built up of Si_3O_9 (Ge_3O_9) rings which are linked through isolated MO_6 octahedra (figure 6) forming wide tunnels where the A ions are located. It must be pointed out that no deviation from stoichiometry has been observed for those oxides in spite of the presence of tunnels.

The silicates of the milarite family $A_xM_3M'_2Si_{12}O_{30}$ ($A = K, Na, Ba, Rb$; $M = Zn, Mn, Al, Te, Cu, Mg$; $M' = Mg, Mn, Fe, Cu, Li$) exhibit variable insertion rates ranging from $x = 1$ to $x = 3$. In those hexagonal oxides, the framework is almost only tetrahedral. The SiO_4 tetrahedra form hexagonal $Si_{12}O_{30}$ crowns (figure 7a), connected through rings of MO_4 tetrahedra and $M'O_6$ octahedra. In those rings the MO_4 tetrahedra and $M'O_6$ octahedra share their edges. The stacking of the $Si_{12}O_{30}$ crowns

Figure 5. Structure of the oxide $K_{10}Nb_{22}Ge_4O_{68}$, the second member of the inter-growth $(A_3M_8O_{21}) \cdot A_{6-x}M_6Ge_4O_{26}$.

Figure 6. Projection of the structure of the benitoite $KNbSi_3O_9$ on to the (001) plane.

Figure 7. The milarite host-lattice $M_3M'_2\text{Si}_{12}\text{O}_{30}$: (a) view along the direction perpendicular to c , (b) view along c .

along c delimits two sorts of tunnels, inside and outside of the crowns respectively, where the A ions are located (figure 7b).

The important family of ionic conductors $\text{Na}_3M\text{Si}_4\text{O}_{12}$ ($M = \text{Fe, In, Se, Y}$ and $\text{Ln} = \text{Ln to Sm}$) are also characterized by a mainly tetrahedral framework. The host lattice of these oxides which is formed of tetrahedral rings $\text{Si}_{12}\text{O}_{30}$, connected through MO_6 octahedra (figure 8) delimits two sorts of tunnels, inside and outside the rings respectively. It has been shown that the Na^+ ions located outside the rings are mobile contrary to those located inside.

Figure 8. Projection of the structure of the ionic conductor $\text{Na}_5\text{MSi}_4\text{O}_{12}$ on to the (001) plane.

3. Mixed frameworks with tetrahedral 'phosphate' groups (Magneli 1948; Kierkegaard 1962; Kihlberg 1963; Middlemis 1978; Giroult *et al* 1981, 1982; Domenges *et al* 1982, 1983, 1984, 1985; Hervieu and Raveau 1982, 1983; Labbe *et al* 1982; Leclaire *et al* 1983, 1985b; Benmoussa *et al* 1984; Goreaud *et al* 1985; Hervieu *et al* 1985; Masse *et al* 1985)

The PO_4 tetrahedra seem to adapt octahedral frameworks much more easily than the SiO_4 groups. Nevertheless the nature of M ions of the octahedral lattice is important: most of the three-dimensional frameworks can be obtained by association of PO_4 tetrahedra with WO_6 , MoO_6 and VO_6 octahedra.

The numerous family of phosphate tungsten bronzes can be considered as one of the most representative examples of adaptability of phosphate groups to an octahedral framework which is in fact that of ReO_3 . The relationships between the different series of phosphate tungsten bronzes can easily be understood by considering the great ability of the PO_4 tetrahedron to replace an octahedron without changing the geometry of the ReO_3 -type framework. The starting point of the structural chemistry of these bronzes can be represented by layers of the ReO_3 -type which are one octahedron thick along $[001]_{\text{ReO}_3}$ and n octahedra wide along $[100]_{\text{ReO}_3}$, bordered by simple PO_4 tetrahedra along the latter direction (figure 9a). Two ways of association of these layers along the direction perpendicular to their mean plane can be considered. In the first one two adjacent identical layers are stacked in such a way that WO_6 octahedra share their corners with other octahedra only, leading to the formation of diphosphate groups (figure 9b), whereas in the second manner two successive layers are stacked up by corner-sharing their polyhedra such that two tetrahedra belonging to two different layers are never connected (figure 9c). Thus, two sorts of slabs can be distinguished: ReO_3 -type slabs bordered with diphosphate groups which can also be represented by figure 9a, and ReO_3 -type slabs bordered by simple PO_4 tetrahedra stacked according to figure 9c, leading to the scheme presented in figure 9d.

The lateral connection of the ReO_3 -type slabs bordered with diphosphate groups can be carried out in two different ways (figure 10) which differ from each other only by a

Figure 9. ReO_3 -type slabs of the phosphate bronzes bordered with (a) PO_4 tetrahedra; their two ways of stacking leading to (b) diphosphate groups, and (c) single PO_4 tetrahedra. (d) The other representation of the stacking according to (c).

rotation of 180° of one layer out of two around the direction perpendicular to the slabs. This first type of association leads to the diphosphate tungsten bronze with hexagonal tunnels (DPTB_H) (figure 10b) and to the diphosphate tungsten bronze with pentagonal tunnels (DPTB_P) (figure 10c) respectively. The DPTB_H , $A_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ ($A = \text{K, Rb, Tl, Ba, } x \sim 1$), thus form an important family whose different m -members differ only by the number m of octahedra which characterize the ReO_3 -type slab; the size of their hexagonal tunnels which are characterized by angles of 120° and 90° , makes them comparable to the HTB . The DPTB_P , whose composition may be formulated as $(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ or $\text{K}_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$, have never been isolated in the form of pure samples, but have been observed as microcrystals by high resolution electron microscopy. Semi-regular sequences are often observed involving diphosphate planes as shown by the micrograph of figure 11a; the structure of such junctions (figure 11b) forming pentagonal tunnels was confirmed by simulation (figure 11c).

The lateral connection of the ReO_3 -type slabs bordered with simple PO_4 tetrahedra can also be connected in two different ways (figure 12) which differ also from each other only by the rotation of one slab out of two by 180° around an axis perpendicular to the slabs. Consequently two monophosphate bronze families have been isolated: the monophosphate tungsten bronzes with pentagonal tunnels (MPTB_P) $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ (figure 12b) and the monophosphate tungsten bronzes with hexagonal tunnels (MPTB_H), $A_x(\text{PO}_2)_4(\text{WO}_3)_{2m}$ ($A = \text{Na, K, } x = 2$) (figure 12c); as for the DPTB series the different members of these series differ from one another only by the number m of octahedra which determine the width of the ReO_3 -type slabs.

The great flexibility of such mixed frameworks are shown by the HREM study of the barium DPTB_H . For instance besides the perfect integral m -members (figure 13), one observes for non integral m -values intergrowths of different m -members (figure 14), and

Figure 10. Lateral connection of the ReO_3 -type slabs bordered with (a) diphosphate groups, leading to the diphosphate tungsten bronzes with (b) hexagonal tunnels (DPTB_H), and to (c) the diphosphate tungsten bronzes with pentagonal tunnels (DPTB_P).

the possibility of stopping the propagation of the phosphate planes leading to wide ReO_3 -type regions (figure 15), or of shifting phosphate planes with respect to one another in two adjacent regions of a crystal (figure 16). It is worth noting that the presence of one diphosphate group in the ReO_3 matrix leads to the formation of dislocations (figure 17). The adaptability of those mixed frameworks to the shear structures is also remarkable as shown from the regular lateral intergrowth of the $\{102\}$ C.S. planes with diphosphate planes (figure 18) and more complex associations of different shear planes with diphosphate planes as shown in figures 19 and 20.

The great ability of the WO_6 octahedra to be connected to PO_4 tetrahedra to form a tunnel structure is also found in the oxides $\text{P}_8\text{W}_{12}\text{O}_{52}$, $\text{CsP}_8\text{W}_8\text{O}_{40}$ and NaWPO_6 . The host lattice of the oxide $\text{P}_8\text{W}_{12}\text{O}_{52}$ (figure 21) formed of ribbons of ReO_3 -type connected to P_2O_7 groups, shows that various tunnels—with a pentagonal and hexagonal section—can be empty as in MPTB_P . The bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$ whose framework is built up from ReO_3 -type columns, connected through diphosphate groups is remarkable for its octagonal tunnels (figure 22) which are among the widest known in oxides with a mixed framework. Nevertheless no deviation from stoichiometry has

been observed for the Cs^+ ion located in the tunnels of this latter oxide. In the same way the phosphotungstate NaPWO_6 and the isomorphous oxide NaPMoO_6 , are stoichiometric in spite of the fact that they exhibit a tunnel structure. The host lattice of these compounds is characterized by infinite mixed chains in which one octahedron alternates with one PO_4 tetrahedron (figure 23a); laterally these chains are linked together in such a way that every tetrahedron of one chain shares one corner with an octahedron of the adjacent chain forming an helicoidal arrangement of the polyhedra (figure 23b). The structure of the phosphomolybdates $\text{PbMo}_2\text{P}_2\text{O}_{12}$ and

Figure 11. (a) and (b).

Figure 11 (c).

Figure 11. Diphosphate tungsten bronzes with pentagonal tunnels in the system $(P_2O_4)_2(WO_3)_{2m}$: (a) low resolution image showing a regular distribution of WO_3 -slabs in the mean sequence 48·91 (b) HREM micrograph of the twin boundary in a $(P_2O_4)_2(WO_3)_{2m}$ crystal and (c) its fitness with the calculated image for a $-400 \text{ \AA}$ defocus value.

Figure 12. Lateral connection of the ReO_3 -type slabs bordered with (a) single PO_4 tetrahedra, leading to (b) the monophosphate tungsten bronzes with hexagonal tunnels ($MPTB_H$) and to (c) the monophosphate bronzes with pentagonal tunnels ($MPTB_P$).

Figure 13. (a) An HREM image of $\text{Ba}(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{12}$ ($m = 6$) projected down the $[010]$ direction at about $-600 \text{ \AA}$ underfocus. The white spots correspond to perovskite (P) and hexagonal (H) tunnels respectively. (b) Idealized structure of $m = 6$.

$\text{BaMo}_2\text{P}_2\text{O}_{12}$ is very similar to that of NaPWO_6 , the mixed chains of octahedra and tetrahedra form the same helicodal arrangement. The main differences concern the tilting and the distortion of the polyhedra.

The recent study of the ternary oxides of molybdenum and phosphorus shows that molybdenum can also participate in the formation of tunnel structures involving PO_4 tetrahedra. $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ and $A\text{Mo}_2\text{P}_3\text{O}_{12}$ ($A = \text{K}, \text{Ti}, \text{Rb}$) characterized by the pentavalent and tetravalent states of molybdenum are two examples of such structures. The host lattice of the oxide $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ is very complex (figure 24); it is built up from corner-sharing MoO_6 octahedra, PO_4 tetrahedra and diphosphate groups P_2O_7 .

Figure 14. HREM images of intergrowths in the $\text{DPTB}_H \text{Ba}(\text{P}_2\text{O}_4)_4(\text{WO}_3)_{2m}$: (a) disordered crystal corresponding to the intergrowth of $m = 8, 9$ and 10 members, (b) ordered intergrowth of the members $m = 8$ and 9 .

Figure 15. (a) Termination of the 'diphosphate rows' in an $m = 11$ member of the potassium DPTB_H, and (b) idealized drawing of such a phenomenon.

Every MoO_6 octahedron shares five corners with the PO_4 and P_2O_7 groups, the sixth corner being free. It is worth noting that each P_2O_7 group shares two oxygen atoms with the same octahedron. In this framework the P_2O_7 and PO_4 groups form different layers. Although the ' O_6 ' octahedron surrounding the molybdenum ion is almost regular, the metal ion is strongly off-centre so that its coordination is better described as

Figure 16. (a) Series of adjacent defects in a potassium DPTB_H crystal, $m = 12$. An additional ' P_2O_7 ' row' appears. The adjacent rows swing (labelled C) in the neighbouring of the defect. (b) Idealized drawing of the shift of a tunnel-row.

a

b

Figure 17. HREM micrograph showing (a) the formation of a dislocation in a ReO_3 matrix, due to (b) the presence of a diphosphate group.

a MoO_5 pyramid. The size of the tunnels where the K^+ ions are located is close to those observed in octahedral structures.

The molybdenophosphate $\text{AMo}_2\text{P}_3\text{O}_{12}$ has its host lattice built up from corner-sharing PO_4 tetrahedra, diphosphate groups P_2O_7 and MoO_6 octahedra forming hexagonal tunnels where the A ions are located (figure 25). This structure is characterized by chains of polyhedra in which units of two corner-sharing octahedra alternate with P_2O_7 groups as in the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$. The similarity of this

Figure 18. (a) Micrograph of a thin crystal of $\text{DPTB}_H \text{K}(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ ($m = 19$) showing a quasi regular sequence of $\{102\}$ CS planes and (b) idealized drawing of the corresponding structure.

structure with the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$ is shown in figure 26. In both structures one observes similar double chains (figure 26b) in which every P_2O_7 group shares two corners with a Mo_2O_{11} unit formed of two octahedra. However, the relative orientation of two successive chains is different in both structures. Moreover the $\text{P}_8\text{W}_8\text{O}_{40}$ framework (figure 26c) is only built up from these double chains, whereas in the $\text{Mo}_2\text{P}_3\text{O}_{12}$ host lattice these double chains are linked through simple PO_4 tetrahedra (figure 26b). The structure of $\text{TlMo}_2\text{P}_3\text{O}_{12}$ is also closely related to that of the hexagonal tungsten bronze of Magneli.

Figure 19. Complex association of diphosphate planes and crystallographic shear planes showing: lateral intergrowths of $\{102\}$ CS planes and diphosphate planes, longitudinal intergrowths of $\{102\}$ CS planes and diphosphate planes, formation of $\{103\}$ CS planes in the ReO_3 -type matrix.

Consideration of this host lattice along another direction shows that it can be described as a stacking of identical layers (figure 27) of polyhedra which are characterized by hexagonal rings deduced from those of HTB by replacing two octahedra by two PO_4 tetrahedra.

The oxide $\text{V}_2\text{P}_2\text{O}_9$ represents the limit case of the tunnel structures characterized by a mixed framework. In such a lattice (figure 28) chains of ReO_3 -type are associated by the edges of their octahedra forming pairs. These double files are connected through P_2O_7 groups as in the diphosphate bronzes. Consequently this framework delimits square tunnels and diamond-shaped tunnels as in phosphate tungsten bronzes. It must also be pointed out that the vanadium ion is off centered in its octahedron so that it is more exactly characterized by a pyramidal coordination.

4. Mixed frameworks involving silicophosphate groups (Hagman and Kierkegaard 1968; Goodenough *et al* 1976; Leclaire *et al* 1984, 1985a, 1986)

The possibility of associating SiO_4 and PO_4 tetrahedra to MO_6 octahedra in order to build a three-dimensional framework characterized by tunnels is not obvious if one

Figure 20. Complex association of diphosphate planes and crystallographic shear planes: detail of an HREM micrograph taken from a crystal $\text{K}(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ with $m = 38$. Zones I and II illustrate different types of interactions between diphosphate planes and shear planes. Zone III shows a hair-pin like contrast.

Figure 21. Structure of the oxide $\text{P}_8\text{W}_{12}\text{O}_{52}$.

Figure 22. Structure of the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$.

Figure 23. NaPWO_6 . (a) The infinite chains built up from WO_6 octahedra and PO_4 tetrahedra. (b) Lateral connection between the mixed chains forming an octahedral arrangement.

Figure 24. The host lattice of the molybdenophosphate $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$.

Figure 25. The host lattice of the molybdenum phosphate $\text{TiMo}_2\text{P}_3\text{O}_{12}$.

takes into account the great rigidity of the SiO_4 and PO_4 tetrahedra. Three examples of such frameworks are given by the silicophosphates $AM_3\text{P}_6\text{Si}_2\text{O}_{25}$, $\text{V}_3\text{P}_3\text{SiO}_{19}$ and $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$.

The hexagonal silicophosphates $AM_3\text{P}_6\text{Si}_2\text{O}_{25}$ ($A = \text{K, Rb, Tl, Cs}$; $M = \text{Mo, Ti, Sn}$) form a large family which is in fact represented by the oxide $\text{KMo}_3\text{P}_{5.8}\text{Si}_2\text{O}_{25}$. The corner-sharing polyhedra which form the host-lattice of these oxides (figure 29) is characterized by tetrahedral units $\text{P}_6\text{Si}_2\text{O}_{25}$ which share their corners with MoO_6 octahedra. The tetrahedral units are built up of disilicate groups which share their corners with 2×3 PO_4 tetrahedra. This three-dimensional network delimits tunnels running along the $[100]$ and $[110]$ directions. Consequently, these oxides are characterized by an intersecting tunnel structure and can exhibit ion exchange properties.

The hexagonal vanadosilicophosphate $\text{V}_3\text{P}_3\text{SiO}_{19}$ can be considered as a limiting case owing to the very small size of its tunnels as shown from the projection of its

Figure 26. Comparison of the structure of the molybdenophosphate $\text{TiMo}_2\text{P}_3\text{O}_{12}$ with that of the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$. (a) The infinite chains built up from diphosphate groups and Mo_2O_{11} octahedral units. Relative dispositions and modes of connection of these chains (b) in the oxide $\text{TiMo}_2\text{P}_3\text{O}_{12}$ and (c) and in the bronze $\text{CsP}_8\text{W}_8\text{O}_{40}$.

structure on to the (001) plane (figure 30a). This oxide exhibits a great similarity with the true tunnel structure $\text{KM}_3\text{P}_6\text{Si}_2\text{O}_{25}$ (figure 30b): its framework is also built up from tetrahedral units $\text{P}_6\text{Si}_2\text{O}_{25}$ sharing their corners with VO_6 octahedra, but it differs from the silicomolybdate by the existence of P_4O_{13} units built up from four

Figure 27. Similarity of $\text{TlMo}_2\text{P}_3\text{O}_{12}$ with the HTB structure: the framework is built up from the stacking of identical layers of the polyhedra forming hexagonal rings.

Figure 28. Structure of the vanadophosphate $\text{V}_2\text{P}_2\text{O}_9$.

Figure 29. The host lattice of the hexagonal silicophosphate $KM_3P_6Si_2O_{25}$.

Figure 30 (a)

Figure 30. Projection of (a) the structure of the vanadosilicophosphate $V_3P_5SiO_{19}$ on to the (001) plane compared to (b) the one of $KM_3P_6Si_2O_{23}$. (c) Three-dimensional view of the host-lattice of $V_3P_5SiO_{19}$.

corner-sharing tetrahedra. The three-dimensional view of this structure (figure 30c) shows another particularity of this structure: the presence of octahedral clusters composed of two face-sharing octahedra; these clusters form infinite chains with the PO_4 tetrahedra extending along c , which can be compared to the strings $[\text{MoP}_2\text{O}_{15}]_3$ built up of three octahedra and six tetrahedra observed in the oxide $\text{AM}_3\text{P}_6\text{Si}_2\text{O}_{25}$.

The silicophosphates $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ could be classified as phosphates as well as silicates since their homogeneity range extends from $x = 0$ to $x = 3$. In these compounds each ZrO_6 octahedron shares its six corners with SiO_4 and/or PO_4 tetrahedra, and each tetrahedron shares its four corners with four octahedra as shown in figure 31a. This mixed framework $\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ does not really form tunnels but large cavities (figure 31b) where the Na^+ ions are located; however these cavities communicate with one another so that Na^+ ions can move through the structure, involving superionic conductivity properties for these materials. It is worth noting that zirconium may be replaced by titanium or germanium.

5. Other examples of mixed frameworks of octahedra and tetrahedra (Lloyd *et al* 1976; Stone and Bursill 1977; Bursil 1979; Bursill and Stone 1981; Gasperin 1981; Agafonov 1985)

Besides the silicates, germanates and phosphates, few oxides with a mixed framework involving tetrahedra and octahedra are known, if one excepts the oxygen-deficient perovskites. The niobate, $\text{Cs}_2\text{Nb}_4\text{O}_{11}$, is an interesting example owing to the great size

Figure 31. $\text{NaZr}_2(\text{PO}_4)_3$. (a) Three-dimensional view of the structure along the C_R direction of the rhombohedral cell. (b) Projection of half the unit cell along the a_R axis.

Figure 32. The host-lattice of the niobate $\text{Cs}_2\text{Nb}_4\text{O}_{11}$.

of its tunnels; the important family of oxides $\text{Ga}_4\text{O}_6(\text{MO}_2)_n$ ($M = \text{Ti, Ge}$) is worth describing owing to its analogy with the shear structures and the DPTB.

The host-lattice of the niobate $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ (figure 32) is mainly built up of corner and edge-sharing octahedra; however a small number of NbO_4 tetrahedra participate in the structure. A striking similarity with the pyrochlore framework is observed as shown from the hexagonal tunnels running in different directions. The main difference with pyrochlores concerns the groups of two edge-sharing octahedra and their association with NbO_4 tetrahedra leading to the formation of wide tunnels where the Cs^+ ions are located; these tunnels can be compared to those observed in $\text{CsP}_8\text{W}_8\text{O}_{40}$ and $\text{AM}_3\text{P}_6\text{Si}_2\text{O}_{25}$. Like the pyrochlores this oxide is characterized by a true intersecting tunnel structure which should exhibit ion exchange properties.

The structure of $\beta\text{-Ga}_2\text{O}_3$ which exhibits an anionic close-packing can also be considered as the limiting case of a tunnel structure: its framework (figure 33a) which is built up from structural units of Ga_4O_{24} formed of two GaO_4 tetrahedra and two edge-sharing GaO_6 octahedra, delimits diamond shaped tunnels. These latter are very similar to those of the hypothetical structure MO_2 (figure 33b) obtained by a simple tilting of the octahedra in the MO_2 rutile form (figure 33c). The close relationships between the two structures, rutile and $\beta\text{-Ga}_2\text{O}_3$, are confirmed by the ability of the Ga_4O_{24} units to fit the rutile framework. Ga_4O_{24} units can be introduced into the TiO_2 framework in the form of rows forming hexagonal tunnels which are empty. These rows delimit rutile slabs which are n octahedra wide; thus a large family, $\text{Ga}_4\text{O}_6(\text{MO}_2)_n$, can be predicted in which n is an odd number which characterizes the number of octahedra corresponding to the width of the rutile slab; Ga_4GeO_8 , $\text{Ga}_4\text{Ge}_3\text{O}_{12}$, $\text{Ga}_4\text{Ti}_5\text{O}_{16}$ correspond to the first, second and third members of this series whereas the oxide $\text{Ga}_4\text{Ti}_{21}\text{O}_{48}$ represents the member $m = 21$ (figure 34a, b, c). The similarity of this structural family with the shear structures and with the diphosphate tungsten bronzes must be pointed out: the ' $[\text{Ga}_4\text{O}_6]_\infty$ planes' correspond to the 'phosphate planes' or to the shear planes whereas the rutile slabs can be replaced by ReO_3 -type slabs in the DPTB. It is worth noting that the geometry of the ' Ga_4O_{24} ' units does not allow the obtaining of an even number of octahedra for the rutile slabs; nevertheless the possibility of existence of even- n members resulting from the intergrowth of two odd- m members can be considered as shown for the hypothetical member $m = 4$ (figure 34d). The particular behaviour of the first member Ga_4GeO_8 is also remarkable: the ' Ga_4O_{24} ' units share their corners in

Figure 33. Comparison of (a) the $\beta\text{-Ga}_2\text{O}_3$ structure with (b) the hypothetical MO_2 oxide derived from (c) the rutile TiO_2 framework by tilting of the octahedra. One Ga_4O_{24} unit is circled.

Figure 34. The three first odd members of the series $\text{Ga}_4\text{O}_6(\text{MO}_2)_n$ (a) $n = 1$, (b) $n = 3$ and (c) $n = 5$ and (d) the hypothetical even- m member $m = 4$ corresponding to the intergrowth of the members $n = 3$ and $n = 5$. The Ga_4O_6 units are hatched.

one direction forming ' $\beta\text{-Ga}_2\text{O}_3$ '-type ribbons, so that an intergrowth between this oxide and $\beta\text{-Ga}_2\text{O}_3$ could be considered.

6. Conclusion

Oxides with a three-dimensional mixed framework built up from octahedra and tetrahedra correspond to a rather recent field of investigation which seems rather promising. The adaptability of phosphate groups to an octahedral framework, especially to WO_6 and MoO_6 octahedra is remarkable, such structural properties

should be used to induce a strong anisotropy in the metallic properties of those bronzes leading either to bidimensional conductors as in DPVB and MPTB or to unidimensional conductors as in $\text{CsP}_8\text{W}_8\text{O}_{40}$. The possibility of SiO_4 and GeO_4 tetrahedra forming a mixed framework seems more limited, owing to their great rigidity, nevertheless they show a good ability to connect with NbO_6 or TaO_6 octahedra. The investigation of mixed frameworks involving 'silicophosphates' groups is quite new, but the formation of an intersecting tunnel structure makes us think that it could be the starting point of the synthesis of tunnel structures intermediate between the octahedral frameworks and the tetrahedral zeolites. Gallium, is characterized by its tendency to form mixed frameworks owing to its ability to take up both octahedral and tetrahedral coordinations; moreover oxides such as $\text{Ga}_4\text{O}_6(\text{TiO}_2)_n$ are potential candidates for intercalation of small ions like Li^+ or Na^+ .

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