sodium ions and having none of the terminal oxygen atoms in common, will give a simple alternative method by which both the sodium and the oxygen content can be made variable, and if they are present at random will undoubtedly provide evidence of disorder. Ordering will most likely occur at intermediate points where the ratio of the two kinds of unit are simple whole numbers.

Such a one (Fig. 5) comprises single units of the sodium tri- and hexatitanates alternating with one another. In one orientation the dimensions of the unit cell are

$$a=46{\cdot}8,\ b=3{\cdot}8,\ c=8{\cdot}7\ \text{Å};\ \beta=105{\cdot}1^\circ,$$

space group $C2/m$ (the average O–O distance again assumed to be 2·75 Å), and with the formula of the asymmetric unit $Na_{10}Ti_{18}O_{41}$, reducing to $Na_{2.2}Ti_4O_{9.1}$. The agreement with the figures in Table 6 for one form of poorly crystallized potassium tetratitanate is quite striking, except for a which is four times greater; a large axis and the likelihood of disorder, however, create difficult problems of identification in single-crystal diffraction films. The formula would approach that of a tetratitanate more closely if some $(Ti_3O_7)^{2-}$ layers were missing, and this would be accompanied by increased disorder and dimensional changes.

Berry *et al.* (1960) provided convincing evidence that potassium hexatitanate is fibrous, and whilst it is undoubtedly isomorphous with the corresponding sodium and rubidium compounds, the crystal structures of these two give no clear explanation of why this should be so except in terms of the closely coordinated octahedral tunnels. The fibrous property of these compounds may perhaps be related to their composition. Any additional $(Ti_3O_7)^{2-}$ sheets present would be expected to improve cleavages, in one direction at least.

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$Na_xTi_4O_8$, an Alkali Metal Titanium Dioxide Bronze

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A chemically inert ternary oxide $Na_xTi_4O_8$ (x approximately 0·8), prepared by the reduction in hydrogen of $Na_2Ti_3O_7$ at 950 °C., is monoclinic, space group $C2/m$, with unit-cell dimensions

$$a=12{\cdot}146,\ b=3{\cdot}862,\ c=6{\cdot}451\ \text{Å};\ \beta=106{\cdot}85^\circ.$$

It has a new kind of AX_2 host lattice with very distorted cubic interstitial positions partly occupied by sodium ions, and is a bronze, a non-stoichiometric oxide with some of the properties of a metal. The host structure is the end member of an homologous series $Me_{2n}O_{5n-2}$, n being here equal to two.

Introduction

In a recent discussion of the crystal chemistry of the alkali metal titanates (Andersson & Wadsley, 1962) we noted the existence of a sequence of structures with the general formula $B_nTi_6O_{10+n}$ $(0 \leq n \leq 4)$, B representing an interstitial position which could hold an alkali-metal ion. The three known members, the low temperature form of Ti_3O_5 $(n=0)$, $Na_2Ti_6O_{13}$ $(n=3)$ and $Na_2Ti_3O_7$ $(n=4)$, all contained common structural features, and the likely existence of addi-

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tional members was mentioned. Of particular interest was $B_2Ti_6O_{12}$ ($n=2$). If it could be made with the structure proposed as a member of the sequence (Fig. 1), the sodium compound of this composition should be a *bronze*, a class of ternary oxide having free electrons in the framework which give it some of the properties of a metal. In view of the readiness with which crystalline $Na_2Ti_6O_{13}$ ($n=3$) was synthesized simply by heating crystalline $Na_2Ti_3O_7$ ($n=4$), presumably by the loss of sodium and oxygen accompanied by the readjustment of the titanium–oxygen framework, it appeared likely that the $n=2$ member might be made in a suitable reducing atmosphere.

This preparative method has indeed produced a bronze, but one with a structure of a different kind, properly belonging to another series of oxides; a brief account of it has appeared elsewhere (Wadsley & Andersson, 1961).

Experimental

Crystalline $Na_2Ti_3O_7$, made by fusing Na_2CO_3 and TiO_2 (anatase) in the molar ratio 1:2 at 1300 °C., was heated in an atmosphere of hydrogen at 950 °C. in a quartz tube for two days. The product consisted of several black phases, one of which became colorless on standing in dilute hydrochloric acid, and this, together with an additional unidentified compound, was dissolved by boiling for several days with a mixture of concentrated hydrofluoric and sulphuric acids. The bronze, which comprised no more than 15% of the reduction product, was unaffected by this treatment. It consisted of very small blue-black electrically conducting crystals with a metallic lustre; they could be attacked very slowly only by prolonged digestion with hot concentrated oxidising acids.

The chemical analysis was a matter of great difficulty, and simply confirmed that sodium was present in a compound consisting chiefly of titanium dioxide. The approximate sodium content was found subsequently by a simple procedure forming part of the X-ray diffraction analysis, and the upper and lower composition limits were defined by the space-group point positions.

The unit-cell constants (Table 1) were determined from a Guinier film internally calibrated with KCl (Table 2). These agreed with the approximate dimensions of the crystal used for the structure determination which was selected before the acid treatment. No reliable measurement of the density could be made, and indeed the composition was considered likely to vary from one crystal to the next. Intensities were recorded on multiple films with copper radiation for the *h0l* and *h1l* levels with an integrating Weissenberg goniometer. The *h2l* and *h3l* levels were also exposed. The measurements made visually with a standard scale were reduced in the usual way. The physical dimensions of the needle-like crystal were 0·45 × 0·05 × 0·04 mm. approximately, and with a linear absorption coefficient of 473·7 cm.$^{-1}$ corresponding to an optimum crystal thickness of 0·04 mm., no absorption corrections were considered necessary. The ionised scattering curves for sodium, titanium and oxygen which were used are enumerated elsewhere (Andersson & Wadsley, 1961); the final *h0l* and *h1l* structure factors sets each incorporated an isotropic temperature factor, $B=0·2$ and 0·6 Å^2 respectively, determined by Wilson's method (1942).

Table 1. *Crystallographic data for* $Na_xTi_4O_8$

Unit cell dimensions:

$a=12·146\pm0·002$, $b=3·862\pm0·002$, $c=6·451\pm0·002$ Å;
$\beta=106·85\pm0·05°$

Systematic absent reflexions: *hkl* with $h+k\neq 2n$
Possible space groups: *C*2, *Cm*, *C*2/*m*
D(calc.): 3·88 g.cm.$^{-3}$
Unit-cell contents: $Na_{1·6}Ti_8O_{16}$

Table 2. *Guinier powder pattern for* $Na_xTi_4O_8$

Cu $K\alpha_1$ radiation (strongest lines only)

I	$\sin^2\theta$ (obs.)	*hk*	$\sin^2\theta$ (calc.)
m	0·01556	001	0·01556
ms	0·04415	110	0·04417
ms	0·06226	002	0·06226
m	0·06452	111	0·06453
s	0·06669	$40\bar{1}$	0·06669
w	0·07029	400	0·07029
ms	0·07911	310	0·07929
ms	0·08030	$31\bar{1}$	0·08049
m	0·09689	$11\bar{2}$	0·09685
s	0·15884	020	0·15912

Structure determination

The *h0l* and *h2l*, as well as the *h1l* and *h3l* reflexions of similar index had similar intensities, with due regard for observational errors. Since the *b* axis is only 3·86 Å in length, it appeared likely that the atoms either were lying within, or were very close to, the mirror planes characteristic of the space group *C*2/*m*, one of the three alternatives given by the systematically absent reflexions (Table 1).

A pseudo-cubic sub-cell appearing on the films was used as evidence of a lattice of atoms approximately in cubic positions, but ordered only in the real cell of lower symmetry; this is a prominent feature of all the alkali titanates and proved to be useful in devising an idealized model of the present structure by an empirical method outlined in detail elsewhere (Andersson & Wadsley, 1961, 1962).

The matrix expressing the relationship,

$$\text{cubic} \rightarrow \text{monoclinic} = 300/010/\bar{\tfrac{1}{2}}0\tfrac{3}{2}\,,$$

defines the orientation of the structural units. The ideal parameters of the titanium and oxygen atoms of the model fitting the data, all of which were assumed to be in the positions 4(*i*), $\pm(x, 0, z)$, for the space group *C*2/*m*, were systematically varied by trial and error, and then refined by electron-density projections on to (010).

Table 3. *Fractional atomic parameters*

Space group $C2/m$ (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0)+

Atom	Point position	x	z
xNa	2(a)	0	0
4Ti_1	4(i)	0·2907 ± 0·0009	0·709 ± 0·002
4Ti_2	4(i)	0·3950 ± 0·0010	0·300 ± 0·002
4O_1	4(i)	0·371 ± 0·003	0·996 ± 0·006
4O_2	4(i)	0·239 ± 0·004	0·358 ± 0·007
4O_3	4(i)	0·430 ± 0·003	0·624 ± 0·007
4O_4	4(i)	0·149 ± 0·004	0·698 ± 0·007

Table 4. *Interatomic distances*

	No.	Length		No.	Length
Ti_1–O_1	1	1·83 Å	Ti_2–$O_3{}^1$	1	2·04 Å
Ti_1–O_2	1	2·17	Ti_2–$O_1{}^1$	1	1·90
Ti_1–O_3	1	1·92	Ti_2–O_2	1	2·04
Ti_1–O_4	1	1·71	Ti_2–$O_4{}^1$	2	2·00
Ti_1–$O_2{}^1$	2	1·99	$O_1{}^1$–O_2	1	3·19
O_1–O_4	1	2·82	$O_1{}^1$–$O_3{}^1$	1	2·90
O_2–O_4	1	2·73	O_2–O_3	1	2·45
O_2–O_3	1	2·45	$O_3{}^1$–O_3	1	2·66
O_1–O_3	1	2·69	O_3–$O_4{}^1$	2	2·79
O_1–$O_2{}^1$	2	2·99	O_2–$O_4{}^1$	2	2·45
O_4–$O_2{}^1$	2	2·45	$O_1{}^1$–$O_4{}^1$	2	2·82
O_2–$O_2{}^1$	2	2·62	$O_3{}^1$–$O_4{}^1$	2	3·21
O_3–$O_2{}^1$	2	2·84	Na–O_1	4	2·48
Ti_2–O_3	1	2·01	Na–O_3	4	3·02

Additional scattering matter at the origin was clearly due to sodium, the peak height corresponding approximately to three quarters of an atom. Owing to atomic overlap it proved difficult to reduce the reliability factor for $h0l$ below 18·5% by difference projections, but two cycles of least-squares refinement, in which the off-diagonal coefficients were neglected only for the completely resolved atoms O_1 and O_3, were more effective. The contributions of the titanium and oxygen atoms were then combined in several

Table 5. *Comparison of observed and calculated structure factors*

hk	F_o	F_c	hk	F_o	F_c	hk	F_o	F_c	hk	F_o	F_c
001	41	$\overline{47}$	$60\bar{2}$	48	$\overline{37}$	$14,0,\bar{2}$	< 19	13	514	< 18	$\bar{2}$
2	99	$\overline{98}$	$\bar{1}$	151	173	$\bar{1}$	19	$\overline{16}$	5	< 17	15
3	150	174	0	48	$\overline{49}$	0	17	16	6	< 19	10
4	52	46	1	78	$\overline{73}$	1	17	27	$71\bar{7}$	< 14	12
5	78	$\overline{75}$	2	94	106	$11\bar{7}$	< 15	$\overline{14}$	$\bar{6}$	24	32
6	43	38	3	35	26	$\bar{6}$	< 18	14	$\bar{5}$	25	$\overline{35}$
7	58	72	4	57	$\overline{55}$	$\bar{5}$	< 17	12	$\bar{4}$	29	$\overline{34}$
8	13	27	5	32	19	$\bar{4}$	< 15	$\overline{12}$	$\bar{3}$	60	77
$20\bar{8}$	< 13	7	6	38	56	$\bar{3}$	< 12	$\overline{10}$	$\bar{2}$	< 15	8
$\bar{7}$	44	$\overline{42}$	$80\bar{7}$	29	22	$\bar{2}$	41	45	$\bar{1}$	98	$\overline{95}$
$\bar{6}$	44	41	$\bar{6}$	35	33	$\bar{1}$	< 7	$\bar{5}$	0	70	70
$\bar{5}$	48	45	$\bar{5}$	< 25	3	0	84	$\overline{82}$	1	51	40
$\bar{4}$	54	$\overline{58}$	$\bar{4}$	< 24	9	1	68	58	2	93	$\overline{82}$
$\bar{3}$	< 22	11	$\bar{3}$	46	41	2	40	33	3	< 18	12
$\bar{2}$	76	77	$\bar{2}$	22	33	3	90	$\overline{70}$	4	54	49
$\bar{1}$	< 15	$\bar{6}$	$\bar{1}$	< 15	$\bar{3}$	4	< 16	11	5	38	$\overline{32}$
0	41	$\overline{52}$	0	22	31	5	51	43	$91\bar{7}$	42	47
1	61	69	1	37	41	6	32	$\overline{23}$	$\bar{6}$	< 16	2
2	43	43	2	< 25	0	7	24	$\overline{17}$	$\bar{5}$	51	57
3	50	$\overline{59}$	3	< 25	19	$31\bar{7}$	56	53	$\bar{4}$	18	$\overline{29}$
4	23	29	4	< 24	21	$\bar{6}$	47	$\overline{50}$	$\bar{3}$	30	$\overline{41}$
5	36	38	5	< 17	6	$\bar{5}$	< 17	1	$\bar{2}$	34	46
6	24	$\overline{31}$	$10,0,\bar{7}$	53	66	$\bar{4}$	109	104	$\bar{1}$	24	31
7	< 17	9	$\bar{6}$	< 22	$\bar{4}$	$\bar{3}$	12	$\overline{25}$	0	38	$\overline{57}$
$40\bar{8}$	< 15	$\bar{9}$	$\bar{5}$	61	55	$\bar{2}$	22	$\overline{23}$	1	< 18	0
$\bar{7}$	45	$\overline{44}$	$\bar{4}$	44	56	$\bar{1}$	97	84	2	47	60
$\bar{6}$	48	47	$\bar{3}$	50	36	0	77	67	3	20	$\overline{32}$
$\bar{5}$	< 24	10	$\bar{2}$	55	$\overline{55}$	1	21	$\overline{36}$	4	26	$\overline{24}$
$\bar{4}$	91	$\overline{79}$	$\bar{1}$	< 25	3	2	< 12	1	$11,1,\bar{6}$	< 13	3
$\bar{3}$	40	33	0	64	66	3	101	102	$\bar{5}$	< 16	12
$\bar{2}$	56	39	1	< 25	$\overline{17}$	4	< 17	$\overline{18}$	$\bar{4}$	< 17	16
$\bar{1}$	78	$\overline{68}$	2	49	$\overline{47}$	5	38	$\overline{35}$	$\bar{3}$	< 18	1
0	44	$\overline{37}$	3	38	53	6	58	60	$\bar{2}$	28	18
1	68	56	4	28	25	7	< 9	9	$\bar{1}$	22	22
2	< 19	$\bar{7}$	$12,0,\bar{6}$	18	20	$51\bar{7}$	< 15	3	0	< 18	$\bar{8}$
3	79	$\overline{74}$	$\bar{5}$	48	48	$\bar{6}$	33	28	1	23	17
4	43	40	$\bar{4}$	47	$\overline{66}$	$\bar{5}$	< 17	9	2	28	22
5	36	36	$\bar{3}$	< 25	$\bar{9}$	$\bar{4}$	< 16	$\bar{4}$	3	16	$\bar{8}$
6	61	$\overline{62}$	$\bar{2}$	66	66	$\bar{3}$	33	40	$13,1,\bar{5}$	17	$\overline{18}$
7	< 10	1	$\bar{1}$	35	$\overline{43}$	$\bar{2}$	42	24	$\bar{4}$	53	58
$60\bar{8}$	49	55	0	42	$\overline{30}$	$\bar{1}$	< 11	1	$\bar{3}$	< 15	1
$\bar{7}$	31	27	1	38	42	0	32	40	$\bar{2}$	50	$\overline{49}$
$\bar{6}$	76	$\overline{73}$	2	< 19	$\bar{2}$	1	< 13	12	$\bar{1}$	44	$\overline{50}$
$\bar{5}$	35	29	3	27	$\overline{29}$	2	18	16	0	37	31
$\bar{4}$	99	117	$14,0,\bar{4}$	< 18	$\overline{10}$	3	24	21	1	54	$\overline{45}$
$\bar{3}$	87	$\overline{97}$	$\bar{3}$	19	29						

sets of structure factors with sodium, the scattering curve of which was weighted by the fraction x, varying at regular intervals between 0·5 and 1·0, and which appears in the asymmetric formula $Na_xTi_4O_8$. The reliability factor, obtained in all cases by including the non-observed reflexions each of which was assigned half the least observable value, reached a minimum of 13·9% at the point of the graph corresponding to $x=0{\cdot}8$. This was accepted as an approximate measure of the sodium content of the compound.

The parameters obtained from the least-squares refinement were next combined in a set of $hl l$ structure factors with values of $y=0$ for all atoms, assuming them all to lie on mirror planes; this gave a reliability index of 16·7%, and the structure, for our purposes, can be described in terms of the space group $C2/m$. It is possible that some of the lighter oxygen atoms may be shifted slightly away from these planes, but as we have pointed out elsewhere (Andersson & Wadsley, 1962) this is a difficult matter to resolve with any finality. With this reservation, therefore, the parameters together with standard deviations enumerated by methods outlined by Cruickshank (1959) are given in Table 3, interatomic distances in Table 4, and F_o and F_c in Table 5. The uncertainty in interatomic distances, averaged for contacts of the same kind, are ±0·04 Å for Ti–O, ±0·05 Å for O–O, and ±0·03 Å for Na–O.

Description

The structure has a framework of titanium–oxygen octahedra (Figs. 2 and 3). The Ti_1–oxygen distances vary between 1·71 Å and 2·17 Å averaging 1·94 Å, whilst the Ti_2–oxygen distances are rather more alike, having the limits 1·90 and 2·04 Å, average 2·00 Å. The shortest oxygen-to-oxygen distances O_3–O_2, O_4–O_2^1 of 2·45 Å correspond to edges which are common to two octahedra. The distances between adjacent titanium atoms vary widely between 2·97 Å for those in the (001) planes to 3·78 Å across octahedral corners. These are similar to distances found in the rutile form of TiO_2, and evidently no metal–to–metal bonds occur. The sodium ion has an environment of eight oxygens at the corners of a very distorted cube, two Na–O_1 bonds being 2·48 Å and two Na–O_3 bonds 3·02 Å, so that it has a pronounced tendency towards square coordination.

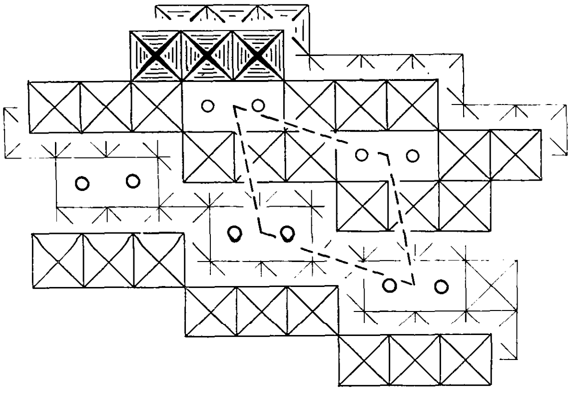


Fig. 1. Possible alkali metal bronze $B_2Ti_6O_{12}$ in idealized form, postulated as a member of the structural sequence $B_nTi_6O_{10+n}$ (B representing an interstitial position marked as a circle). One of the structural units, a treble zig-zag ribbon of octahedra extending out of the plane of the paper, is hatched, and half the unit cell drawn as a broken line. This substance has not yet been found.

There are several ways to describe this structure which enable certain of its features to be emphasized and perhaps clarified.

Its relationship to the other alkali titanates is best expressed in terms of a double zig-zag ribbon of octahedra having common edges (Fig. 4(a)), the ribbons joining

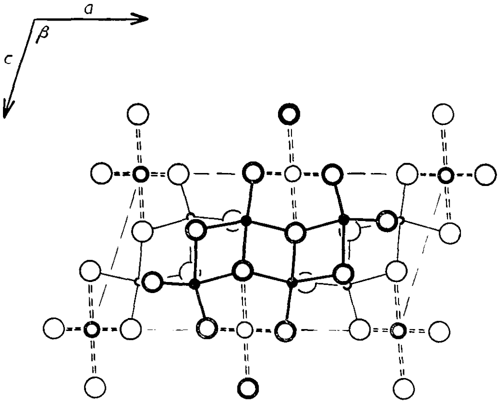


Fig. 2. The positions of the atoms in $Na_xTi_4O_8$. The largest circles are oxygen, the intermediate ones in special positions sodium, and the smallest are titanium. The atoms in heavier outline (black for titanium) are at $y=0$ and the lighter are at $y=\frac{1}{2}$. Bonds from sodium to oxygen are drawn as broken lines and the unit cell is outlined.

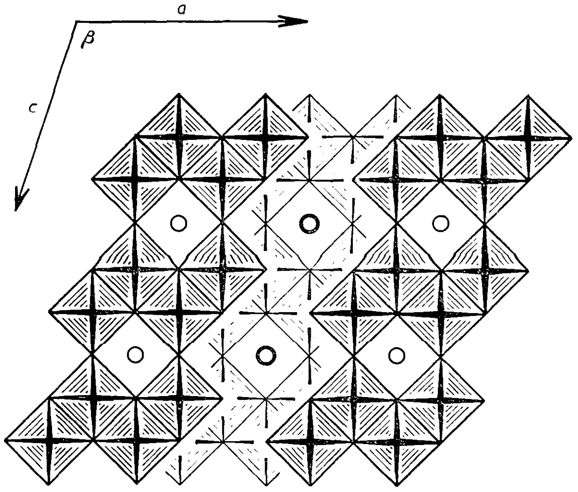


Fig. 3. Structure of $Na_xTi_4O_8$ drawn in idealized form with regular titanium–oxygen octahedra; the circles are sodium atoms. Aspects of this drawing are emphasized in Figs. 4(a), (b), and (c).

corners to form a sheet which is parallel to the c axis; $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ are both constructed of similar kinds of sheet containing treble and not double octahedral ribbons (Andersson & Wadsley, 1962). The structure is then completed by these sheets, alternately reversed, and joined by having additional edges in common. This forms a host framework in which the metal-to-oxygen ratio is 1 : 2, and is a titanium dioxide unrelated to the polymorphs rutile, anatase or brookite. The structure has not previously been found for any known compound of formula AX_2.

Each sodium position is at the centre of a group of four octahedra sharing corners, and in the ideal case will have the same cubic (or twelve-fold) environment as the A atoms in the perovskite structure ABX_3 (Fig. 4(b)). Instead of continuing indefinitely by corner sharing, these sub-units of four in the bronze are condensed, the two non-equivalent octahedra respectively sharing four and five of their edges with neighbouring groups. The effect is to reduce the number of A sites together with the quantity of oxygen in the unit formula, but retaining a resemblance to the simpler lattice in the diffraction data as well as in the structure itself.

Along the a direction the zig-zag ribbons of Fig. 4(a) are joined together by edges (the upper part of Fig. 4(c)). This double octahedral sheet, for convenience called a D unit, is made up by the union of two single octahedral or S sheets (Fig. 4(c), lower), a method of description used previously to discuss the mixed niobium–titanium oxides (Wadsley, 1961). The double unit (D) occurs in V_6O_{13} (Aebi, 1948) where it alternates with single (S) units joined to it by corners. A convenient description of this substance is therefore the sheet sequence

$$-S-D-S-D- .$$

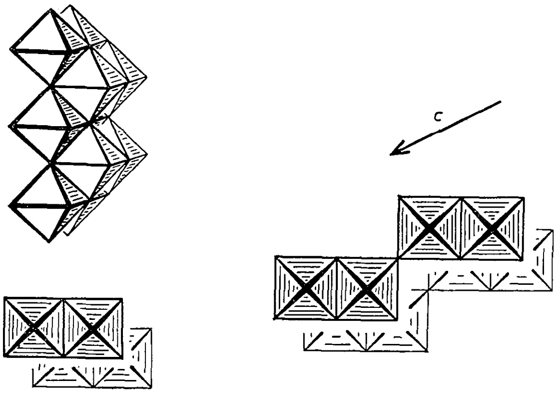
The structure of vanadium pentoxide, whilst it is grossly distorted (Byström, Wilhelmi & Brotzen, 1950) can be represented by single units of the same kind sharing corners,

$$-S-S-S-S .$$

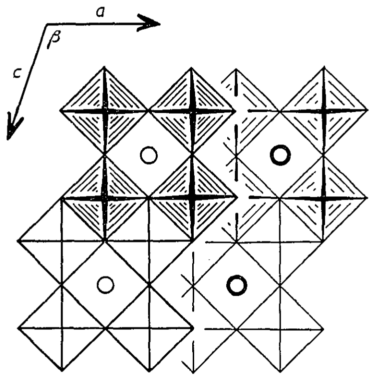
An appraisal of the crystal chemistry of the vanadium oxides led to the idea that perhaps many different sequences of these two units were possible, and could result in a series of ordered structural homologues with the general formula $Me_{2n}O_{5n-2}$ (Wadsley, 1957). The limiting cases would be V_2O_5 itself (n large) and a dioxide MeO_2 ($n = 2$) consisting solely of the D units sharing corners,

$$-D-D-D-D .$$

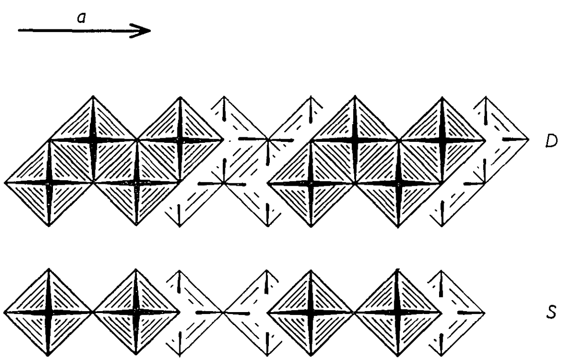
This latter is the host lattice of the titanium bronze; although it contains a different metal ion it is nevertheless closely related in structure to the vanadium-oxides as a member of this series.



(a)



(b)



(c)

Fig. 4(a). The drawings at the left show a zig-zag row of double octahedra, in perspective (upper) and in projection down the axis of elongation (lower). These ribbons can join by having common corners as on the right-hand side; this corresponds to the c direction of Fig. 3.

Fig. 4(b). Part of Fig. 3 in which a group of four octahedra sharing corners and enclosing a sodium ion, essentially a fragment of the ideal perovskite structure, is joined to a similar group $b/2$ down by edge sharing (both groups shaded). Further edge sharing at the same levels by both groups also occurs; these are unshaded.

Fig. 4(c). Double zig-zag ribbons (Fig. 4(a)) have edges in common when viewed along the a direction (upper). These are called D units, and consist of two single, or S sheets (lower) joined together by common edges. The D and/or the S units occur in V_2O_5, V_6O_{13} as well as in $Na_xTi_4O_8$.

Bronzes

The name *bronze* is given to the chemically inert non-stoichiometric ternary oxides of tungsten first described by Wöhler in 1824. There are three known classes of tungsten bronze all of which, represented chemically as A_xWO_3, are based upon WO_3 host lattices of different crystal structure. The simplest is the regular or degenerate perovskite structure, and A may be the univalent ions Na, Li, Cu or Ag. Tetragonal bronzes have been found containing Na, K, Pb^{++} and possibly NH_4^+, whilst others with hexagonal symmetry are confined to K, Rb, Tl or Cs. The guest ions A always occupy positions of appropriate size within the framework.

Cubic bronzes of perovskite structure have been found which do not contain tungsten, La_xTiO_3 (Kestigian & Ward, 1955) and Sr_xNbO_3 (Ridgley & Ward, 1955). Compounds generally accepted as bronzes may have entirely different structures. These include $Na_{2-x}V_6O_{15}$ (Wadsley, 1955) and related compounds (Ozerov, 1959) as well as $Li_{1+x}V_3O_8$ (Wadsley, 1957); $Na_xPt_3O_4$ and $Na_xPd_3O_4$ (Waser & McLanahan, 1951; Scheer, van Arkel & Heyding, 1955), a hexagonal barium tantalate of partly known structure (Galasso & Katz, 1960) and K_xTiO_2 (Wadsley & Andersson, 1961). All of these substances have host frameworks in which additional ions of another kind, in variable amounts, are present in interstitial positions of the appropriate size.

It seems that the *bronze* category is a wide one, but attempts to classify it solely in terms of structure can lead to difficulties. All of these substances, however, have chemical and physical properties which include

(*a*) intense color and lustre; black;
(*b*) metallic conduction; semiconduction;
(*c*) range of chemical composition;
(*d*) resistance to chemical attack by non-oxidising acids.

The metal ion of the host lattice must be capable of dual valency; the electrons liberated by the guest ions are not captured by individual host metal ions, but are distributed instead over the whole structure. These electrons and their mobility confer upon the solid its combination of properties which, despite much recent work, are still imperfectly understood.

In this instance the presence of sodium, which as an impurity or guest atom, may be necessary to form the host lattice, is undoubtedly the reason why $Na_xTi_4O_8$ can be classified as a bronze. The composition limits have not been established experimentally but on space-group requirements would be in the range $0 \le x \le 1$. Additional experiments could be devised in which the well crystallized alkali titanates were reduced under different conditions, or syntheses conducted in sealed tubes, or in which solutions of TiO_2 in fused sodium salts were electrolysed. These could lead either to new compositions of this bronze or to bronzes of similar composition but of different structure as, for example, Fig. 1.

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