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The Structure of Orthorhombic Y_2TiO_5 , an Example of Mixed Seven- and Fivefold Coordination

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Crystals of Y_2TiO_5 , grown by heating the composition $NaYTiO_4$ at 1500°C in air, have the unit-cell dimensions $a = 10.35$, $b = 3.70$, $c = 11.25$ Å, space group $Pnma$, $Z = 4$. The structure was deduced from the Patterson function and refined by three-dimensional Fourier and least-squares methods. The two independent yttrium ions are both in sevenfold coordination, with oxygen atoms forming irregular trigonal prisms capped through one rectangular face. These polyhedra unite by edge-sharing into groups of four extending infinitely in the direction of the short b axis. The groups are held together by the titanium ions which are five-coordinated, with four oxygen ligands from one group and one from the next at the corners of a square pyramid. A number of rare-earth titanates with the same stoichiometry are isomorphous with Y_2TiO_5 . The relationships to the B -type rare-earth oxide, to $YO(OH)$ and to Sr_2PbO_4 structure types are discussed.

Introduction

The mixed-metal oxycompounds formed at high temperature between Ti or Zr and the rare earths were summarized recently by Collongues, Queyroux, Perez y Jorba & Gilles (1965). They reported a number of cubic phases $A_2B_2O_7$ (A trivalent, B quadrivalent) with the pyrochlore structure, a rhombohedral group $A_4B_3O_{12}$ related to UY_6O_{12} (Bartram, 1966) and to $Sc_4Zr_3O_{12}$ (Thorner, Bevan & Graham, 1968), as well as a third family A_2BO_3 existing in both low- and high-temperature modifications. Each of the powder diffraction patterns of low-temperature Y_2TiO_5 , Dy_2TiO_5 and Gd_2TiO_5 was indexed in terms of a monoclinic superlattice $a \approx 3a'$, $b \approx a'$, $c \approx 3a'$, $\beta = 90 - \delta$, originating from a fluorite-type sub-cell of side a' , and conforming to the notion of a phase intermediate in structure and composition between fluorite-type (stoichiometry BO_2) and C -type rare-earth oxide (A_2O_3), both of which are cubic.

We now wish to report that a well-crystallized product, formed as one of the thermal decomposition

products of $NaYTiO_4$, appears to be identical with the low-temperature form of Y_2TiO_5 . This phase was overlooked by Ault & Welch (1966) in their appraisal of the Y_2O_3 - TiO_2 system. The symmetry and unit-cell dimensions are not those given by Collongues *et al.* (1965), however, and the structure determination relates it more to the B (monoclinic) rare-earth oxides than to the C (cubic) form.

Experimental

$NaYTiO_4$, which is readily prepared by solid-state reaction between Y_2O_3 , TiO_2 and sodium oxalate at 1300°C in a sealed system, is related to a number of titanates with the K_2NiF_4 structure (Mumme, Reid & Wadsley, 1967). It decomposes on heating in air at 1500°C into a heterogeneous product containing a number of small clear colourless needle-like crystals, which proved from this structure analysis to have the composition Y_2TiO_5 . The crystallographic constants in Table 1 were determined from the separation of the α_1 - α_2 doublet for a number of spots in the back-reflex-

Table 1. *Crystallographic data for Y_2TiO_5*

Symmetry: orthorhombic	
Unit-cell dimensions	$a = 10.35 \pm 0.01 \text{ \AA}$ $b = 3.70 \pm 0.01$ $c = 11.25 \pm 0.01$
Systematically absent reflexions	$0kl$ with $k+l \neq 2n$ $hk0$ with $h \neq 2n$
Possible space groups	$Pnma$ (No. 62), $Pn2_1a$ (No. 33)
D_x	4.73 g.cm^{-3}
Z	4
μ	537 cm^{-1}

ion region of Weissenberg films by a simple variant of Main & Woolfson's (1963) method.

The identity of this phase with the Y_2TiO_5 of Collongues *et al.* (1965) was established by a roundabout procedure. Waring & Schneider (1965) prepared Sm_2TiO_5 , Eu_2TiO_5 and Gd_2TiO_5 , noted the similarity of the powder patterns, and yet were unable to confirm the unit-cell assignment of Collongues *et al.* They kindly sent a specimen of Gd_2TiO_5 to us, and a Guinier pattern of it was readily indexed in terms of an orthorhombic unit cell with the dimensions $a = 10.48$, $b = 3.76$, $c = 11.33 \text{ \AA}$, the missing reflexions being characteristic of the space group $Pnma$. Gd_2TiO_5 is clearly isostructural with the crystals prepared by thermally decomposing $NaYTiO_4$ (Table 1) and both are members of a group of titanates M_2TiO_5 containing a number of the rare earths, M.

Intensities were collected with a crystal 0.08 mm long (corresponding to the b direction) and between 0.02 and 0.03 mm in average cross-section. μr was in the range 1.2–1.4 and absorption corrections were unnecessary. Exposures for the levels hkl , $k=0$, 1 and 2 were made on multiple films with filtered copper radiation using an integrating Weissenberg camera, and measurements were made visually with a standardized scale of timed exposures having the same spot shape. Approximate scaling between levels was made initially by Wilson's (1942) method, and adjusted in between refinement cycles by comparing F_o with F_c . Scattering curves for Y^{3+} and Ti^{4+} , corrected with Cromer's (1965) values for $\Delta f'$ and $\Delta f''$ were taken from Cromer & Waber (1965), and the values for doubly ionized oxygen from Suzuki (1960). The weighting scheme for the least-squares refinement was that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), and the matrices were inverted with the block-diagonal approximation. All calculations were made on the Division's Elliott 803 computer using the programming system of Daly, Stephens & Wheatley (1963).

The principal structural features were determined in projection to (010), as no extensive overlap of atoms is possible with a projection axis only 3.70 Å long. The derivation of the structure depended upon fixing the positions of two independent yttrium atoms, one titanium and five oxygen atoms in the asymmetric unit, all of which were assumed to lie in the mirror planes

at $y = \frac{1}{4}$ or $y = \frac{3}{4}$. Only one set of metals consistent with the Patterson projection $P(uw)$ were found, and their coordinates were improved and the five oxygen atoms located directly and without assumptions by reiteration of electron density and structure factor calculations based on the $h0l$ data. Preliminary bond length calculations were helpful in assigning the y parameters for

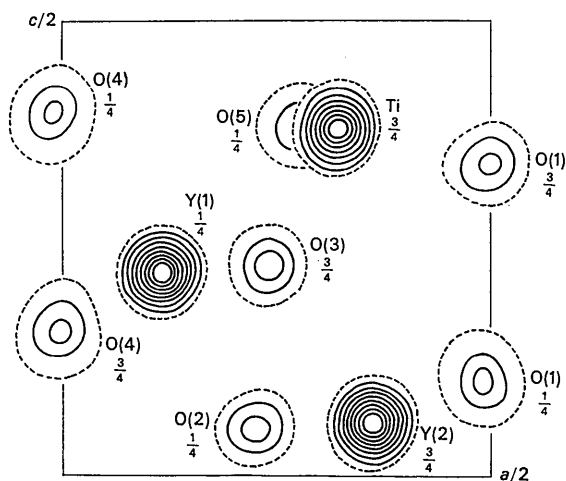


Fig. 1. Superimposed electron density sections at $y = \frac{1}{4}$ and $\frac{3}{4}$. Contours drawn at intervals of 2.5 electrons for Ti and O, and 5 electrons for the two yttrium atoms. Zero contour dotted.

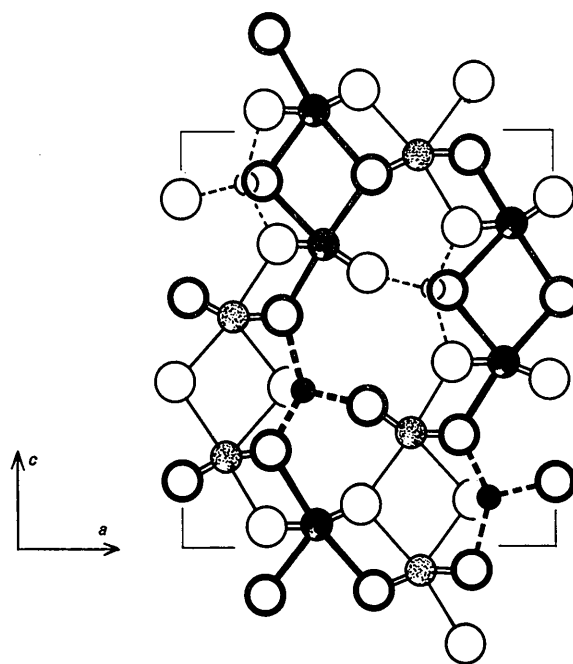


Fig. 2. Structure of Y_2TiO_5 . Oxygen atoms are the largest circles, yttrium atoms are stippled and titanium atoms are the smallest circles, open and black. Heavier outlines or shading represents an atom at $y = \frac{3}{4}$, lighter at $y = \frac{1}{4}$. The bonds between titanium and oxygen are drawn as dashed lines.

all atoms. These were confirmed by three-dimensional Fourier sections coinciding with the mirror planes (Fig. 1), and the positions were refined together with individual isotropic temperature factors, by a number of least-squares cycles using all of the data except for five reflexions of low indices, severely affected by extinction, which were omitted. Refinement was stopped when the shift of each variable was less than one quarter of its standard deviation. No attempt was made either to reduce the symmetry to $Pn2_1a$ or to correct for extinction. The final R value of 12.2% was rather high, but a three-dimensional difference synthesis con-

tained no peak or trough greater than $0.5 e. \text{Å}^{-3}$. A comparison between F_o and F_c is given in Table 2, and the atomic parameters, the temperature factors, and their e.s.d.'s in Table 3. The structure is illustrated by Fig. 2.

Discussion

Both yttrium atoms are seven-coordinated to oxygen, but the polyhedra, which are similar to each other, are not easy to define. One description is a cube of oxygen atoms from which one is missing and with some relaxation of three of the remaining seven [Fig. 3(a)]. In

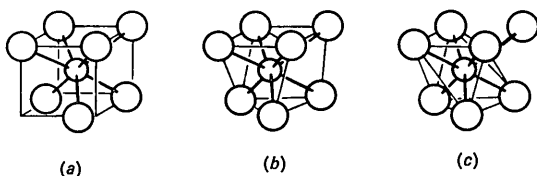


Fig. 3. Coordination of yttrium in Y_2TiO_5 : (a) as a cube with one oxygen atom missing and with some rearrangement of the remainder; (b) as a distorted trigonal prism with a seventh oxygen atom bonded through a face; (c) as an octahedron with one additional oxygen atom.

Table 3. Fractional atomic coordinates for Y_2TiO_5
Space group $Pnma$ (No. 62). All atoms in point position $4c$.
E.s.d.'s are given in brackets.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Y(1)	0.1156 (3)	$\frac{1}{4}$	0.2231 (3)	0.51 (6) Å ²
Y(2)	0.1366 (3)	$\frac{3}{4}$	0.5578 (3)	0.43 (6)
Ti	0.1745 (8)	$\frac{1}{4}$	0.8806 (7)	0.72 (13)
O(1)	0.4947 (32)	$\frac{1}{4}$	0.1024 (29)	1.2 (6)
O(2)	0.2229 (31)	$\frac{1}{4}$	0.0449 (28)	0.9 (6)
O(3)	0.2594 (30)	$\frac{1}{4}$	0.7340 (27)	0.9 (6)
O(4)	0.5085 (28)	$\frac{3}{4}$	0.6601 (26)	0.8 (5)
O(5)	0.2690 (34)	$\frac{1}{4}$	0.3833 (30)	1.4 (7)

Table 2. Observed and calculated structure factors

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	2	28	-27	7	0	8	74	-65	4	1	4	56	55	1	2	12	71	-95
0	0	4	20	20	7	2	9	79	80	4	4	1	5	28	24	2	24	46	33
0	0	6	12	-144	7	4	10	12	12	4	4	1	11	14	14	2	47	25	201
0	0	8	56	-55	7	6	11	27	58	4	4	1	15	35	37	2	56	28	79
0	0	10	79	-31	8	8	12	36	151	4	4	1	19	57	50	2	68	26	44
0	0	12	30	37	8	10	13	45	79	4	4	1	23	90	88	2	82	46	44
0	0	14	44	-33	8	12	14	54	257	4	4	1	27	107	100	2	96	34	25
0	0	16	29	-26	8	14	15	63	227	4	4	1	31	124	117	2	110	207	-25
0	0	18	44	-41	8	16	16	72	267	4	4	1	35	141	134	2	124	46	-44
0	0	20	87	84	8	18	17	81	63	4	4	1	39	158	151	2	138	34	-25
0	0	22	156	-156	8	20	18	90	123	4	4	1	43	175	164	2	152	207	-25
0	0	24	87	-84	8	22	19	99	213	4	4	1	47	192	173	2	166	46	-44
0	0	26	156	156	8	24	20	108	303	4	4	1	51	209	192	2	180	34	-25
0	0	28	44	-41	8	26	21	117	393	4	4	1	55	226	201	2	194	46	-44
0	0	30	87	84	8	28	22	126	483	4	4	1	59	243	210	2	208	34	-25
0	0	32	156	-156	8	30	23	135	573	4	4	1	63	260	219	2	222	46	-44
0	0	34	44	-41	8	32	24	144	663	4	4	1	67	277	228	2	236	34	-25
0	0	36	87	84	8	34	25	153	753	4	4	1	71	294	237	2	250	46	-44
0	0	38	156	-156	8	36	26	162	843	4	4	1	75	311	246	2	264	34	-25
0	0	40	44	-41	8	38	27	171	933	4	4	1	79	328	255	2	278	46	-44
0	0	42	87	84	8	40	28	180	1023	4	4	1	83	345	264	2	292	34	-25
0	0	44	156	-156	8	42	29	189	1113	4	4	1	87	362	273	2	306	46	-44
0	0	46	44	-41	8	44	30	198	1203	4	4	1	91	379	282	2	320	34	-25
0	0	48	87	84	8	46	31	207	1293	4	4	1	95	396	291	2	334	46	-44
0	0	50	156	-156	8	48	32	216	1383	4	4	1	99	413	300	2	348	34	-25
0	0	52	44	-41	8	50	33	225	1473	4	4	1	103	430	309	2	362	46	-44
0	0	54	87	84	8	52	34	234	1563	4	4	1	107	447	318	2	376	34	-25
0	0	56	156	-156	8	54	35	243	1653	4	4	1	111	464	327	2	390	46	-44
0	0	58	44	-41	8	56	36	252	1743	4	4	1	115	481	336	2	404	34	-25
0	0	60	87	84	8	58	37	261	1833	4	4	1	119	498	345	2	418	46	-44
0	0	62	156	-156	8	60	38	270	1923	4	4	1	123	515	354	2	432	34	-25
0	0	64	44	-41	8	62	39	279	2013	4	4	1	127	532	363	2	446	46	-44
0	0	66	87	84	8	64	40	288	2103	4	4	1	131	549	372	2	460	34	-25
0	0	68	156	-156	8	66	41	297	2193	4	4	1	135	566	381	2	474	46	-44
0	0	70	44	-41	8	68	42	306	2283	4	4	1	139	583	390	2	488	34	-25
0	0	72	87	84	8	70	43	315	2373	4	4	1	143	600	399	2	502	46	-44
0	0	74	156	-156	8	72	44	324	2463	4	4	1	147	617	408	2	516	34	-25
0	0	76	44	-41	8	74	45	333	2553	4	4	1	151	634	417	2	530	46	-44
0	0	78	87	84	8	76	46	342	2643	4	4	1	155	651	426	2	544	34	-25
0	0	80	156	-156	8	78	47	351	2733	4	4	1	159	668	435	2	558	46	-44
0	0	82	44	-41	8	80	48	360	2823	4	4	1	163	685	444	2	572	34	-25
0	0	84	87	84	8	82	49	369	2913	4	4	1	167	702	453	2	586	46	-44
0	0	86	156	-156	8	84	50	378	3003	4	4	1	171	719	462	2	600	34	-25
0	0	88	44	-41	8	86	51	387	3093	4	4	1	175	736	471	2	614	46	-44
0	0	90	87	84	8	88	52	396	3183	4	4	1	179	753	480	2	628	34	-25
0	0	92	156	-156	8	90	53	405	3273	4	4	1	183	770	489	2	642	46	-44
0	0	94	44	-41	8	92	54	414	3363	4	4	1	187	787	498	2	656	34	-25
0	0	96	87	84	8	94	55	423	3453	4	4	1	191	804	507	2	670	46	-44
0	0	98	156	-156	8	96	56	432	3543	4	4	1	195	821	516	2	684	34	-25
0	0	100	44	-41	8	98	57	441	3633	4	4	1	199	838	525	2	698	46	-44
0	0	102	87	84	8	100	58	450	3723	4	4	1	203	855	534	2	712	34	-25
0	0	104	156	-156	8	102	59	459	3813	4	4	1	207	872	543	2	726	46	-44
0	0	106	44	-41	8	104	60	468	3903	4	4	1	211	889	552	2	740	34	-25
0	0	108	87	84	8	106	61	477	3993	4	4	1	215	906	561	2	754	46	-44
0	0	110	156	-156	8	108	62	486	4083	4	4	1	219	923	570	2	768	34	-25
0	0	112	44	-41	8	110	63	495	4173	4	4	1	223	940	579	2	782	46	-44
0	0	114	87	84	8	112	64	504	4263	4	4	1	227	957	588	2	796	34	-25
0	0	116	156	-156	8	114	65	513	4353	4	4	1	231	974	597	2	810	46	-44
0	0	118	44	-41	8	116	66	522	4443	4	4	1	235	991	606	2	824	34	-25
0	0	120	87	84	8	118	67	531	4533	4	4	1	239	1008	615	2	838	46	-44
0	0	122	156	-156	8	120	68	540	4623	4	4	1	243	1025	624	2	852	34	-25
0	0	124	44	-41	8	122	69	549	4713	4	4	1	247	1042	633	2	866	46	-44
0	0	126	87	84	8	124	70	558	4803	4	4	1	251	1059	642	2	880	34	-25
0	0	128	156	-156	8	126	71	567	4893	4	4	1	255	1076	651	2	894	46	-44
0	0	130	44	-41	8	128	72	576	4983	4	4	1	259	1093	660	2	908	34	-25
0	0	132	87	84	8	130	73	585	5073	4	4	1	263	1110	669	2	922	46	-44
0	0	134	156	-156	8	132	74	594	5163	4	4	1	267	1127	678	2	936	34	-25
0	0	136	44	-41	8	134	75	603	5253	4	4	1	271	1144	687	2	950	46	-44
0	0	138	87	84	8	136	76	612	5343	4	4	1	275	1161	696	2	964	34	-25
0	0	140	156	-156	8	138	77	621	5433	4	4	1	279	1178	705	2	978	46	-44
0	0	142	44	-41	8	140	78	630	5523	4	4	1	283	1195	714	2	992	34	-25
0	0	144	87	84	8	142	79	639	5613	4	4	1	287	1212	723	2	1006	46	-44
0	0	146	156	-156	8	144	80	648	5703	4	4	1	291	1229	732	2	1020		

this way the coordination resembles that of Zr in ZrO_2 (McCullough & Trueblood, 1959). Another is to relate the polyhedron to a trigonal prism with a seventh oxygen bonded to the metal through the centre of one rectangular face [Fig. 3(b)], and this is the configuration we have chosen. A third alternative [Fig. 3(c)] shows the resemblance to an irregular octahedron with the addition of a seventh atom. The yttrium–oxygen distances for Y(1) vary between 2.29 and 2.40 Å and for Y(2) between 2.32 and 2.38 Å, all ± 0.03 Å (Table 4). Coordination numbers of 6 (octahedral), 7, 8 and 9 have been recorded for yttrium in oxy-, hydroxy- and oxyhalide compounds, and a comparison of bond lengths for a representative collection from the recent literature is given in Table 5, the Y–O bond increasing with coordination number. The 7-, 8-, and 9-coordi-

nated polyhedra are most conveniently represented as the additions of seventh, eighth and ninth atoms to one or more of the three rectangular faces of a trigonal prism.

The irregularity of the yttrium environments in Y_2TiO_5 may be attributed in part to the proximity of the titanium atom. This has fivefold coordination. Four of its neighbours O(2), O(3) and O(5) (twice) are square planar and are already bonded to Y(1) and Y(2) from a double group consisting of the two polyhedra sharing edges. The fifth, O(4), is from the next double group and forms the apex of a square pyramid of oxygen atoms. Titanium is displaced by about 0.05 Å from the centre of the square base towards this apex, and the Ti–O(4) distance of 1.78 Å is the shortest of the five (Table 4). There is no sixth atom closer to

Table 4. *Interatomic distances* (Å)

The e.s.d.'s for Y–O and for Ti–O are all ± 0.03 Å, and ± 0.04 Å for O–O. The figures in brackets following the bond lengths are the numbers of these distances within a single coordination polyhedron.

Y(1)–O(1)	2.33 (1)	Y(2)–O(1)	2.32 (1)	Ti–O(2)	1.91 (1)
–O(2)	2.29 (1)	–O(3)	2.35 (1)	–O(3)	1.87 (1)
–O(5)	2.40 (1)	–O(5)	2.38 (1)	–O(4)	1.78 (1)
–O(3)	2.26 (2)	–O(1')	2.35 (2)	–O(5)	1.94 (2)
–O(4)	2.36 (2)	–O(2)	2.35 (2)	O(5)–O(2)	2.58 (2)
O(2)–O(4)	3.29 (2)	O(3)–O(2)	2.82 (2)	–O(3)	2.52 (2)
–O(3)	2.82 (2)	–O(1')	3.54 (2)	–O(4')	2.99 (2)
O(3)–O(4)	2.71 (2)	O(2)–O(1')	2.89 (2)	O(2')–O(4')	3.20 (2)
–O(5)	2.52 (2)	–O(5)	2.58 (2)	O(3)–O(4')	2.86 (2)
O(1)–O(4)	3.24 (2)	O(1')–O(1'')	2.95 (2)		
–O(5)	2.84 (1)	O(5')–O(1'')	2.84 (1)		
O(3)–O(3)	3.70*	O(2)–O(2)	3.70*		
O(4)–O(4)	3.70*	O(1)–O(1)	3.70*		

* *b*-axis length.

Table 5. *Yttrium–oxygen distances*

Compound	Coordination number	Y–O distances		Reference
		Range	Average	
Y_2O_3	6	2.26–2.35 Å	2.30 Å	Paton & Maslen (1965)
Y_2BeO_4	6	2.21–2.34	2.29	Harris & Yakel (1967)
Y_2TiO_5	7	2.29–2.40	2.32	This study Y(1)
		2.32–2.38	2.35	This study Y(2)
YO(OH)	7	2.24–2.44	2.33	Christensen (1965)
$Y_3Fe_5O_{12}$	8	2.37–2.43	2.40	Geller & Gilileo (1957)
$Y(OH)_2Cl$	8	2.31–2.39	2.36	Klevtsova & Klevtsov (1966)
$Y(OH)_3$	(6O+2Cl) 9	2.40–2.44	2.42	Christensen, Hazell & Nilsson (1967)

Table 6. *Five-coordinated Ti–O distances*

Compound	Ti–O distances		Reference
	Range	Average	
Y_2TiO_5	1.78–1.94 Å	1.89 Å	This study
$K_2Ti_2O_5$	1.57–2.00	1.85	Andersson & Wadsley (1961)
$Ba_2TiSi_2O_8$	1.66–2.00	1.93	Moore & Louisnathan (1967)
Dichlorodiphenoxy-titanium(IV) (3 oxygen, 2 chlorine ligands)	1.74–2.12 (oxygen only)		Watenpaugh & Caughlan (1966)

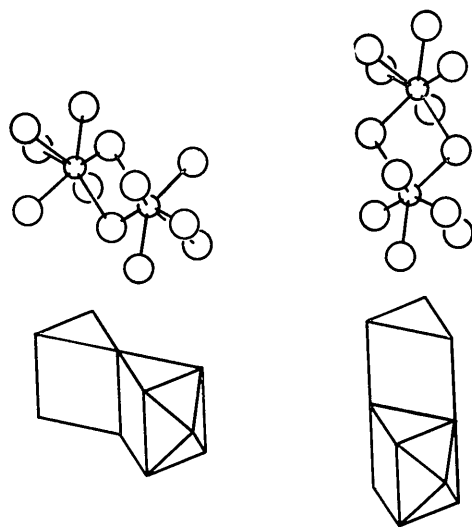


Fig. 4. (below) Two ways of joining seven-coordinated polyhedra by a common edge. (above) The same as atoms, the smaller being the metal and the larger the oxygen atoms.

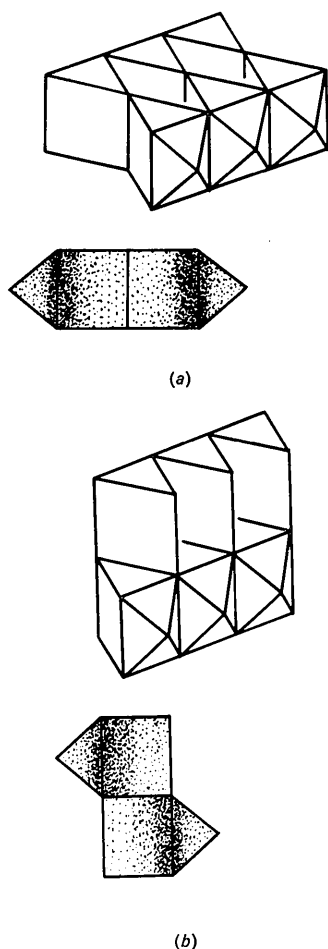


Fig. 5. (a) and (b) Both units of Fig. 4 extended indefinitely: (above) in perspective; (below) in projection down the repeat direction.

Ti than O(1), which is 3.89 Å away and is clearly unbonded.

Fivefold coordination for Ti^{4+} can no longer be considered a rarity. It was first found by Andersson & Wadsley (1961) in the hygroscopic layer compound $K_2Ti_2O_5$, and has subsequently been identified in the ester dichlorodiphenoxytitanium(IV) (Watenpaugh & Caughlan, 1966) as well as in two minerals, fresnoite $Ba_2TiSi_2O_8$ (Moore & Louisnathan, 1967; Masse, Grenier & Durif, 1967) and lamprophyllite $(Ba, Sr, K)-Na(Ti, Fe)TiSi_2O_7(O, OH, F)_2$ (Woodrow, 1964). Y_2TiO_5 as well as these minerals is very stable, and evidently the reactive nature of the other two compounds is not simply due to an unstable coordination of Ti, as might at first be supposed. Ti-O distances are given in Table 6 for all of these compounds except lamprophyllite, its structure so far having been determined only in one projection. In this mineral, in fresnoite and in Y_2TiO_5 the coordination is square pyramidal, and in all cases the shortest distance is from the metal to the oxygen at the apex. There are two short Ti-O bond lengths of 1.57 and 1.67 Å in $K_2Ti_2O_5$ where the coordination of Ti, and also in the case of the ester, is described as trigonal bipyramidal. An unambiguous decision between these two modes is not always practicable or meaningful, however, and may simply be a matter of semantics.

Sevenfold coordination

There is a good deal of growing evidence that metal-oxygen octahedra tend to aggregate by edge-sharing into groups extending infinitely through a crystal in one and sometimes two directions. These groups, or structural building blocks, are able to unite with themselves through common corners or edges, to form three-dimensional structures which are restricted in number by the configuration of the group, as well as by the presence of additional ions of specific sizes within the interstices between the groups (Wadsley, 1967). It may therefore be worth while to see if these simplifying working 'rules' can be extended to the trigonal prism having a seventh atom additionally bonded through a rectangular face.

While it would be a useful exercise to list exhaustively all possible ways of joining these figures together, as Aurivillius & Lundgren (1965) have recently done for the 8-coordinated square Archimedean antiprism, we confine this discussion to a number of structures already determined in order to keep it within reasonable bounds. These include $Y(OH)_3$ (Schubert & Seitz, 1946; Christensen, Hazell & Nilsson, 1967), and $YO(OH)$ (Klevtsova & Klevtsov, 1964; Christensen, 1965), high-pressure Y_2O_3 (Hoekstra & Gingerich, 1964) with the *B*-type rare-earth oxide structure determined for Sm_2O_3 by Cromer (1957), and also the phases isostructural with Sr_2PbO_4 including Ca_2PbO_4 , Ca_2SnO_4 (Trömel, 1965, 1967) and Mn_2GeO_4 (Wadsley, Reid & Ringwood, 1968) but for which no yttrium isotope has yet been found.

We can extract two features which are common to these four structures and also to Y_2TiO_5 . These are illustrated in Fig. 4, showing two of a number of possible ways of joining the seven-coordinated polyhedra by common edges. These two units unite with themselves to form groups of two different kinds, both extending indefinitely through a structure with a repeat distance equal to an oxygen-oxygen separation (Fig. 5).

Sr_2PbO_4 and its isotypes contain only one kind of group [Fig. 5(a)], joined together by edges. The Sr atoms are the seven-coordinated atoms (or more nearly six-coordinated), and the Pb atoms are situated in octahedral positions between the groups (Fig. 6). Both groups of Fig. 5 form the basic structure of the B-type rare-earth oxide (Fig. 7). One-third of the metals are in the octahedral positions between the groups, and their coordination number is therefore six, and not seven, as often stated (*Structure Reports*, 1957).

The groups are also able to form much larger composite units. Fig. 8, containing both of the elements of Fig. 5, is the fundamental structural unit of Y_2TiO_5 and its isotypes, which, as we have already seen, is grossly distorted by the presence of the Ti atoms binding them together in a way so as to conserve space (Fig. 9).

Fig. 5(b) can also be extended in a second direction to become an infinite two-dimensional sheet (Fig. 10). The structure of $YO(OH)$ consists of these sheets arranged in parallel and bonded through two oxygen atoms and by hydrogen ions (Fig. 11). The similarity between $YO(OH)$ and $Y(OH)_3$, where the yttrium is 9-coordinated – having two more oxygen atoms beyond the two remaining rectangular faces – has been discussed by Klevtsova & Klevtsov (1964) for the dehydration reaction



It is clear to us that by no means all of the structures which can be generated by the close union of these polyhedra have been found. This may be due to the difficulty of synthesizing compounds containing the metals – apart from sodium – which are able to assume this particular coordination, Sr, Ca, Mn^{2+} , Y, Gd, Dy and presumably more of the rare earths. All of these can be expected to form mixed oxide phases only at very high temperatures, and the difficulties of making crystals large enough for unambiguous X-ray studies can be overcome with normal laboratory equipment only by tricks of synthesis such as we have used in the present case. Finally the similarity between the environment of Y and Zr in oxides, mentioned earlier, suggests a close study of the relations of the structures in Figs. 6, 7, 8 and 11 to those of pyrochlore ($Y_2Ti_2O_7$ or $Y_2Zr_2O_7$), where the coordination is a mixture of six and eight, and ZrO_2 where it is seven.

We are grateful to Dr A.F.Reid for preparing the crystals.

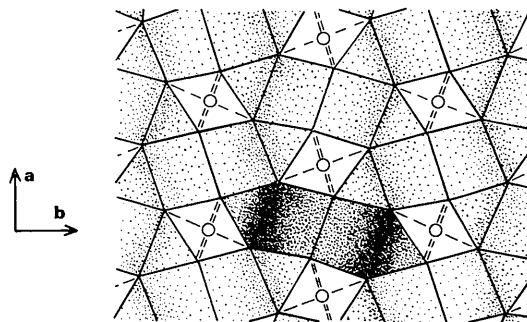


Fig. 6. Sr_2PbO_4 structure type, consisting of the groups of Fig. 5(a), centred on the Sr atoms, joined by edges leaving octahedral holes for Pb (circles). One group is more heavily stippled.

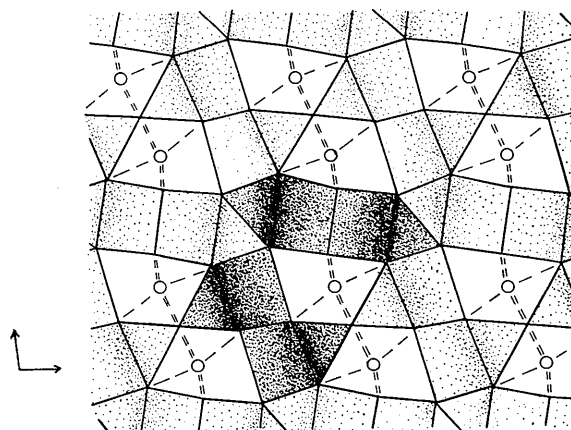


Fig. 7. Structure of Sm_2O_3 (or of high-pressure Y_2O_3), the B-rare-earth-oxide type. The more heavily stippled groups emphasize two different varieties in Fig. 5, and the circles are the metals in an octahedral environment.

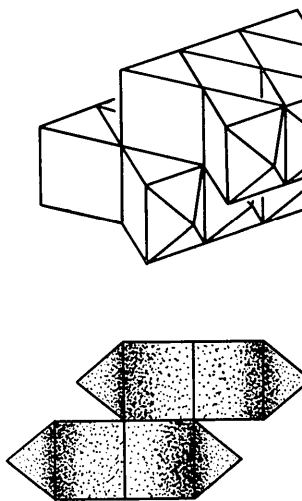


Fig. 8. Composite of both units of Fig. 5; (above) in perspective, and (below) in projection down the repeat direction.

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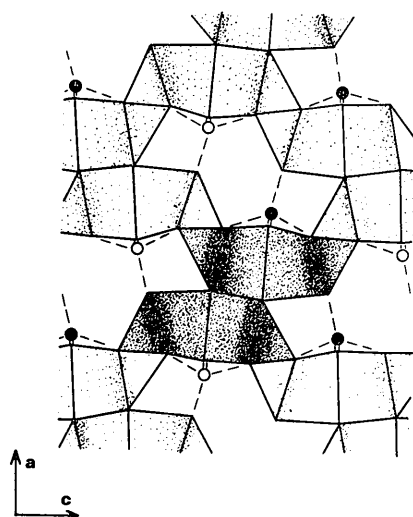


Fig. 9. Structure of Y_2TiO_5 containing the composite groups of Fig. 8, considerably distorted. The Ti atoms are drawn as circles, with their bonds to oxygen as dashed lines. This Figure is rotated through 90° with respect to Fig. 2 in order to conform to Fig. 8.

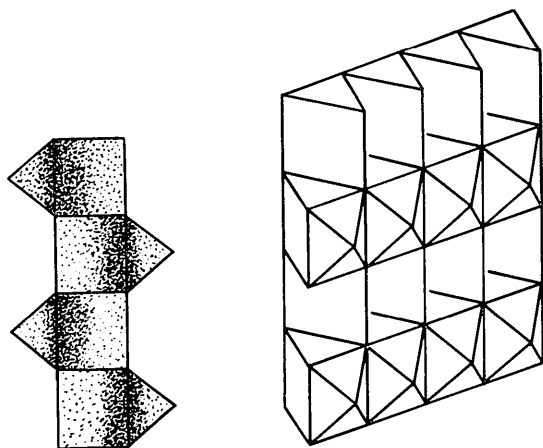


Fig. 10. Formation of a two-dimensional infinite sheet from the groups in Fig. 5(b). (left) in projection; (right) in perspective.

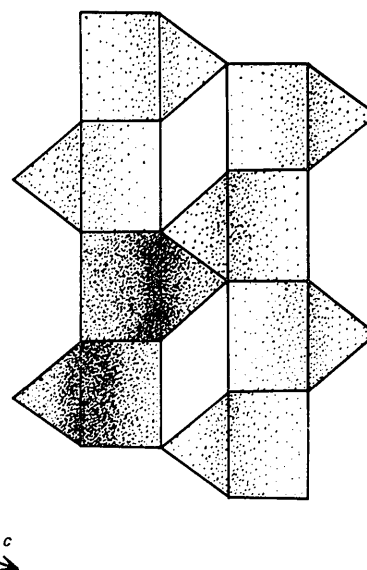


Fig. 11. Structure of $YO(OH)$, made up from the union of the sheets in Fig. 10 joined by edges. Hydrogen atoms are presumably located in the holes.

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