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Double Oxides Containing Niobium, Tantalum, or Protactinium. III. Systems Involving the Rare Earths

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Those regions of the systems R_2O_3–M_2O_5 (R = rare earth or other trivalent metal, M = Nb, Ta, or Pa) rich in M_2O_5 have been investigated. The niobium and tantalum systems yield series of compounds RM_3O_9 which have a form of perovskite structure. Cell constants for these and, in the cases of $LaNb_3O_9$ and $LaTa_3O_9$, structure analyses based on single-crystal data are presented. The unit cells of a few compounds RM_5O_{14} are also reported. The protactinium systems do not resemble those of niobium and tantalum but extensive solid solutions of fluorite structure are formed. Cell parameters are presented and their variation with the size of the R ion and with the R to Pa ratio is discussed.

Introduction

Protactinium, though properly an *f*-block element, resembles by its predominant quinquevalency the *d*-block elements niobium and tantalum, as cerium and thorium resemble the elements of the titanium group. A study of the extent and limits of chemical similarity between these elements should thus be instructive and assist in the understanding of the role of *f*-electrons in chemical bonding. The present study has shown no resemblances between the structures of solid compounds of protactinium and those of niobium and tantalum within the field of investigation. It is noteworthy that within this field, in all the products of this and previous investigations protactinium is in an 8-coordinate environment – which, to the extent that the bonding is covalent, indicates *f*-orbital involvement (Kettle & Smith, 1967) – whereas niobium and tantalum in phases of corresponding formula occupy octahedrally coordinated sites.

Mixed-oxide systems involving rare earth oxides with niobium, tantalum, and protactinium pentoxides have received attention from a number of workers. Niobium and tantalum compounds of the type RMO_4 with the monoclinic fergusonite structure have been prepared by Komkov (1959), Krylov, Sanatina & Shtol'ts (1961), Keller (1962), and Rooksby & White (1963). More recently Keller (1964) reported the formation of fluorite type compounds $RPaO_4$. On the rare earth rich side of the niobium and tantalum systems, Rooksby & White (1964) prepared, by solid-state reaction, phases of the type R_3MO_7 with two structures. The lanthanum and neodymium compounds formed the orthorhombic weberite structure while those of samarium, gadolinium, dysprosium, yttrium, and scandium gave a cubic fluorite or pyrochlore structure. No systematic investigation of compounds existing in the M_2O_5-rich fields appears to have been made at the time of initiating our work.

In the present investigation we have examined the formation of the compounds and solid solutions in the M_2O_5-rich regions of the rare earth oxide systems, and the possibility of forming similar compounds with the trivalent oxides of scandium, aluminum, gallium, and indium.

Experimental

Preparative and X-ray techniques were as described in part I (Whiston & Smith, 1965) with the following additions. Protactinium pentoxide was supplied from the Chemistry Division, Atomic Energy Research Establishment, Harwell, and contained 0·4% niobium as its principal impurity. All protactinium preparations were carried out on a scale of about 5 to 15 mg in glove-boxes, using the standard techniques for handling α-active materials. Samples for powder photography on the Guinier camera could be removed from the glove-boxes as they were completely sealed with 'Sellotape' and 'Bostikote'. Guinier patterns were used for the derivation of accurate cell constants of niobium and tantalum compounds as well as for those of protactinium.

Single-crystal diffraction data for structure analysis were collected by use of molybdenum radiation and a multiple film technique. Intensities were estimated visually and corrected by standard procedures for Lorentz and polarization effects. As the linear absorption coefficients were rather high (105 and 535 cm^{-1} for $LaNb_3O_9$ and $LaTa_3O_9$ respectively) an absorption correction was made, by a Gaussian integration procedure based on the method of Busing & Levy (1957). All computations were carried out on the University of Sheffield's Mercury computer. Further details of experimental conditions are given by Iyer (1965).

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RM_3O_9 compounds of perovskite structure

The niobium series

Roth (1961) prepared a compound $LaNb_3O_9$ with a distorted perovskite structure. Powder X-ray diffraction patterns showed the compound to have orthorhombic symmetry. Single-crystal Weissenberg patterns did not show the orthorhombic symmetry but appeared tetragonal. More recently Masuno (1964) prepared $LaNb_3O_9$ and indexed its powder pattern on an orthorhombic (pseudotetragonal) cell with the *a* and *b* dimensions double those reported by Roth. While our investigations were in progress Dyer & White (1964) examined the formation of intermediate oxides in the systems R_2O_3–Nb_2O_5 and R_2O_3–Ta_2O_5. They reported the formation of perovskite-type phases for lanthanum to neodymium oxides with niobia and lanthanum to gadolinium oxides with tantala, all the products having composition ranges from $2R_2O_3+3M_2O_5$ to $R_2O_3+3M_2O_5$. Recently the unit cells of the compounds RM_3O_9 have been reported independently by Rooksby, White & Langston (1965) and by Keller (1965*b*). The two sets show small differences in the reported cell parameters and, more significantly, a few disagreements as to the true symmetry of the structures. Our results, presented below, agree closely with those of Keller.

We have prepared perovskite-type compounds of the general formula RNb_3O_9 from lanthana, ceria, praseodymia, and neodymia. These compounds melted between 1360 and 1400 °C. No such perovskite-type phase was observed with any of the rare earths from samaria onwards or with scandia, alumina, gallia, or india. The Guinier pattern of $LaNb_3O_9$ showed all reflexions with $h \neq k$ split into two lines of approximately equal intensity, and was indexed on the basis of an orthorhombic cell with the *a* and *b* dimensions very nearly equal. The doubling of these dimensions reported by Masuno was not necessary. Weissenberg photographs obtained from single crystals did not reveal any deviation from orthorhombic symmetry or any superlattice reflexions, thus confirming Roth's conclusions. The observed density of 5·08 g.cm^{-3} agrees well with the calculated value of 5·14 g.cm^{-3} for one formula unit of $La_{2/3}Nb_2O_6$ per cell. The lattice parameters of all the compounds are listed in Table 1, and show good agreement with the values published by Keller (1965*b*).

Table 1. *Lattice parameters of compounds* RNb_3O_9

P indicates powder data, *S* single-crystal data.

	Cell parameters	*c/2a*	*U*
$LaNb_3O_9$ (*P*, *S*)	$a=3·911\pm0·005$ Å $b=3·917\pm0·005$ $c=7·908\pm0·002$	1·0110	121·2 Å^3
$CeNb_3O_9$ (*P*)	$a=3·901\pm0·005$ $b=3·917\pm0·005$ $c=7·886\pm0·01$	1·0108	120·5
$PrNb_3O_9$ (*P*, *S*)	$a=3·891\pm0·005$ $b=3·915\pm0·005$ $c=7·862\pm0·01$	1·0103	119·8
$NdNb_3O_9$ (*P*, *S*)	$a=3·878\pm0·005$ $b=3·907\pm0·005$ $c=7·840\pm0·01$	1·0108	118·8

The tantalum series

Compounds of perovskite structure of the composition RTa_3O_9 were prepared from lanthana, ceria, praseodymia, neodymia, samaria, gadolinia, dysprosia, holmia, erbia, and yttria. These compounds melted between 1640 and 1680 °C. No compound of perovskite structure was obtained from scandia, alumina, gallia. or india. The lattice parameters are listed in Table 2.

Table 2. *Lattice parameters of compounds* RTa_3O_9

P indicates powder data, *S* single-crystal data.

	Cell parameters	*c/2a*	*U*
$LaTa_3O_9$ (*P*, *S*)	$a=3·918\pm0·001$ Å $c=7·913\pm0·001$	1·0098	121·5 Å^3
$CeTa_3O_9$ (*S*)	$a=3·915\pm0·005$ $c=7·878\pm0·008$	1·0061	120·7
$PrTa_3O_9$ (*P*, *S*)	$a=3·895\pm0·005$ $b=3·910\pm0·005$ $c=7·836\pm0·008$	1·0059	119·3
$NdTa_3O_9$ (*P*, *S*)	$a=3·876\pm0·005$ $b=3·916\pm0·005$ $c=7·829\pm0·006$	1·0099	118·8
$SmTa_3O_9$ (*P*, *S*)	$a=3·882\pm0·002$ $b=3·896\pm0·002$ $c=7·785\pm0·005$	1·0027	117·7
$GdTa_3O_9$ (*S*)	$a=3·874\pm0·003$ $c=7·795\pm0·003$	1·0061	117·0
$DyTa_3O_9$ (*S*)	$a=3·847\pm0·001$ $c=7·769\pm0·003$	1·0097	115·0
$HoTa_3O_9$ (*S*)	$a=3·841\pm0·005$ $c=7·756\pm0·005$	1·0096	114·4
YTa_3O_9 (*S*)	$a=3·824\pm0·005$ $c=7·758\pm0·005$	1·0144	113·5
$ErTa_3O_9$ (*P*)	$a=3·825\pm0·005$ $c=7·754\pm0·005$	1·0136	113·5

We have observed no range of composition for these RM_3O_9 compounds. The cell constants show a number of interesting features. In the niobium series the orthorhombic distortion (*b/a* – representing the deviation from tetragonal symmetry) increases progressively as R changes from lanthanum to neodymium: the *b* dimension remains almost constant, while *a* and *c* decrease with the radius of R. The ratio *c/2a* remains nearly constant, *i.e.* in this series *a* and *c* are related similarly to the size of the rare earth ion but *b* is not. In the tantalum series these effects are complicated by the changes from tetragonal to orthorhombic and back again. The *c/2a* ratio passes through two minima where these changes occur at $CeTa_3O_9$ and $SmTa_3O_9$. The cause of the changes is obscure. In both series of compounds the effect of the lanthanide contraction is reflected in the unit cell volumes.

Structure analyses

As these compounds belong to the perovskite structure type and contain one unit of $R_{2/3}M_2O_6$ per unit cell, there must be 1·33 vacant *A* sites in the cation lattice. The cell dimensions ($a \simeq b \simeq c/2 \simeq 3{\cdot}9$ Å) give no clue as to the distribution of the $\frac{2}{3}$ R ion between the two available *A* sites nor to the possible displacements of the *B* ions or oxygen atoms from their ideal positions. In order to examine the nature of the distortion and the distribution of vacancies in the cation lattice, three-dimensional structure analyses were carried out for the two analogous compounds $LaNb_3O_9$ and $LaTa_3O_9$.

Single crystals of $LaNb_3O_9$ were prepared by cooling a melt of the compound from 1375 °C at 15 °C per hour down to 1000 °C and annealing the crystals at this latter temperature for a week. A pale yellow platy crystal of volume slightly less than 0·01 mm^3 was selected for collection of data.

No measurable difference between the *a* and *b* dimensions was observed in the single-crystal photographs in contrast to the powder photographs obtained with the Guinier camera. Therefore tetragonal symmetry was assumed for the structure analysis. This may be justified by the following considerations. Careful examination of the X-ray films did not show any visually estimable difference in intensity between the *hkl* and *khl* reflexions. Thus, although deviation from tetragonal symmetry is indicated by the Guinier pattern, structure solutions in the tetragonal and orthorhombic systems should lead to the same parameters. Also the difference between the *a* and *b* dimensions of the orthorhombic cell (0·007 Å) is much smaller than the final uncertainty of the oxygen positions we obtained.

180 unique reflexions from the layers 0*kl* to 3*kl* were collected on Weissenberg films. Seven of these were subsequently removed because of extinction effects. No systematic absences were observed: so the possible space groups were $P4$, $P\bar{4}$, $P4/m$, $P4mm$, and $P4/mmm$. The first three of these require that $F_{hkl} \neq F_{\bar{h}kl}$. To test this condition *hk*0 and *hk*3 were taken, but no difference between the intensities of the *hkl* and $\bar{h}kl$ reflexions could be found. The remaining choice of space groups is thus between $P4mm$ and $P4/mmm$.

Positional parameters for the lanthanum and niobium atoms were derived from a two-dimensional Patterson projection along [100]. These were refined with isotropic vibration parameters to $R = 0{\cdot}19$, when a difference Fourier synthesis revealed the oxygen atoms. The oxygen positions thus derived using $P4mm$ proved to be related by a mirror plane perpendicular to [001] and so the centrosymmetric space group $P4/mmm$ was adopted. Refinement was carried out, initially with unit weights and isotropic vibrations, and finally with logical weights (weight varying from 0·5 to 1·0 to 0·2 with increasing F_{obs}) and anisotropic vibrations to a final reliability index of 0·098. Final positional shifts were less than 1/20 of the corresponding estimated standard deviations.

The final parameters are listed in Tables 3 and 4, and observed and calculated structure factors in Table 5. The negative vibrational parameters of two of the oxygen atoms evidently reflect some residual absorption errors in the data. Apart from these the vibrational parameters are rather small, as is commonly observed for closely packed ionic materials with high melting points. The NbO_6 distorted octahedron is illustrated in Fig. 1.

Table 3. *Positional parameters for* $LaNb_3O_9$ *in* $P4/mmm$ $(Z=\frac{2}{3})$

	x/a	y/b	z/c	e.s.d. (z in Å)
$\frac{2}{3}$ La in (*a*)	0	0	0	
2 Nb in (*h*)	0·5	0·5	0·26163	0·0038
4 O(1) in (*i*)	0	0·5	0·22582	0·024
1 O(2) in (*c*)	0·5	0·5	0	
1 O(3) in (*d*)	0·5	0·5	0·5	

Table 4. *Vibrational parameters for* $LaNb_3O_9$

Temperature factor =

$$2^{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{31}lh+b_{12}hk)}$$

b_{23}, b_{31}, and b_{12} are systematically zero.

	b_{11}	b_{22}	b_{33}
La	0·00253	0·00253	0·00099
Nb	0·01367	0·01367	0·00535
O(1)	0·02402	−0·00985	0·00897
O(2)	0·05088	0·05088	−0·00249
O(3)	0·09178	0·09178	0·00509

From its lattice constants it is evident that $LaTa_3O_9$ is isostructural with $LaNb_3O_9$ although it does not show any orthorhombic distortion. Structure analysis for the tantalum compound followed essentially the same sequence used for the niobium one but, because of greater absorption effects, agreement was never so good and anisotropic thermal vibration parameters were not used. The results obtained were similar to those for $LaNb_3O_9$ except for O(2) and O(3). No meaningful vibration parameters could be refined for these atoms in their special onefold positions (*c*) and (*d*) and the peaks obtained for them by Fourier synthesis were toroidal in shape with a minimum of density at these special positions on the fourfold axis and maximum density in a ring of radius about 0·05 Å in the *xy* plane. We concluded that these oxygen atoms are displaced from the special positions in a disordered manner, and approximated this disorder by placing them in the eightfold positions (*p*) and (*q*). They were not further refined. The final *R* index was 0·145. Atom parameters are listed in Table 6, observed and calculated structure factors in Table 7, and the dimensions of the distorted octahedron are shown in Fig. 2.

Table 5. $|F_{\text{obs}}|$ *and* $|F_{\text{calc}}|$ *for* LaNb_3O_9

•	0	0	
3		1601	1777
5		880	880
6		801	785
7		1539	1689
8		2370	2669
11		1451	1407
12		1584	1394
•	0	1	
0		2136	2583
1		1530	1940
3		1049	801
4		1736	1586
5		2179	2060
6		2653	2740
8		614	561
9		1817	1688
10		1769	1539
13		1194	1188
14		749	787
•	0	2	
1		1274	1353
2		1612	1742
3		1589	1545
4		3186	4167
5		837	755
6		913	607
7		1703	1539
8		2415	2384
11		1401	1313
12		1476	1279
•	0	3	
0		1498	1209
1		1372	1313
2		2484	3028
3		846	611
4		1066	894
5		1776	1630
6		2270	2235
9		1554	1451
10		1476	1365
13		1017	1070
•	0	4	
0		3134	3288
1		1077	947
2		1257	1004
3		1417	1158
4		2676	2780
7		1539	1204
8		2013	1601
11		1070	1066
12		864	1044
•	0	5	
1		1035	930
2		2320	2012
5		1566	1209
6		1871	1612
9		1206	1147
10		995	1087
•	0	6	
0		2117	2128
1		687	699
2		698	562
3		905	813
4		2060	1853
7		855	850
8		953	1289
•	0	7	
2		1377	1275
5		654	907
6		846	1092
•	1	1	
1		1266	1163
2		310	65
3		2317	2408
4		3109	3488
7		2262	2227
8		2414	2306
11		1535	1663
12		1385	1408
•	1	2	
0		1841	1710
1		1666	1509
2		2918	3547
3		846	702
4		1372	1196
5		1881	1777
6		2414	2495
9		1575	1535
10		1460	1442
13		1143	1119
•	1	3	
0		2796	2926
1		987	922
3		1755	1744
4		2625	2601
7		1940	1831
8		2080	1880
11		1361	1454
12		1133	1205
•	1	4	
0		991	905
1		1133	1055
2		2764	2565
3		682	585
4		773	681
5		1420	1290
6		1940	1942
9		1257	1220
13		769	942
•	1	5	
0		1969	1893
1		709	695
3		1269	1224
4		1912	1747
7		1675	1368
8		1277	1365
11		668	1158
12		557	943
•	1	6	
1		773	758
2		1831	1793
5		872	897
6		1197	1421
•	1	7	
0		991	1187
3		872	880
4		889	1125
•	2	2	
0		3534	4413
1		1230	1154
2		1435	1386
3		1456	1391
4		3510	3531
5		719	676
6		759	587
7		1488	1405
8		2242	2141
11		1206	1215
12		1251	1186
•	2	3	
0		1156	992
1		1331	1172
2		2717	2743
3		734	561
4		893	732
5		1657	1468
6		2117	2060
9		1448	1346
10		1353	1288
13		872	1016
•	2	4	
0		2770	2952
1		929	879
2		972	885
3		1167	1069
7		1209	1121
9		1537	318
•	2	5	
1		1031	872
2		1914	1877
5		1130	1124
6		1501	1520
9		941	1077
10		677	1039
•	2	6	
0		1825	1973
3		792	766
4		1525	1726
7		759	810
8		893	1215
•	2	7	
2		1097	1214
•	3	3	
0		2390	2308
1		637	792
3		1535	1430
4		2214	2096
7		1591	1554
8		1591	1590
11		1215	1292
12		893	1056
•	3	4	
0		687	627
1		1056	911
2		2252	2127
5		1425	1144
6		1716	1665
9		1124	1088
10		933	1090
•	3	5	
0		1727	1619
3		1059	1077
4		1539	1500
7		1254	1215
8		1094	1206
•	3	6	
2		1539	1559

Table 6. *Positional and vibrational parameters for* LaTa_3O_9 *in* $P4/mmm$

$Z=\frac{2}{3}$: B is to the base e.

	x/a	y/b	z/c	e.s.d. (z in Å)	B (Å^2)
$\frac{2}{3}$ La in (a)	0	0	0		1·162
2 Ta in (h)	0·5	0·5	0·26040	0·006	0·948
4 O(1) in (i)	0	0·5	0·22617	0·05	2·710
1 O(2) in (p)	0·505	0·510	0		2·513
1 O(3) in (q)	0·505	0·510	0·5		2·513

Thus the perovskite-type unit cell of the RM_3O_9 compounds contains two $B\text{O}_6$ octahedra of equal size but, while one of the A sites is occupied by $\frac{2}{3}$ of an R atom, the other is vacant. The B ions are displaced from the centres of the octahedra, which themselves suffer distortion so as to retain only one of their four-fold axes. These two effects lead to kinked O–B–O chains in the x and y directions with angles of about 164°. Similar off-centred octahedra with resulting kinked metal–oxygen chains are observed in such perovskites as BaTiO_3 and PbTiO_3, though in these cases the octahedra are much more nearly regular. The niobium–oxygen distances found in the present study are similar to those reported for niobium pentoxide by Gatehouse & Wadsley (1964).

The orthorhombic distortion in LaNb_3O_9 may arise from slight displacements of O(2) and O(3), differing in the x and y directions, from their special positions in the tetragonal unit cell. The resulting differences in scattering amplitude between reflexions hkl and khl would then be extremely small, as was observed. Similar displacements but with disordering of the x and y directions could account for the LaTa_3O_9 structure observed.

An interesting feature of this cation-deficient perovskite structure is the large void at $0,0,\frac{1}{2}$. This point is rather more than 2·75 Å from the nearest oxygen atom and could easily accommodate an atom of more than 1 Å radius. The failure to prepare RNb_3O_9 compounds for the heavier rare earths beyond neodymium is also surprising, since the tantalum compounds are readily formed. The reason may lie in the different electronic structures of the niobium and tantalum ions. The present series of RTa_3O_9 compounds shows clear evidence of the existence of off-centred tantalum–oxygen octahedra for which experimental data have previously been scanty.

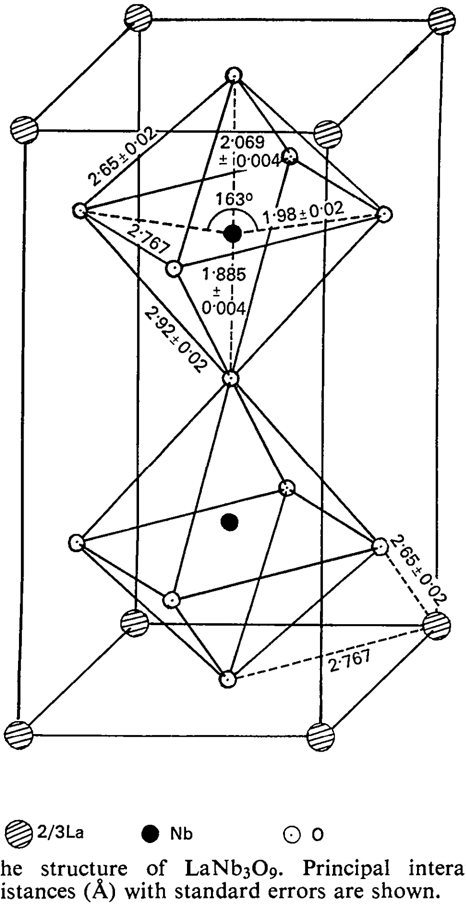

Fig. 1. The structure of LaNb_3O_9. Principal interatomic distances (Å) with standard errors are shown.

RM_5O_{14} compounds

The possible existence of $LaNb_5O_{14}$ was postulated by Masuno (1964), though no X-ray data were presented. Dyer & White (1964) have reported its formation and that the structure is related to that of β-Nb_2O_5.

$LaNb_5O_{14}$

An appropriate mixture of lanthana and niobia fired at 1300°C gave a product with a complicated powder pattern, which could not be indexed. Pale yellow well-formed needles were obtained by slowly cooling a melt of the compound from 1360°C. Similar crystals could be obtained by decomposition on cooling a melt of $LaNb_3O_9$ from above 1400°C. The orthorhombic unit cell had

$$a=3{\cdot}87,\ b=12{\cdot}56,\ c=19{\cdot}86\ \text{Å}\ ,$$

and possible space groups $Pmc2_1$ or (with interchange of a and c) $Pma2$. The measured density of 5·4 g.cm^{-3} is in reasonably good agreement with 5·70 g.cm^{-3} calculated for four formula units per cell. The structure does not appear to be similar to that of β-Nb_2O_5.

$GaNb_5O_{14}$

This compound was prepared from the oxides at 1300°C. The powder pattern contained many lines and was not indexed but single-crystal studies showed an orthorhombic lattice with

$$a=3{\cdot}81,\ b=20{\cdot}67,\ c=28{\cdot}62\ \text{Å}\ ,$$

and space group $Cmc2_1$. The measured density was 4·42 g.cm^{-3} that calculated for eight formula units per cell was 4·48 g.cm^{-3}. Work on the structure of this compound is continuing.

$LaTa_5O_{14}$

Powder patterns showed this phase to be similar to its niobium analogue. Thick needle-shaped crystals, grown from a melt at 1650°C, confirmed the structural similarity. The tantalum compound has

Table 7. $|F_{\text{obs}}|$ *and* $|F_{\text{calc}}|$ *for* $LaTa_3O_9$

•	0	0	
3		3082	2198
4		7651	7528
6		2955	2904
7		2426	2250
8		3442	3781
10		1457	1338
11		1566	1785
12		1694	1720
•	0	1	
0		5336	5597
1		2530	2079
4		4113	3967
5		2875	2559
6		4856	4493
8		2434	2093
9		2303	2164
10		2283	2376
11		698	907
12		763	915
13		978	1468
14		903	1045
15		592	696
•	0	2	
1		1299	1078
2		4856	4043
3		1853	1827
4		5679	5901
6		2568	2489
7		2023	1981
8		3512	3289
10		1260	1212
11		1321	1611
12		1397	1542
15		821	1044
•	0	3	
0		2572	3360
1		1031	1268
2		4782	4732
4		2947	2752
5		1942	1842
6		3528	3403
8		1817	1631
9		1833	1694
10		2043	1910
12		781	753
13		1105	1205
14		931	862
•	0	4	
2		2235	2434
3		1470	1195
4		3588	3621
6		2218	1717
7		1720	1397
8		2520	2200
10		1174	910
11		1125	1183
12		1121	1137
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5		1348	1109
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8		1021	1071
9		1199	1097
10		1370	1267
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4		1663	1987
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4		765	923
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2		568	729
4		819	997
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6		3074	2241
7		3407	2564
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9		1007	1018
10		1217	1258
11		1764	1859
12		1770	1659
15		997	1128
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14		873	949
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7		2295	1908
8		2945	2614
10		1120	1035
11		1538	1483
12		1461	1335
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3		891	973
4		2128	2484
6		1637	1230
7		1725	1109
8		2047	1679
10		1282	724
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12		1525	901
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6		1628	1567
8		935	810
9		936	817
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6		786	820
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2		3316	3304
3		1347	1567
4		4251	4892
6		2384	2169
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8		3046	2873
10		1091	1098
11		1250	1450
12		1290	1386
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1		1052	1070
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5		1632	1602
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12		838	685
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8		2173	2024
10		1101	831
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12		1197	1031
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4		1273	1496
5		1100	989
6		2603	1923
8		1128	973
9		1397	995
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4		879	909
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12		1303	1092
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2		2637	2808
4		1875	1669
5		1566	1109
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9		1486	1097
10		1723	1267
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7		1470	940
8		1901	1378
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2		1481	1655
4		1045	1009
6		1444	1294
•	3	7	
0		875	1253
2		600	790
4		985	1117
•	4	4	
0		1854	2560
4		1748	2218

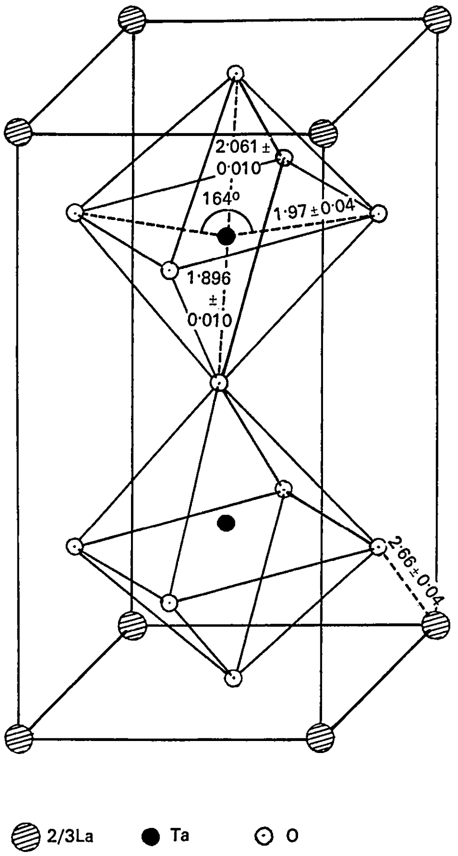

Fig. 2. The structure of $LaTa_3O_9$. Principal interatomic distances (Å) with standard errors are shown. The disorder is represented by antiparallel displacements of O(2) and O(3).

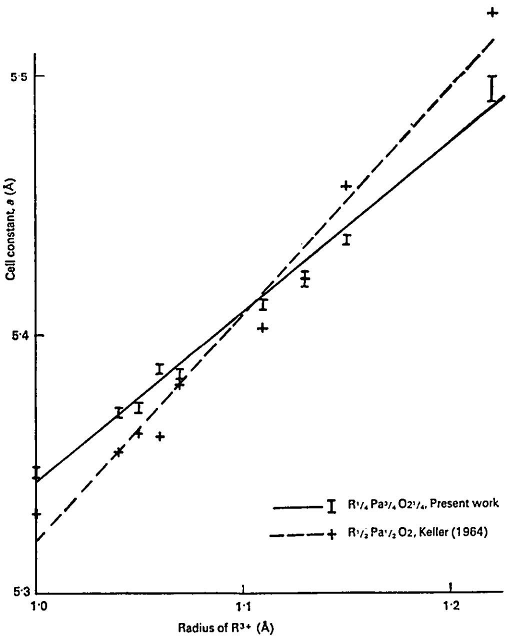

Fig. 3. Unit-cell constants of $R_xPa_{1-x}O_{2\cdot5-x}$.

$a=3{\cdot}81$, $b=12{\cdot}72$, and $c=19{\cdot}98$ Å.

These three were the only RM_5O_{14} compounds formed by niobium or tantalum with any of the rare earths (including scandium and yttrium), aluminum, gallium, or indium.

The systems R_2O_3–Pa_2O_5

Keller's (1964, 1965*a*) studies on the rare earth–Pa_2O_5 systems showed the formation of compounds $RPaO_4$ with the fluorite structure, and the solubility of the corresponding rare earths in these. The solubility of R_2O_3 in $RPaO_4$ was reported as a function of the cell constant of the fluorite phase and of the reaction temperature. Although the possible extension of the fluorite phase into the protactinium-rich part of the systems was suggested, no experiments were reported on this. We presented a preliminary report on the Pa_2O_5-rich part of these systems after seeking possible RPa_3O_9 compounds analogous to the niobium and tantalum ones described in the earlier part of this paper (Iyer & Smith, 1965): we now give these results in full.

1:3 mixtures of lanthana, neodymia, samaria, gadolinia, dysprosia, holmia, erbia, ytterbia, and yttria with protactinium pentoxide were fired at 1350°C. The Guinier patterns of all the products showed cubic symmetry, with significant differences of cell constant from protactinium pentoxide. [Pure Pa_2O_5 on heating to 1350°C is transformed to a hexagonal phase and does not reform the cubic phase on cooling or on annealing (Roberts & Walter, 1965).] These products we obtained may thus be regarded as part of a series of extensive solid solutions of rare earths in cubic fluorite-type protactinium pentoxide. Many oxides and fluorides crystallizing in the fluorite structure show large concentrations of anion defects, both vacancies and interstitial anions (Roberts, 1963). Our fluorite-type phases $R_2O_3.3Pa_2O_5$ may therefore be expected to contain interstitial oxygen ions, and should be written as $(R_{0\cdot25}Pa_{0\cdot75})O_{2\cdot25}$.

The lattice parameter of this phase decreases linearly with the radius of the rare earth ion as shown in Table 8 and Fig. 3. The cell parameters of the $(R_{0\cdot5}Pa_{0\cdot5})O_2$ phases reported by Keller are also shown in Fig. 3 and exhibit a similar trend. It is interesting to observe that

Table 8. *Lattice parameters of* $R_xPa_{1-x}O_{2\cdot5-x}$ (Å)

R	$x=0{\cdot}5$ (Keller, 1964)	$x=0{\cdot}25$ (Present work)	Mean cation radius ($x=0{\cdot}5$)
La	5·525 ± 0·002	5·495 ± 0·005	1·040
Nd	5·458 ± 0·002	5·437 ± 0·002	1·005
Sm	5·422 ± 0·002	5·422 ± 0·003	0·995
Gd	5·403 ± 0·002	5·412 ± 0·002	0·985
Dy	5·381 ± 0·002	5·385 ± 0·002	0·965
Ho	5·362 ± 0·002	5·372 ± 0·002	0·955
Y	5·361 ± 0·002	5·387 ± 0·002	0·960
Er	5·355 ± 0·002	5·370 ± 0·002	0·950
Yb	5·331 ± 0·002	5·347 ± 0·002	0·930

the two lines cross. That is, for the rare earths lanthanum to samarium the composition $MO_{2\cdot 25}$ shows a smaller cell volume than MO_2, whereas from gadolinium to ytterbium the reverse is true. This would appear to be packing effect. The greater oxygen content of $(R_{0\cdot 25}Pa_{0\cdot 75})O_{2\cdot 25}$ as compared with $(R_{0\cdot 5}Pa_{0\cdot 5})O_2$ will tend to increase the unit-cell size but the increased proportion of Pa^{5+} (which is smaller than any of the R^{3+} used) in the cation lattice will have the opposite tendency. Which of these effects is the greater depends on the radius of the rare earth ion: both are illustrated by the data for various compositions in the samarium and ytterbium systems listed in Table 9. For compositions richer in protactinium than those listed, a rhombohedral phase was observed in the samarium system and a hexagonal one in the ytterbium system. It was not determined whether these were the hexagonal and rhombohedral phases of Pa_2O_5 observed by Roberts & Walter (1965) or solid solutions of rare earth in these.

Table 9. *Lattice parameters* (Å) *of* $R_xPa_{1-x}O_{2\cdot 5-x}$

e.s.d.'s are all 0·002 Å.

x	R = Sm	R = Yb
0·5	5·435	5·270
0·33	5·430	
0·29	5·428	
0·25	5·422	5·347
0·16	5·413	5·379
0·10	5·405	

It is noteworthy that the two lines of Fig. 3 cross in the region of gadolinium, at which point the mean cation radius for the composition MO_2 [*i.e.* $0\cdot 5(r_{R^{3+}}+r_{Pa^{5+}})$] is close (0·985 Å for Gd^{3+}) to the theoretical limit (0·966 Å) for anion contact in the fluorite structure. Above this limit the only contacts are cation–anion ones and changes in composition reflect the change of mean cation radius: below the limit there are anion–anion contacts and the changes of cell parameter reflect the increasing numbers of oxygen ions. (We have used Goldschmidt radii for all ions except Pa^{5+}, for which we use 0·86 Å. The derivation of this value is to be published in a subsequent paper.)

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