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Pyrochlore-Related Phases in the Lead Oxide–Tantalum Oxide System

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Pyrochlore-related phases in the $PbO-Ta_2O_5$ system were reinvestigated. Three such phases are described: cubic $Pb_{1.5}Ta_2O_{6.5}$ with a narrow range of composition, rhombohedral $Pb_{22}Ta_{18}O_{67}$, and orthorhombic $Pb_{14}Ta_{10}O_{39}$. A new pyrochlore-related structure is proposed for the orthorhombic phase. There is also a range of rhombohedral solid solution, which may be metastable only. The existence of the previously reported $Pb_2Ta_2O_7$ is not confirmed.

Introduction

Previous studies of the $PbO-Ta_2O_5$ system (*1–6*) or the analogous $PbO-Nb_2O_5$ system (*1, 3, 6, 7*) have indicated the existence of a number of phases with structures apparently related to that of pyrochlore. The type structure was originally described many years ago (*8, 9*). It is characterized by a 3-dimensional framework of corner-linked octahedra. Different features of this arrangement and its relationship to other structures have been emphasized by various authors (*1, 10–12*), but perhaps the most characteristic feature is the presence of a tetrahedron of corner-linked octahedra which Nyman *et al.* (*13*) have termed the "pyrochlore unit."

In the $PbO-Ta_2O_5$ system the pyrochlore-related phases are generally considered to be cubic $Pb_{1.5}Ta_2O_{6.5}$ with a defect pyrochlore structure, rhombohedral $Pb_2Ta_2O_7$ (this is the ideal pyrochlore composition) and $Pb_5Ta_4O_{15}$, and tetragonal $Pb_3Ta_2O_8$. However, it is not clear whether the two rhombohedral compositions are distinct compounds with a complete range of solid solubility, or merely the approximate extremes of a nonstoichiometric phase. Except in the case of the cubic phase, it is only the fluorite-related subcells which are known with any confidence and crystal structures are certainly not known. Even for the cubic phase, as Subbarao (*2*) points out, the specific composition $Pb_{1.5}Ta_2O_{6.5}$ for a defect phase which might be expected to have a range of composition poses an interesting problem in crystal chemistry.

There are also some results not in accord with this general picture. Weaver and Li (*14*) reported a tetragonal variant of $Pb_{1.5}Ta_2O_{6.5}$ prepared as a single crystal by flux growth, but the proposed indexing of a powder pattern from the material is inconsistent with the space group determined from the single-crystal data. Brusset *et al.* (*15, 16*) have described monoclinic unit cells for $Pb_2Nb_2O_7$ and $Pb_5Nb_4O_{15}$ on the basis of single-crystal X-ray data, but it does not seem possible to reconcile the proposed

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cells with the fluorite-type subcells which are undoubtedly present in these phases.

Most recently Bernotat-Wulf and Hoffmann (*17*) (hereafter contracted to BWH) have given a substantially new picture of the pyrochlore-related phases in the PbO–Nb_2O_5 system. Five such phases were obtained from melts: cubic $Pb_{1.5}Nb_2O_{6.5}$, three rhombohedral phases $Pb_2Nb_2O_7$, $Pb_{30}Nb_{26}O_{95}$, and $Pb_{22}Nb_{18}O_{67}$, and orthorhombic $Pb_{14}Nb_{10}O_{39}$. Structures for the first four were determined from single-crystal data: the postulated defect-pyrochlore structure for the cubic phase was confirmed, and structures for the rhombohedral phases derived from the ideal pyrochlore type by periodic faulting on (111) planes were established. No structure was postulated for the orthorhombic phase.

Because of the uncertainties in the existing literature, and because pyrochlore-related phases in general and defect-pyrochlores in particular have potential as solid-state electrolytes (*18*), the PbO–Ta_2O_5 system was reinvestigated over the composition range in which pyrochlore-related phases are reputed to occur, with particular emphasis on the crystal structures of the phases present. In addition a few PbO–Nb_2O_5 compositions were examined to confirm analogies with the corresponding tantalates, and to facilitate the determination of some crystal data. Broadly, the results obtained confirm those of BWH for the niobates and extend them to the tantalates, though there are some differences of detail.

Experimental Technique

The starting materials were Nb_2O_5 (Koch-Light, 99.9%), optical-grade Ta_2O_5 (Kawecki Berylco Industries Inc.), and yellow PbO (BDH Analar, 99.0%) which, after firing at 800°C to decompose some basic lead carbonate initially present, contained only the orthorhombic polymorph.

Samples were prepared by conventional ceramic techniques: weighed quantities of the component oxides were thoroughly mixed, pressed into pellets, and fired in electric furnaces. Because of the volatility of PbO, some samples were encapsulated in gold for firing at temperatures up to 950°C or in platinum for firing above that temperature. All samples were weighed before and after firing to check on evaporation losses and to calculate compositional changes where necessary, assuming that only PbO was lost.

The phases present after firing were identified by powder X-ray diffraction using a Guinier camera. When accurate lattice parameters were required a little ThO_2 (a = 5.5972 Å) was mixed with the specimen as an internal standard. Intensity data were obtained from some films using a scanning microdensitometer coupled to a chart recorder: peak areas were measured with a planimeter.

Densities were determined pycnometrically with water as the immersion fluid. For the samples prepared in this study the precision was estimated to be about ½–1%. However, systematic errors, e.g., closed porosity, tend to reduce the measured densities, so that measured densities which are less than the corresponding X-ray values are probably not significant unless the discrepancy exceeds 5%.

Results

A. Stable Phases

Because of the volatility of PbO at elevated temperatures, it is necessary to distinguish between thermodynamically stable phases, i.e., those phases which are stable in a closed system, and phases which are also stable (or effectively so over reasonable time spans) when evaporation is not specifically prevented. In this study only three thermodynamically stable pyrochlore-related phases were identified in the $PbO-Ta_2O_5$ system above 700°C. These are described in detail below.

(*i*) *The cubic defect-pyrochlore phase.* This phase, previously considered to be a line compound, was found to have a narrow range of composition, indicated by small but definite lattice parameter changes from 10.5471(3) Å when the phase coexisted with $PbTa_2O_6$, to 10.5550(2) Å when the phase coexisted with a PbO-rich rhombohedral phase (figures in parentheses denote the estimated standard deviation in the last place quoted). From these parameter changes the composition range was estimated to be about $Pb_{1.3}Ta_2O_{6.3}$ to $Pb_{1.5}Ta_2O_{6.5}$.

The phase is thermodynamically stable to at least 1200°C, the highest temperature used in this study. In air it is stable at 1000°C, but at 1100°C it decomposes slowly by evaporation of PbO to the Ta_2O_5-rich tetragonal $PbTa_2O_6$, which is not pyrochlore related.

In an attempt to find a crystallographic basis for the rather narrow composition range of this reputedly defect structure, a sample prepared initially at 850°C was heated for 6 days at 1200°C in platinum to facilitate possible ordering. There was some weight loss at this stage which altered the nominal composition to $Pb_{1.445}Ta_2O_{6.445}$. The sample was very well crystallized, but neither powder X-ray diffraction nor electron diffraction showed any reflection, sharp or diffuse, other than those allowed by the space group $Fd3m$ for the pyrochlore structure.

Powder X-ray integrated intensity data were collected from the sample, and are given in Table I. Using this data, the postulated defect-pyrochlore structure was refined to a weighted residual, R_w, of 1.87% using the program POWDER (*19*). The parameters varied, and their refined values and esd's are given in Table II. Within the limits of experimental error, the composition derived from the structure refinement, $Pb_{1.34(2)}Ta_2O_{6.24(12)}$, was consistent with all the lead being present as Pb^{2+}. However, there was a significant difference between the composition derived from the X-ray data and the nominal composition given above: there were no observed weight losses during the specimen preparation which would account for this discrepancy, but the possibility that a weight was incorrectly recorded at some stage could not be excluded. Support for the X-ray-derived value was obtained by electron probe microanalysis of the sample which yielded a value of 1.350(5) : 2 for the Pb : Ta atomic ratio; also the lattice parameter of the sample, a = 10.5492(5) Å, suggested a PbO content below that of the nominal composition. Also worthy of comment is the large temperature factor for the Pb atom, 1.1(2) on a scale with an arbitrary origin chosen to make B(Ta) = O: this might be expected in a partially disordered structure in which the individual Pb atoms are randomly displaced from their ideal sites.

The density of the sample used in the crystal structure determination was not measured, but that of a larger sample of nominal composition $Pb_{1.5}Ta_2O_{6.5}$ prepared at 850°C was determined; the measured value of 8.62 g · cm^{-3} was in satisfac-

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $Pb_{1.34}Ta_2O_{6.34}$

$h\ k\ l$	I/I_0	d_{obs}	$h\ k\ l$	I/I_0	d_{obs}
1 1 1	7	6.091	5 5 1	1	1.4771
3 1 1	2	3.180	7 1 1		
2 2 2	100	3.044	5 5 3	1	1.3734
4 0 0	42	2.638	7 3 1		
4 2 2	1	2.1534	8 0 0	9	1.3185
3 3 3	2	2.0297	6 6 0	0.4	1.2438
5 1 1			8 2 2		
4 4 0	47	1.8642	6 6 2	29	1.2102
5 3 1	1	1.7828	8 4 0	26	1.1795
5 3 3	1	1.6086	7 5 3	0.6	1.1579
6 2 2	59	1.5902	9 1 1		
4 4 4	16	1.5222	9 3 1	0.8	1.1060

TABLE II

REFINED STRUCTURAL PARAMETERS FOR $Pb_{1.34}Ta_2O_{6.34}$

Lattice parameter a = 10.5492(5) Å
Overall isotropic temperature factor B_0 = −0.92(10)

Atom	Site	Occupancy	B	x	y	z
Ta	16(c)	1.0	0.0	0	0	0
Pb	16(d)	0.671(8)	1.10(19)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O1	48(f)	1.0	0.52(89)	0.310(3)	$\frac{1}{8}$	$\frac{1}{8}$
O2	8(b)	0.24(12)		$\frac{3}{8}$	$\frac{3}{8}$	$\frac{1}{8}$

Note. Figures in parentheses denote the estimated standard deviations in the last places quoted.

tory agreement with the X-ray value of 8.77 g · cm^{-3} for the defect-pyrochlore model.

On the basis of the evidence above, it is concluded that the $Pb_{1.5}Ta_2O_{6.5}$ phase does have a defect-pyrochlore structure, but there is a distinct composition range which corresponds to about one-quarter to one-third of the lead sites being randomly vacant. Thus the question posed by Subbarao (*2*) concerning why this defect phase should have a precise composition does not really arise.

(*ii*) *Rhombohedral* $Pb_{22}Ta_{18}O_{67}$. This compound, which was previously described as $Pb_5Ta_4O_{15}$, was formed in a pure state when samples containing at least the stoichiometric amount of PbO were heated in air at 850°C for a sufficient time (say, 7 days); under these conditions any excess PbO evaporated.

The composition was established by measuring the weight loss from samples with an initial composition of 5PbO + $2Ta_2O_5$, and was confirmed by crystallographic data. The erroneous composition previously given for the compound is readily understood when it is noted that the weight change in passing from one composition to the other is only about 1%. Also, if evaporation is prevented the residual PbO in a sample with overall composition 5PbO + $2Ta_2O_5$ is very hard to detect by X-ray powder methods: not only is there little PbO present, but the grinding involved in preparing a powder specimen facilitates a polymorphic transition in PbO and seriously degrades its crystallinity.

The compound is thermodynamically stable to at least 950°C, but on heating in air at 1000°C it decomposes by evaporation of PbO to the cubic phase with a lattice parameter of 10.5551(5) Å, i.e., the PbO-rich extreme of the defect-pyrochlore. No intermediate phases were detected during the decomposition.

The X-ray powder pattern of the compound showed strong subcell reflections characteristic of a rhombohedrally distorted fluorite-type cell (this distorted cell is most conveniently described as a rhombohedrally centered hexagonal cell, with a cell content which is three-fourths that of the parent fluorite cell). In addition, there were much weaker reflections which were indexed on the basis of a rhombohedral cell with hexagonal a axis twice and c axis five times those of the subcell. From this it was inferred that the unit cell contained 60 cations, and hence 1.5 formula units. The density calculated for this model was 9.54 g · cm^{-3}, which is in fair agreement with the measured value of 9.23 g · cm^{-3}. Crystal data for this compound, and for the other pyrochlore-related phases observed in this study, are given in Table III.

Electron diffraction patterns confirmed

TABLE III

CRYSTAL DATA FOR SOME PYROCHLORE-RELATED PHASES IN THE $PbO-Ta_2O_5$ AND $PbO-Nb_2O_5$ SYSTEMS

Phase		Lattice Parameters (Å)		Axial relationship to fluorite cell		
(M = Nb or Ta)	Symmetry	$PbO-Nb_2O_5$	$PbO-Ta_2O_5$			
$Pb_{1.3}Ta_2O_{6.3}$–	Cubic		a = 10.4731(3)–	2	0	0
$Pb_{1.5}Ta_2O_{6.5}$	*Fd*3*m*		10.5550(2)	0	2	0
				0	0	2
30PbO : $13Ta_2O_5$	Rhombohedral		a = 3.7349(5)	$\frac{1}{2}$	$-\frac{1}{2}$	0
s/s limit			c = 9.548(3)	0	$\frac{1}{2}$	$-\frac{1}{2}$
at 850°C				1	1	1
$Pb_{22}M_{18}O_{67}$	Rhombohedral	a = 7.4607(3)	a = 7.4602(2)	1	−1	0
		c = 48.134(5)	c = 48.129(3)	0	1	−1
				5	5	5
$Pb_{14}M_{10}O_{39}$	Orthorhombic	a = 7.5218(4)	a = 7.5128(4)	1	−1	0
	*B**b*	b = 7.5374(4)	b = 7.5304(14)	1	1	0
		c = 32.510(2)	c = 32.587(1)	0	0	6

the relationship of the unit cell to the subcell, but also showed diffuse streaks parallel to the c^* axis, indicating some disorder and suggesting that in a fully ordered crystal the c axis would be a multiple of that required to account for the sharp reflections. The smallest multiple which permits an integral number of formula units in the unit cell (a necessary condition for a fully ordered structure) is two. This doubling of the c axis is in accord with the data for $Pb_{22}Nb_{18}O_{67}$ given by BWH.

For comparison, a sample of $Pb_{22}Nb_{18}O_{67}$ was prepared by heating the component oxides for 7 days at 950°c in gold. The powder diffraction pattern was very similar to that of the tantalate, though the supercell reflections were much stronger and rather more numerous. This is to be expected since Pb and Ta have very similar scattering factors for X rays, so that ordering of these cations contributes little to the intensity of the supercell reflections. Details of the powder patterns of both the tantalate and the niobate are given in Table IV.

Intensity calculations for the X-ray powder patterns of both the niobate and the tantalate were made on the basis of the structure proposed by BWH for the niobate. In both cases the agreement between observed and calculated intensities was excellent.

(*iii*) *Orthorhombic* $Pb_{14}Ta_{10}O_{39}$. The evidence for this compound, which is considered to be the phase previously described as tetragonal $Pb_3Ta_2O_8$, is not wholly satisfactory. Reflections corresponding to a minor phase with an orthorhombic, but almost tetragonal, distortion of a fluorite-type cell were observed from a number of PbO-rich samples fired at temperatures ranging from 650°C in air to 915°C in gold. The formation of the phase was rather inconsistent and repetitions under nominally similar conditions gave very different yields. Similar difficulties were apparently encountered by Vandenborre *et al.* (*6*), who concluded that best results were obtained by using a substantial excess of PbO which was subsequently dissolved in nitric acid.

The best yield in this study, a sample containing about 70% of the phase, was obtained by heating a sample with overall

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR $Pb_{22}M_{18}O_{67}$ PHASES

$Pb_{22}Ta_{18}O_{67}$					$Pb_{22}Nb_{18}O_{67}$	
d_{obs}	I/I_0	h	k	l	I/I_0	d_{obs}
		0	0	6	1	8.00
6.38	0.1	1	0	1	6	6.40
		0	1	2	0.8	6.25
5.71	0.1	1	0	4	0.9	5.69
		0	1	5	0.8	5.36
4.010	0.1	0	0	12		
		1	1	0	0.4	3.733
		1	1	3	1	3.627
3.621	0.1	0	1	11		
3.383	0.1	1	1	6	3	3.380
3.209	25	0	0	15	28	3.207
		0	2	4	0.5	3.121
3.063	100	2	0	5	100	3.059
2.726	0.1	1	0	16	0.5	2.728
2.682	51	0	2	10	47	2.682
2.598	0.1	2	0	11	0.7	2.600
2.439	0.4	2	1	1	3	2.439
2.393	0.1	2	1	4	2	2.394
2.357	0.1	1	0	19	2	2.361
		2	0	14		
		1	2	8	0.2	2.259
		0	1	20		
		0	2	16	0.6	2.200
2.178	0.1	2	1	10		
2.155	0.1	3	0	0	0.2	2.154
		1	2	11	2	2.132
		3	0	6	0.4	2.080
		3	0	9	0.9	1.998
		0	2	19	0.6	1.994
		1	2	14		
1.952	0.3	1	1	21	0.8	1.951
1.9299	23	2	0	20	23	1.9302
1.8970	0.1	3	0	12	0.7	1.896
		2	1	16		
1.8650	28	2	2	0	29	1.8652
		2	2	6	0.5	1.816
		1	3	1	0.9	1.790
1.6537	10	0	2	25	12	1.6539
1.6122	28	2	2	15	26	1.6121
1.6044	3	0	0	30	4	1.6039
1.5928	15	0	4	5	15	1.5931
1.5314	12	4	0	10	13	1.5313
1.3411	7	0	4	20	8	1.3412
1.2652	4	2	0	35	5	1.2654
1.2375	5	4	0	25	6	1.2374
1.2163	8	2	2	30	10	1.2163
1.2112	12	4	2	5	15	1.2113
1.1834	10	2	4	10	12	1.1835
1.1276	2	0	2	40	4	1.1275
1.0888	7	4	2	20	12	1.0889

composition 3PbO + Ta_2O_5 for 4 months at 840°C in gold, with two intermediate regrinding stages: in addition to the orthorhombic phase, $Pb_{22}Ta_{18}O_{67}$ and PbO were present in the sample. This sample enabled the subcell parameters to be determined accurately, but provided no information about the presumed supercell.

By comparison, the niobate analog was easily prepared. A sample with overall composition 3PbO + Nb_2O_5 fired for 8 days at 950°C in gold yielded the desired phase with just a trace of residual PbO. X-Ray powder diffraction patterns indicated the same distortion of a fluorite subcell as with the tantalate, but numerous extra reflections enabled the supercell to be determined also. The axes of this orthorhombic cell are related to those of the fluorite subcell by the matrix (1 −1 0/1 1 0/0 0 6). This relationship was confirmed by electron diffraction which also showed the diffraction symbol to be $A{*}{*}a$ or $B{*}{*}b$. If the shorter of the two similar axes is chosen as the a axis the diffraction symbol required for satisfactory indexing of the powder pattern is $B{*}{*}b$, the alternative being unacceptable. This is a minor point of difference with BWH, who, with the same choice regarding axial lengths, concluded that the diffraction symbol was $A{*}{*}a$.

Since there are 48 cation sites in the unit cell (given that it is fluorite related) and the diffraction symbol requires them to be occupied in groups of four, the only possible composition for the phase in the vicinity of $3PbO \cdot Nb_2O_5$ is $Pb_{14}Nb_{10}O_{39}$ with two formula units in the unit cell. Other similar compositions would require cation vacancies, but these can be excluded since the measured density of $7.97 \mathrm{g} \cdot \mathrm{cm}^{-3}$ is in good agreement with the X-ray density of $8.024 \mathrm{g} \cdot \mathrm{cm}^{-3}$ for the proposed compound.

BWH did not propose a structure for $Pb_{14}Nb_{10}O_{39}$. However, it may be seen that by substituting Pb for Nb in every sixth (001) cation layer of a hypothetical

$Pb_2Nb_2O_7$ cubic pyrochlore (which does not actually exist under normal conditions), a structure with the required composition, symmetry, and lattice parameters can be developed. This structure is illustrated in Fig. 1, which shows the suggested cation arrangement, and the consequent framework of NbO_6 octahedra. Intensities calculated from this model agreed well with measured powder intensity data, and a weighted residual, R_w, of 10.3% was obtained refining scale and an overall temperature factor only. Attempts to further refine the structure were not successful due possibly to high correlations between atomic coordinates and the presence of false minima. Also, the number of anions in the proposed cell is not divisible by four so that a fully ordered structure would require at least a doubling of the unit cell. A full structure determination will therefore require high-quality single-crystal data.

Intensity calculations for the tantalate, using the same model for the structure, indicated that all the supercell reflections would probably be too weak to detect in Guinier photographs. It therefore seems reasonable to assume, in the absence of evidence to the contrary, that the orthorhombic niobate and tantalate are analogous, on the basis of the similarity of the subcells. Powder diffraction data for these phases are given in Tables V and VI.

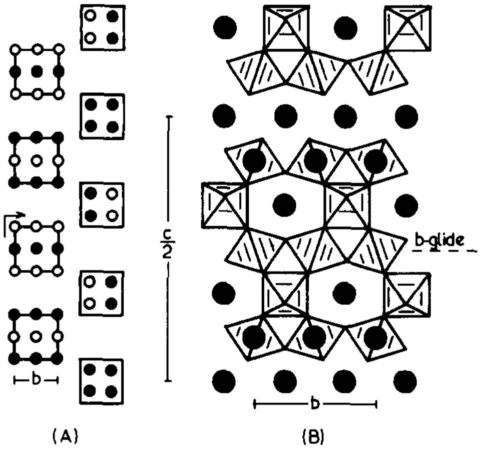

FIG. 1. Proposed structure for $Pb_{14}Nb_{10}O_{39}$ and $Pb_{14}Ta_{10}O_{39}$. (A) Cation arrangement in successive (001) layers. (B) View in [100] direction showing configuration of MO_6 octahedra. Solid circles denote lead atoms. There is a direct correspondence between the cation layers shown in projection in (A) and viewed "edge on" in (B).

B. Metastable Phases

Despite the fact that rhombohedral $Pb_2Ta_2O_7$ has been reported a number of times (*1–3*, *20*), no evidence for the compound was found in this study. All attempts to prepare the compound by solid-state reaction of the component oxides failed, and in each case yielded a mixture of the cubic defect-pyrochlore and a poorly crystalline rhombohedral phase in the approximate ratio of 1 : 2. From this ratio, the composition of the pyrochlore, and the overall composition of the sample, it was deduced that the composition of the rhombohedral phase was about 30PbO · $13Ta_2O_5$. The lattice parameters were similar to those of the subcell of $Pb_{22}Ta_{18}O_{67}$, but with a slightly

TABLE V

X-RAY POWDER DIFFRACTION DATA FOR $Pb_{14}Ta_{10}O_{39}$

h	k	l	I/I_0	d_{obs}	h	k	l	I/I_0	d_{obs}
0	2	6	100	3.091	4	4	0	7	1.3298
2	0	6							
0	0	12	9	2.7155	2	4	18	12	1.2327
					4	2	18		
2	2	0	33	2.6596	0	6	6	5	1.2231
2	2	12	24	1.9002	6	0	6	5	1.2202
0	4	0	12	1.8831	4	4	12	7	1.1943
4	0	0	11	1.8783	2	6	0	5	1.1906
0	2	18	9	1.6312	6	2	0	6	1.1882
2	0	18							
2	4	6	35	1.6075	0	4	24	5	1.1009
4	2	6		1.6056	4	0	24		
0	4	12	7	1.5472	2	6	12	6	1.0903
4	0	12	6	1.5449	6	2	12	6	1.0886

Note. Powder pattern indexed by anology with $Pb_{14}Nb_{10}O_{39}$. All the observed lines from the tantalate can be indexed on the basis of an *I*-centered orthorhombic cell with a = 3.7565(2), b = 3.7658(2), c = 5.4311(6) Å.

TABLE VI

X-RAY POWDER DIFFRACTION DATA FOR $Pb_{14}Nb_{10}O_{39}$

h	k	l	I/I_0	d_{obs}	h	k	l	I/I_0	d_{obs}
0	0	2	0.9	16.26	0	1	16	0.5	1.9623
0	0	4	0.4	8.130	2	2	12	24	1.8988
0	1	2	2	6.838	0	4	0	9	1.8848
1	0	3	4	6.179	4	0	0	9	1.8803
0	1	4	0.8	5.530	1	2	15	0.5	1.8229
0	2	0	0.4	3.763	4	1	2	0.3	1.8134
2	0	0			3	2	9	0.6	1.8076
0	2	2	0.5	3.669	1	4	3	0.8	1.8026
2	0	2			4	1	4	0.4	1.7808
0	2	4	0.4	3.420	2	3	10	0.9	1.7579
2	0	4			2	1	16	0.5	1.7397
2	1	2	0.3	3.296	0	2	18	11	1.6285
1	0	9	0.7	3.259	2	0	18		
1	2	3	2	3.219	2	4	6	33	1.6088
0	2	6	100	3.091	4	2	6		1.6071
2	0	6			0	4	12	5	1.5469
0	1	10	0.7	2.984	4	0	12	6	1.5448
0	0	12	10	2.7092	0	0	24	2	1.3548
2	2	0	30	2.6621	4	4	0	6	1.3312
2	2	2	0.3	2.628	2	4	18	13	1.2316
2	1	8	0.3	2.593	4	2	18		
2	2	4	0.4	2.531	0	6	6	4	1.2240
0	3	2	0.2	2.4833	6	0	6	5	1.2213
1	2	9	3	2.4645	2	2	24	6	1.2074
3	0	3	2	2.4426	4	4	12	6	1.1947
0	3	4	1	2.4011	2	6	0	5	1.1916
2	1	10	2	2.3387	6	2	0	6	1.1895
1	0	15	0.4	2.0827	0	4	24	5	1.0995
2	3	2	0.6	2.0731	4	0	24		
3	2	3	2	2.0500	2	6	12	6	1.0908
2	3	4	0.5	2.0239	6	2	12	6	1.0892

longer *a* axis and shorter *c* axis: there were no detectable supercell reflections. Between the composition $30PbO \cdot 13Ta_2O_5$ and the compound $Pb_{22}Ta_{18}O_{67}$ there appears to be complete solid solubility.

Two experimental results cast doubt on the stability of this disordered rhombohedral phase. As noted above, when $Pb_{22}Ta_{18}O_{67}$ is heated in air at 1000°C to evaporate PbO it transforms directly to the cubic pyrochlore without the formation of any intermediate rhombohedral phase. Also, when $Pb_{22}Ta_{18}O_{67}$ was reacted with about 3% by weight of Ta_2O_5 the products were about 10% of cubic pyrochlore and 90% of an ordered rhombohedral $Pb_{22}Ta_{18}O_{67}$-type phase with a *c* axis of 48.107(7) Å, which is slightly but significantly different from that of $Pb_{22}Ta_{18}O_{67}$, which suggests that the compound may be able to dissolve a little Ta_2O_5 without becoming disordered.

Conclusions

Three stable pyrochlore-related phases occur in the $PbO-Ta_2O_5$ system. These are (i) a cubic phase with a defect-pyrochlore structure with a composition range of $Pb_{1.3}Ta_2O_{6.3}$ to $Pb_{1.5}Ta_2O_{6.5}$ approximately, (ii) an ordered rhombohedral compound $Pb_{22}Ta_{18}O_{67}$, and (iii) an orthorhombic (pseudotetragonal) compound $Pb_{14}Ta_{10}O_{39}$. All three phases are analogous to lead niobates described by Bernotat-Wulf and Hoffmann (*17*).

A structure based on that of pyrochlore is proposed for $Pb_{14}Ta_{10}O_{39}$ and the analogous niobate. This structure gives a good semiquantitative account of the intensities in the powder diffraction patterns of both compounds, but could not be refined satisfactorily using powder data.

Samples with an overall composition of $2PbO:Ta_2O_5$ were two-phase mixtures even after extended firings, so that the existence as a stable phase of the widely reported $Pb_2Ta_2O_7$ is not confirmed.

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