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Formation and transformation of cubic $3PbO \cdot 2Ta_2O_5$ solid solution

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The formation of lead tantalates in the PbO-rich region is studied using the powders prepared by the simultaneous hydrolysis of lead and tantalum alkoxides. Cubic $3PbO \cdot 2Ta_2O_5$ solid solutions crystallize at low temperatures from amorphous materials between 60 and 75 mol% PbO. The lattice parameter, *a*, increases linearly from 1.0545 to 1.0705 nm with increasing PbO. At higher temperatures the solid solutions above 66.67 mol% PbO are transformed into those of rhombohedral $2PbO \cdot Ta_2O_5$. Rhombohedral $5PbO \cdot 2Ta_2O_5$ is formed at ~850 to 900 °C by transformation of $2PbO \cdot Ta_2O_5$ solid solution corresponding to 71.43 mol% PbO. The existence of previously reported $3PbO \cdot Ta_2O_5$ is not confirmed.

1. Introduction

Previous studies of the $PbO–Ta_2O_5$ system indicated the existence of a number of compounds related to the pyrochlore structure [1–6]. The compounds were considered to be cubic $3PbO \cdot 2Ta_2O_5$, rhombohedral $2PbO \cdot Ta_2O_5$ and $5PbO \cdot 2Ta_2O_5$, and tetragonal $3PbO \cdot Ta_2O_5$. The last compound was always prepared with a trace of PbO [2, 3, 6]. They were formed by the solid-state reaction of PbO and Ta_2O_5. Because of the vaporization of PbO at elevated temperatures, many of the experiments were carried out in sealed platinum tubes. Recently, Scott [7] studied the compound formation from initial compositions of $5PbO + 2Ta_2O_5$ and $3PbO + Ta_2O_5$ and showed that the compounds so far denoted as $5PbO \cdot 2Ta_2O_5$ and $3PbO \cdot Ta_2O_5$ were determined to be $22PbO \cdot 9Ta_2O_5$ (rhombohedral) and $14PbO \cdot 5Ta_2O_5$ (orthorhombic), respectively.

A systematic study of compound formation in the PbO-rich region of this system was attempted using amorphous materials prepared from alkoxides. The existence of $5PbO \cdot 2Ta_2O_5$ was established. On the other hand, $22PbO \cdot 9Ta_2O_5$ and $14PbO \cdot 5Ta_2O_5$ reported by Scott [7] and $3PbO \cdot Ta_2O_5$ were not confirmed to exist. Cubic $3PbO \cdot 2Ta_2O_5$ solid solutions were formed in the range 60 to 75 mol% PbO. The compounds $2PbO \cdot Ta_2O_5$ and $5PbO \cdot 2Ta_2O_5$ were found to form by transformation of the solid solutions. The formation of alkoxy-derived lead tantalates is reported here.

2. Experimental procedure

Tantalum isopropoxide, $Ta(OC_3H_7)_5$ (99.999% pure, Kojundo Kagaku Kenkyujo, Saitama, Japan), was used. Lead isopropoxide, $Pb(OC_3H_7)_2$, was synthesized by the reaction of anhydrous lead acetate (99.9% pure) with sodium isopropoxide in the presence of excess analytical grade 2-propanol [8, 9].

$$Na + C_3H_7OH \rightarrow NaOC_3H_7 + 1/2H_2 \quad (1)$$

$$Pb(CH_3COO)_2 + 2NaOC_3H_7 \xrightarrow[C_3H_7OH]{82\,^\circ C,\ 10\,h} Pb(OC_3H_7)_2 + 2CH_3COONa\downarrow \quad (2)$$

After as-received sodium was cleaned by removing the superficial crust, it was used in the preparation of sodium isopropoxide. Lead isopropoxide was filtered to a clear solution. The mixed alkoxides were heated under reflux for 5 h and then hydrolysed by adding distilled water at room temperature. The temperature was slowly increased to 75 °C while the resulting suspensions were stirred. The hydrolysis products of the various compositions shown in Table I were separated from the suspensions by filtration, washed ten times in hot water, and dried at 120 °C under reduced pressure. The powders obtained are termed starting powders A to H. The average particle size of all starting powders, determined by electron microscopy, was ≈ 80 nm. Atomic absorption analysis indicated that the sodium content in the starting powders was < 400 p.p.m.

Thermal analyses (thermogravimetric (TG), differential thermal analysis (DTA)) were conducted in air at a rate of $10\,^\circ C\,min^{-1}$; α-alumina was used as the reference for the DTA. The starting powders and specimens, obtained from DTA studies and then quenched, were examined by X-ray diffraction (XRD) analysis using nickel-filtered Cu*K*α radiation. Interplanar spacings were measured with the aid of an internal standard of silicon, and unit cell values were determined by a least-squares refinement.

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TABLE I Chemical composition of starting powders, crystallization temperature of $3PbO \cdot 2Ta_2O_5$ phase, and phase transformation temperature of $3PbO \cdot 2Ta_2O_5$ into $2PbO \cdot Ta_2O_5$

Starting powder	Composition (mol %)		Mole ratio, PbO : Ta_2O_5	Crystallization temperature (°C)	Transformation temperature (°C)
	PbO	Ta_2O_5			
A	60	40	3 : 2	515–630	
B	66.67	33.33	2 : 1	480–580	780–850*
C	70	30		440–540	765–800
D	70.97	29.03	22 : 9	435–530	760–795
E	71.43	28.57	5 : 2	425–520	750–780
F	73.68	26.32	14 : 5	415–510	735–770
G	75	25	3 : 1	405–495	730–770
H	77.78	22.22		400–490	740–790

* Determined by X-ray analysis.

3. Results and discussion

3.1. Identification of starting powder

The starting powders A to G were amorphous. On the other hand, powder H contained a small amount of $Pb_3(CO_3)_2(OH)_2$ [10]. According to the previous data [9], the hydrolysis product of lead isopropoxide is crystalline PbO. It can, therefore, be presumed that free PbO, formed by hydrolysis, was reacted with H_2O and CO_2 in air during the course of the washing and drying processes, resulting in $Pb_3(CO_3)_2(OH)_2$.

3.2. Existence of $5PbO \cdot 2Ta_2O_5$

It is important to confirm if the compounds described as $5PbO \cdot 2Ta_2O_5$ and $3PbO \cdot Ta_2O_5$ are $22PbO \cdot 9Ta_2O_5$ and $14PbO \cdot 5Ta_2O_5$, respectively. When powder D was heated at 950 °C, the final product was a mixture of $2PbO \cdot Ta_2O_5$ and $5PbO \cdot 2Ta_2O_5$. Single-phase $5PbO \cdot 2Ta_2O_5$ was prepared from powder E. These results suggest that $5PbO \cdot 2Ta_2O_5$ exists in this system. On the other hand, no formation of $14PbO \cdot 5Ta_2O_5$ and $3PbO \cdot Ta_2O_5$ from powders F and G, respectively, was recognized throughout the heating processes; mixtures of $5PbO \cdot 2Ta_2O_5$ and tetragonal PbO (litharge) were obtained as final products. Details will be described later.

3.3. Thermal analysis

Thermogravimetric data showed weight losses of 10.1 to 11.4% to 210 °C for all starting powders; these are

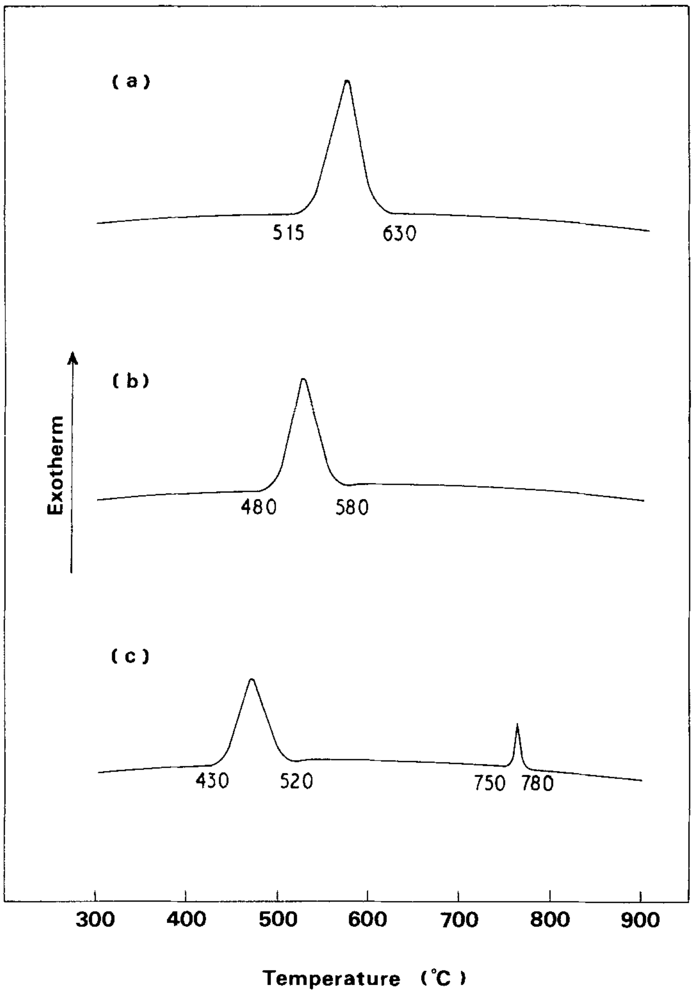

Figure 1 Differential thermal analysis curves for starting powders (a) A, (b) B, and (c) E.

due to the release of organic residues from the parent alcohol, absorbed water, and hydrated water. In the DTA curve for powder H, two small endothermic peaks were observed at 230 to 285 °C and 330 to 375 °C. They occurred from the decomposition of $Pb_3(CO_3)_2(OH)_2$ for the former peak and Pb_2OCO_3 [11] for the latter peak. Fig. 1 shows the DTA curves > 300 °C for powders A, B, and E. All DTA curves in the temperature range 400 to 630 °C reveal large exothermic peaks resulting from the crystallization of $3PbO \cdot 2Ta_2O_5$ ($3PbO \cdot 2Ta_2O_5$ solid solution), although the peaks decreased successively in height from powders A to H. The crystallization temperature of each starting powder is listed in Table I; with increasing PbO the crystallization was shifted to lower temperatures. Powders C to H showed the second exothermic peaks at higher temperatures; they were found to result from the transformation of the solid solutions of $3PbO \cdot 2Ta_2O_5$ into $2PbO \cdot Ta_2O_5$. The transformation, as well as crystallization, was shifted to lower temperatures with increasing PbO, except for powder H.

3.4. Formation of $3PbO \cdot 2Ta_2O_5$ solid solution

The starting powders A to G, being amorphous, did not exhibit significant change in structure up to the temperatures of the large exothermic peaks. The specimens at temperatures above the peaks gave the XRD pattern of only $3PbO \cdot 2Ta_2O_5$ phase. As described above, a small amount of $Pb_3(CO_3)_2(OH)_2$ was present in powder H. The decomposition of the compound proceeded in two stages: $Pb_3(CO_3)_2(OH)_2 \rightarrow Pb_2OCO_3 \rightarrow PbO$ (tetragonal). The tetragonal-to-orthorhombic PbO phase transformation occurred at ~500 °C. A mixture of the $3PbO \cdot 2Ta_2O_5$ phase and orthorhombic PbO was obtained when powder H was heated at 520 °C. These results indicate that $3PbO \cdot 2Ta_2O_5$ solid solutions were formed between 60 and 75 mol % PbO. The X-ray data for pure $3PbO \cdot 2Ta_2O_5$ prepared from powder A were in agreement with those reported [12]; the lattice parameter *a* was estimated as a cubic unit cell with *a* = 1.0545 nm. Compositional changes result in a significant variation in the cell dimensions. Fig. 2 shows the variation of lattice parameters of the $3PbO \cdot 2Ta_2O_5$ phase; their values increased linearly from 1.0545 to 1.0705 nm with increasing PbO.

3.5. Formation of $2PbO \cdot Ta_2O_5$

Cubic $3PbO \cdot 2Ta_2O_5$ solid solutions were observed up to the temperatures of the second exothermic peaks. They were transformed into $2PbO \cdot Ta_2O_5$ solid solutions at temperatures shown in Table I. Although no thermal activity for powder B was detected in the DTA, $2PbO \cdot Ta_2O_5$ was formed at ~ 780 to

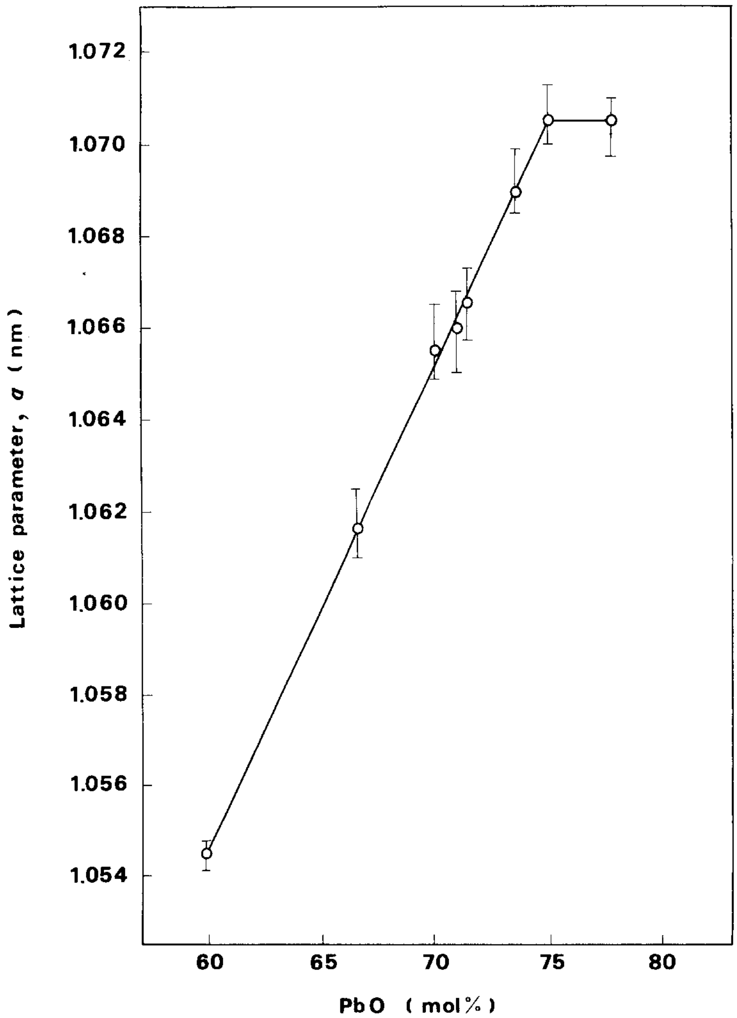

Figure 2 Lattice parameters for $3PbO \cdot 2Ta_2O_5$ phase as a function of composition.

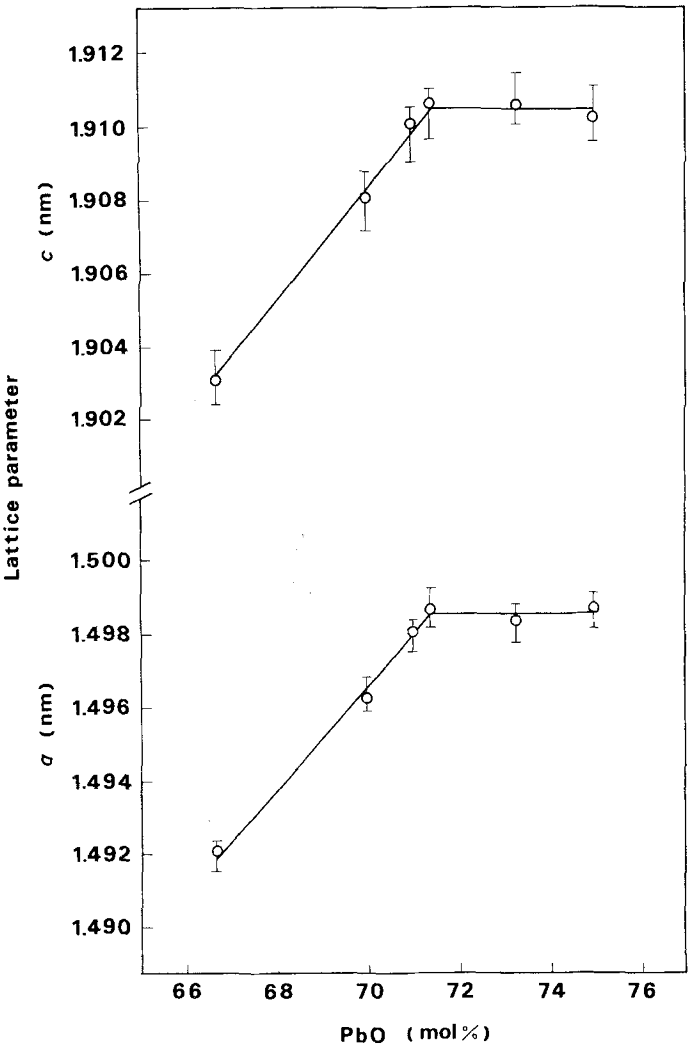

Figure 3 Lattice parameters for $2PbO \cdot Ta_2O_5$ phase as a function of composition.

850 °C. The crystal structure had a rhombohedral symmetry with $a = 1.492$ nm and $c = 1.903$ nm ($a = 1.070$ nm, $\alpha = 88°26'$); the data were in agreement with those ($a = 1.493$ nm, $c = 1.905$ nm) reported previously [3]. The effect of solid solutions on structure is shown in Fig. 3. The changes in lattice parameters a and c as a function of composition were the same as those of cubic $3PbO \cdot 2Ta_2O_5$ solid solutions.

3.6. Formation of $5PbO \cdot 2Ta_2O_5$

The compound $5PbO \cdot 2Ta_2O_5$ was formed at ~850 to 900 °C by transformation of $2PbO \cdot Ta_2O_5$ solid solution from powder E. The X-ray data for $5PbO \cdot 2Ta_2O_5$ are shown in Table II; although the d values were in agreement with those reported [3], the strongest line and the intensity ratio of the lines were different from each other. It was classified into the rhombohedral system with $a = 1.491$ nm and $c = 1.925$ nm ($a = 1.074$ nm, $\alpha = 87°57'$). The solid solutions from powders C and D after heating at 900 °C were transformed into $5PbO \cdot 2Ta_2O_5$ with the formation of $2PbO \cdot Ta_2O_5$. The specimens from powders F to H were $5PbO \cdot 2Ta_2O_5$ containing small amounts of tetragonal PbO transformed from the solid solutions (the formation of the tetragonal phase suggests that PbO melted after transformation). The existence of $3PbO \cdot Ta_2O_5$ was reported by several investigators [2, 3, 6]. Subbarao [2] first described that heating the specimen below ~700 °C with 75 mol% PbO gave $3PbO \cdot Ta_2O_5$ plus a trace of PbO, hence the labelling of this compound is tentative. Later Kemmler-Sack and Rüdorff [3] reported the formation of $3PbO \cdot Ta_2O_5$ containing a trace of PbO by heating for 48 h at 900 to 930 °C. Moreover, Vandenborre *et al.* [6] studied the compound formation from $5PbO + Ta_2O_5$ by heating for 48 h at

TABLE II X-ray data for $5PbO \cdot 2Ta_2O_5$[a]

$5PbO \cdot 2Ta_2O_5$[a]				$5PbO \cdot 2Ta_2O_5$[b] [3]	
d_{obs} (nm)	d_{calc} (nm)	I/I_0	hkl	d_{obs} (nm)	I/I_0
0.321	0.321	37	006	0.321	80
0.306	0.306	100	402	0.306	90
0.2681	0.2681	57	044	0.269	100
0.2432	0.2432	< 2	226	0.2435	10
0.2254	0.2254	< 2	217		
0.2067	0.2066	< 2	520	0.2064	10
				0.1995	10
0.1929	0.1929	26	408	0.1927	80
0.1864	0.1864	28	440	0.1862	80
0.1760	0.1760	< 2	622	0.1758	10
0.1653	0.1653	13	04*10*	0.1652	30
0.1612	0.1612	27	446	0.1610	80
0.1592	0.1592	15	082	0.1590	60
0.1530	0.1530	11	804	0.1529	30

[a] Rhombohedral: $a = 1.491$ nm, $c = 1.925$ nm.
[b] Rhombohedral: $a = 1.491$ nm, $c = 1.924$ nm.

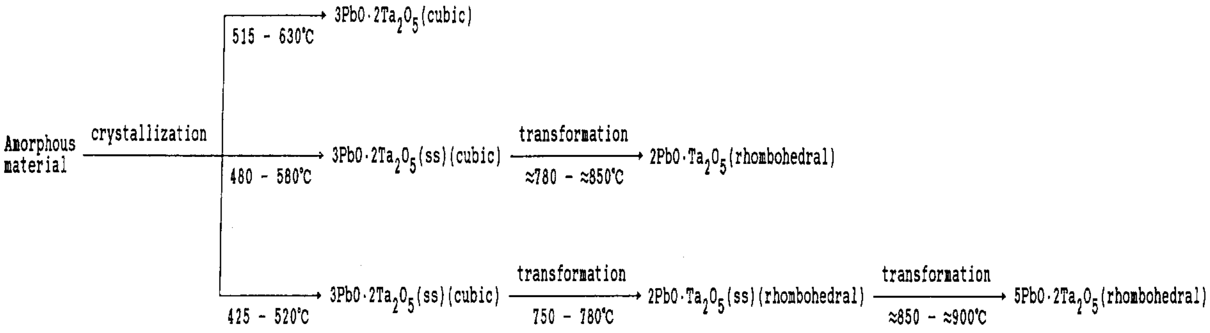

Figure 4 Formation of lead tantalates in the PbO-rich region.

900 °C and reported that the product removed excess PbO by nitric acid after the reaction showed a similar XRD pattern to that of $3PbO \cdot Ta_2O_5$. In the present study, no compounds corresponding to $3PbO \cdot Ta_2O_5$ and $14PbO \cdot 5Ta_2O_5$ from powders F to H were prepared even after heating for 48 h at 900 and 950 °C (to prevent the vaporization of PbO, the experiments were carried out in sealed platinum tubes) mixtures of $5PbO \cdot 2Ta_2O_5$ and tetragonal PbO were obtained.

4. Conclusion

The formation of alkoxy-derived lead tantalates in the PbO rich region can be summarized by Fig. 4.

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