JOURNAL OF SOLID STATE CHEMISTRY **107**, 93–100 (1993)

Synthesis and Polymorphism of PdP_2O_6

A. WATANABE* AND S. TAKENOUCHI

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki, 305 Japan

AND J.-P. WIGNACOURT, P. CONFLANT, M. DRACHE, AND J.-C. BOIVIN

Laboratoire de Cristallochimie et Physicochimie du Solide, URA CNRS 452, ENSCL et USTL, BP108, 59652 Villeneuve d'Ascq, France

Received December 7, 1992; in revised form March 1, 1993; accepted March 2, 1993

Transparent needlelike brownish-yellow single crystals of PdP_2O_6 have been grown in air under P_2O_5-rich composition in the system $PdO–P_2O_5$. It crystallizes in the orthorhombic system, the possible space group *Pmna* or *P2na*, with a = 12.4904(9) Å, b = 4.5759(5) Å, c = 4.2344(3) Å, and Z = 2. This phase changes into a monoclinic phase under heating conditions. The quenchable monoclinic phase has the possible space group $P2_1/m$ or $P2_1$ with a = 13.156(2) Å, b = 5.1630(7) Å, c = 8.1426(9) Å, and β = 97.46(1)°. A transition temperature depends entirely on a heating rate, e.g., at 908°C at a rate of 10°C min^{-1}, or over 660–735°C at a rate of 20°C hr^{-1}. Moreover the monoclinic phase tends to be decomposed into Pd metal as the final product, depending on not only a temperature but a heating rate. Isothermal heat treatments show that the orthorhombic phase might be a metastable state and the monoclinic phase a stable state at lower temperatures.

Introduction

Palladium (II) mixed oxides have appeared in only a small number of binary systems between palladium (II) oxide and another oxide because of the characteristics of PdO as a noble metal oxide, viz., easy decomposition at 800°C and less reactivity with the other oxide. To date, it is known that each system of PdO with the following oxide has generated a single mixed oxide or a few oxides: alkaline metal oxide (*1*), alkaline-earth metal oxide (*2, 3*), lanthanoid oxide (*4–6*), Cr_2O_3 (*7*), CoO (*7*), Rh_2O_3 (*7*), CuO (*8*), CdO (*3*), PbO (*3, 9, 10*), or Bi_2O_3 (*11, 12*). In addition, Lazarev and Shaplygin (*11*) examined each reaction of PdO with the pentavalent oxides V_2O_5, Nb_2O_5, Ta_2O_5, or Sb_2O_5; as a result, PdO did not react with any of them. On the other hand, Palkina *et al.* (*13*) determined a structure of PdP_2O_6 which was prepared from the system $PdCl_2–H_3PO_4$ (85% conc.). The crystal structure consists of an infinite chain of PO_4 tetrahedra and each Pd atom surrounded by four oxygen atoms forming a square plane. However, they (*13*) did not characterize their product any more. Thus, we reexamined the preparation of compound PdP_2O_6 in the system $PdO–P_2O_5$ free from chlorine and hydrogen, and characterized PdP_2O_6 by X-ray diffraction and thermal analysis.

Experimental Procedure

The starting materials were 99.9% pure PdO (Kojundo Chemical Laboratory Co., Ltd.) and reagent grade $NH_4H_2PO_4$ (Wako Pure Chemicals). The desired proportions

---

* To whom correspondence should be addressed.

0022-4596/93 $5.00

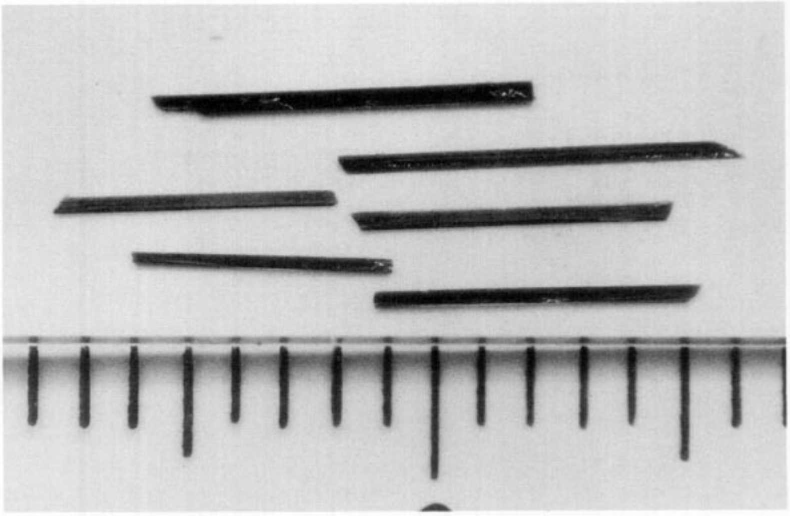

FIG. 1. As-grown needlelike single crystals of PdP_2O_6 (minimum scale = 1 mm).

of $Pd_{1-x}P_{2x}O_{1+4x}$ (where $x = 0.5$ to 0.8) were accurately weighed and thoroughly hand mixed in an agate mortar. Each mixture was placed in a covered gold crucible and heated at 500 to 650°C for 3 hr in air, followed by a slow cooling to room temperature at a rate of 20°C hr^{-1}. A product was always a mixture of needlelike single crystals and a viscous liquid which seems to consist most of P_2O_5. The liquid phase was leached with water from the product. Transparent brownish-yellow single crystals were obtained; they are shown in Fig. 1. At the same time, a small quantity of black powder was recognized visually; it proved to be Pd metal from X-ray powder diffraction (XRPD). Thus, P_2O_5 is also considered to play a role of a low-temperature flux in the present system. Therefore, in numerous cases, the P_2O_5-rich starting composition was selected for the purpose of growing the single crystals positively. Even the product of stoichiometric starting composition (i.e., $x = 0.5$) was the same as above, so that the preparation of polycrystalline sample seems to be difficult.

Chemical analyses of the single crystals were performed using a gravimetric dimethylglyoxime method for the determination of palladium content and using a colorimetric method by a phosphovanadomolybdate procedure for phosphorus content. The probable error was estimated to be ±0.1 wt%.

The density of single crystals was measured at 20°C in kerosene using pycnometer. The accuracy was ±0.10 g cm^{-3}.

The crystal system and the lattice parameters were determined by X-ray diffraction using a Weissenberg camera for single crystals and a diffractometer for a powder which was prepared from pulverization of single crystals. The color of the powder was mustard yellow.

The thermal behavior was checked by a conventional, simultaneous thermogravimetry–differential thermal analysis (TG–DTA) apparatus. A sample holder of alumina was used. A 10–30 mg of pulverized sample underwent heating and cooling cycles usually at a rate of 10°C min^{-1}. The temperature accuracy was ±3°C. Transition temperatures were determined from peaks on DTA curves during the heating cycle. At the same time, the *in situ* measurement of structural change with temperature was also carried out by a Guinier–Lénne camera for high-temperature X-ray diffraction (HTXRD) using Cu $K\alpha$ radiation with operating conditions of a gold-mesh sample holder and a heating rate of 20°C hr^{-1}.

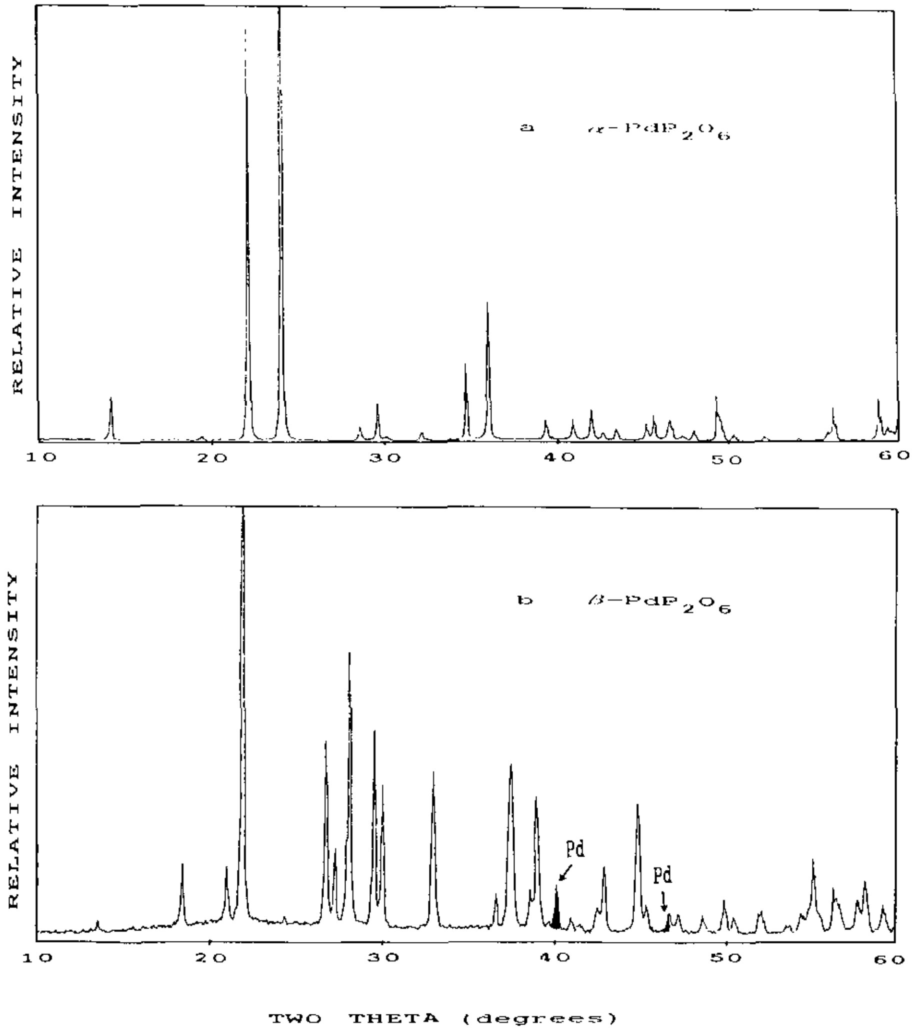

FIG. 2. The room-temperature XRPD patterns of PdP_2O_6: (a) the orthorhombic phase corresponding to the obtained single crystals, maximum scale of the ordinate 4000 cps, and (b) the high-temperature phase quenched to room temperature after being heated at 938°C for 30 min, maximum scale 1000 cps.

Results and Discussion

The chemical analyses gave the following results: 40.4 wt% Pd and 23.5 wt% P. These led to a chemical formula of PdP_2O_6 for the present compound.

The X-ray diffraction study revealed that PdP_2O_6 crystallizes in the possible space group *Pmna* or *P2na* with $a = 12.4904(9)$ Å, $b = 4.5759(5)$ Å, and $c = 4.2344(3)$ Å and that the longitudinal direction of the needlelike crystal is parallel to the orthorhombic *b*-axis. An X-ray powder diffraction pattern is shown in Fig. 2a and diffraction data are listed in Table I. The compound had a density of 3.52 g cm^{-3} to give $Z = 2$, the number of formula units per unit cell. Although the color of single crystals prepared by Palkina *et al.* (*13*) was dark green or almost black, different from the present ones, the lattice parameters and the density were the same as those reported by them. Likewise, the details of the crystal structure determined by us ($R = 3.6\%$ for 985 inde-

TABLE I

X-Ray Powder Diffraction Data for α-PdP_2O_6

h	k	l	d_{calc} (Å)	d_{obs} (Å)	I_{obs}
2	0	0	6.245	6.250	5
0	1	0	4.576	4.577	<1[a]
1	0	1	4.0103	4.0118	51
2	1	0	3.6912	3.6977	100
4	0	0	3.1226	3.1236	2
0	1	1	3.1079	3.1060	1
1	1	1	3.0160	3.0166	4
3	0	1	2.9688	2.9707	<1
2	1	1	2.7824	2.7840	1
4	1	0	2.5793	2.5807	15
3	1	1	2.4906	2.4908	26
0	2	0	2.2880	2.2887	3
4	1	1	2.2028	2.2039	2
5	0	1	2.1516	2.1497	4
2	2	0	2.1484		
0	0	2	2.1172	2.1176	1
6	0	0	2.0817	2.0825	1
2	0	2	2.0051	2.0059	2
1	2	1	1.9873	1.9875	3
5	1	1	1.9452	1.9462	2
0	1	2	1.9215	1.9222	<1
2	2	1	1.9159	1.9167	<1
1	1	2	1.8992	1.9000	1
6	1	0	1.8949	1.8950	1
4	2	0	1.8456	1.8459	5
2	1	2	1.8366	1.8371	2
3	2	1	1.8122	1.8128	1
4	0	2	1.7524	1.7530	<1
4	2	1	1.6919	1.6921	<1
7	0	1	1.6443	1.6445	1
4	1	2	1.6365	1.6363	4
5	2	1	1.5674	1.5673	4
0	2	2	1.5540	1.5541	2
7	1	1	1.5475	1.5477	1
6	2	0	1.5398	1.5399	4
5	1	2	1.5231	1.5250	<1
2	2	2	1.5080	1.5082	<1
6	0	2	1.4844	1.4844	1
2	3	0	1.4818	1.4815	2
8	1	0	1.4777	1.4779	2
1	3	1	1.4257	1.4254	<1
1	0	3	1.4026	1.4026	<1
4	3	0	1.3706	1.3705	2
3	3	1	1.3567	1.3565	2
1	1	3	1.3410	1.3408	<1
7	2	1	1.3353	1.3353	1
9	0	1	1.3188	1.3186	<1
3	1	3	1.2831	1.2829	2
9	1	1	1.2672	1.2673	2
10	0	0	1.2490	1.2487	<1
6	2	2	1.2453	1.2452	1
5	0	3	1.2289	1.2287	1
2	3	2	1.2140	1.2141	1
8	1	2	1.2117	1.2113	1
10	1	0	1.2050	1.2050	<1
1	2	3	1.1958	1.1956	1
4	3	2	1.1505	1.1506	<1
0	4	0	1.1440	1.1440	<1

[a] Observed relative intensity weaker than 1.

pendent reflections) were similar to their results. Therefore, it turns out that both crystals were the same despite the different preparation method and the different color.

Figure 3 exhibits representative TG–DTA curves for heating and cooling cycles. When the specimen is heated up to 940°C, a endothermic peak is observed at 908°C; on cooling, no thermal effect is detected, but in a subsequent heating process, we can again observe the foregoing endothermic peak with somewhat smaller peak area (Fig. 3a). The result seems to denote that a rate of transition in the cooling direction is considerably sluggish, although that in the heating direction is very fast. The sluggishness of this transition in the cooling direction suggests that a high-temperature phase can easily be quenched to room temperature. In fact, Fig. 2b shows a room-temperature XRPD pattern of this phase which was quenched by an air stream after heating at 938°C for 30 min; a very small amount of Pd metal is recognized. The color of the powder changed to brown. Accordingly, the 908°C endothermic peak would seem to indicate a reversible polymorphic transition; hereafter, for convenience, we refer to the orthorhombic phase as α-PdP_2O_6 and to the quenched phase (Fig. 2b) as β-PdP_2O_6.

Making a comparison in Fig. 2, it appears that β-PdP_2O_6 has lower symmetry than α-PdP_2O_6 because of the somewhat complex pattern. To investigate preliminary lattice parameters, Visser's indexing program (*14*) was applied to the observed data listed in Table II. Using these results, the precise

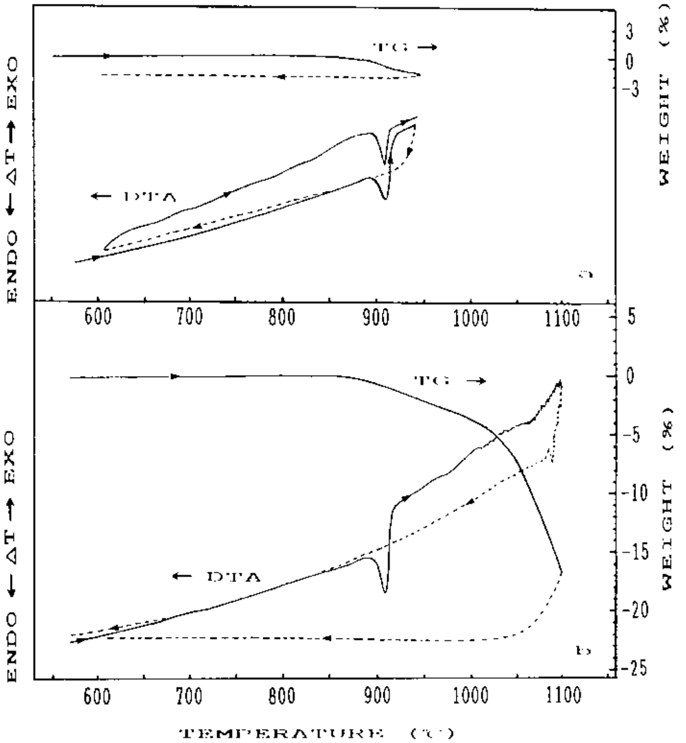

FIG. 3. TG–DTA curves of PdP_2O_6 measured at a rate of 10°C min^{-1} for a heating and cooling cycle: (a) maximum temperature 940°C and (b) maximum temperature 1100°C.

lattice parameters were calculated by the least-squares method. As a result, β-PdP_2O_6 has the monoclinic symmetry with a = 13.156(2) Å, b = 5.1630(7) Å, c = 8.1426(9) Å, and β = 97.46(1)°. We can estimate Z = 4 compared with the lattice parameters of α-PdP_2O_6. The Miller indices given in Table II may be classified as follows: hkl all order, $hk0$ all order, and $00l$ with $l = 2n$. These results lead to the possible space group $P2_1/m$ or $P2_1$.

Figure 3b shows another TG–DTA curve at the maximum temperature of 1100°C. Above 908°C, the DTA curve exhibits no thermal effect besides small vibrations near 1100°C. In contrast, the TG curve points out that a weight loss begins at 880°C and is remarkable above 1015°C. After the measurement, the existence of liquid state at high temperatures was confirmed by the external appearance of the specimen in the sample holder. Apart from the TG–DTA experiment, the α-PdP_2O_6 powder sample wrapped up in a Pt foil was heated at 1136°C for 15 min and then quenched; an XRPD pattern indicated that the product is pure Pd metal. On one hand, it was found that the powder of β-PdP_2O_6 is deliquescent under normal atmospheric conditions; in addition, an XRPD pattern of the deliquescing sample was the same as shown in Fig. 2b. Judging from the results of both TG–DTA and heat-treatment experiments, β-PdP_2O_6 may begin to be decomposed gradually into Pd metal, O_2 gas, and P_2O_5 liquid above 908°C, though a rate of decomposition increases with temperature; in succession, the evaporation of P_2O_5 seems to occur as shown in TG curves (Fig. 3). Also, we can infer that this decomposition causes the decrease in endothermic peak area on the second heating DTA curve shown in Fig. 3a. At higher temperatures

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR β-PdP_2O_6

h	k	l	d_{calc} (Å)	d_{obs} (Å)	I_{obs}
2	0	0	6.522	6.523	3
1	1	0	4.801	4.802	13
1	1	−1	4.2159	4.2162	13
1	1	1	4.0423	4.0421	100
0	0	2	4.0368		
2	0	−2	3.6515	3.6503	4
3	1	0	3.3259	3.3264	33
4	0	0	3.2612	3.2608	15
3	1	−1	3.1889	3.1868	18
1	1	−2	3.1651	3.1648	48
1	1	2	3.0193	3.0195	37
3	1	1	2.9728	2.9744	26
4	0	−2	2.7152	2.7145	28
3	1	2	2.4501	2.4507	7
1	1	−3	2.3969	2.3973	27
2	1	−3	2.3295	2.3295	8
5	1	−1	2.3098	2.3098	25
3	1	−3	2.2019	2.2007	3
0	2	2	2.1748	2.1743	3
5	1	−2	2.1266	2.1263	6
2	2	−2	2.1079	2.1076	12
2	2	2	2.0211	2.0209	23
0	0	4	2.0184	2.0190	22
3	1	3	1.9972	1.9978	6
5	1	2	1.9228	1.9246	5
5	1	−3	1.8716	1.8715	4
4	0	−4	1.8258	1.8256	6
3	1	−4	1.8070	1.8070	4
7	1	−1	1.7581	1.7585	5
5	2	1	1.7551	1.7540	5
1	3	0	1.7062	1.7064	3
4	2	−3	1.6842	1.6848	5
0	3	1	1.6832	1.6812	4
7	1	1	1.6711	1.6728	5
2	3	0	1.6641	1.6640	14
3	1	4	1.6541	1.6558	5
8	0	0	1.6306	1.6314	8
1	0	−5	1.6285	1.6276	7
5	1	−4	1.6211	1.6217	6
6	2	−2	1.5944	1.5951	7
0	2	4	1.5901	1.5910	6
2	2	−4	1.5826	1.5829	10
1	2	4	1.5593	1.5588	5
8	1	0	1.5548	1.5549	5
7	1	2	1.5405	1.5405	3
7	2	0	1.5110	1.5106	10
6	2	2	1.4864	1.4874	6
3	3	2	1.4638	1.4632	3
8	0	2	1.4480	1.4485	3
3	2	4	1.4464	1.4460	3
1	3	3	1.4301	1.4303	3
7	1	−4	1.4116	1.4113	2
5	1	−5	1.4055	1.4055	4
3	3	−3	1.4053		
3	1	5	1.3990	1.4005	4
5	3	1	1.3972	1.3968	4
4	3	2	1.3965		
5	3	−2	1.3851	1.3850	3

than 1100°C, the decomposition is completed and only Pd metal remains. Thus, the room-temperature quenched β-PdP_2O_6 sample must always contain a small quantity of both Pd metal and amorphous P_2O_5. Consequently the deliquescent property in β-PdP_2O_6 might be ascribed to the latter P_2O_5 impurity.

To confirm the above-mentioned structural change including the decomposition, HTXRD was conducted from room temperature up to 930°C. Figure 4 shows a typical result. The α-PdP_2O_6 disappears completely at about 735°C, while the β-PdP_2O_6 appears at about 660°C and disappears at about 815°C. At the maximum temperature of 930°C, the diffraction pattern consists of the lines of Pd metal, those of Au metal for sample holder, and one sharp line which seems to originate from Pd_3P, i.e., $d_{112} = 2.26$ Å (*15, 16*), and seems to be exaggerated by preferred orientation.

It was noted that the α-to-β transition temperature of 908°C by DTA is much higher than that by HTXRD. To explain this difference, we must take the heating rate into account: 10°C min^{-1} = 600°C hr^{-1} in DTA and 20°C hr^{-1} in HTXRD. Figure 5 shows TG–DTA curves of α-PdP_2O_6 measured respectively at extremely different heating rates of 20°C min^{-1} = 1200°C hr^{-1} and 2°C min^{-1} = 120°C hr^{-1}. In the faster heating conditions (Fig. 5a), the DTA curve exhibits one clear peak around 900°C, but the TG curve indicates a negligibly small weight loss. That is, the α phase transforms promptly around 900°C into the β phase with

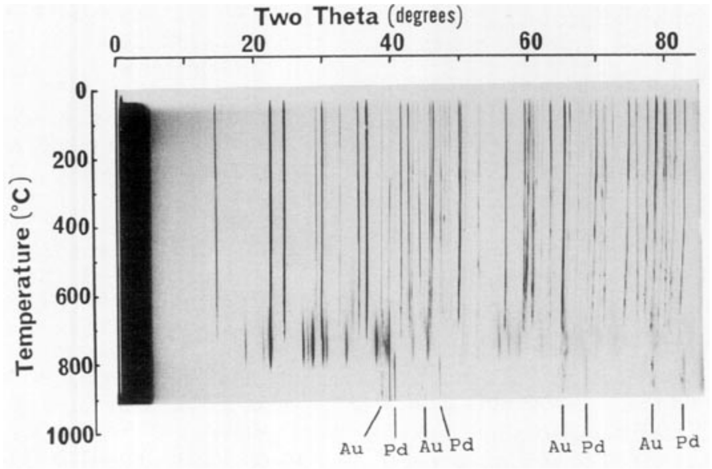

FIG. 4. High-temperature XRPD pattern of PdP_2O_6 using Cu $K\alpha$ radiation.

little decomposition at the rate of 20°C min^{-1}. On the other hand, Fig. 5b shows that the slower heating conditions induces the gradual decomposition at a temperature above 800°C, and that the DTA curve indicates two peaks, one broad and another small one, around 900°C; in light of the HTXRD results, the former broad peak is probably ascribable to both the α and β transition and the subsequent sluggish decomposition of the β phase, and the latter peak to the sudden decomposition of all the β phase. The results of Figs. 3, 4, and 5 show the dependence of the α-to-β transition on heating rate in the same manner as the intermediate metastable phase of Bi_2MoO_6 (*17*).

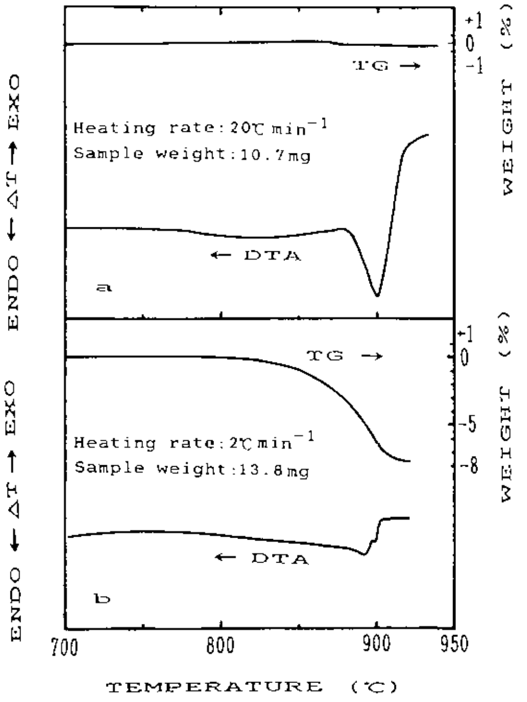

FIG. 5. TG–DTA curves of PdP_2O_6 for heating processes at a rate of (a) 20°C min^{-1} and (b) 2°C min^{-1}.

Furthermore, since DTA does not distinguish between thermodynamically stable and metastable phases, and since the above TG–DTA results of the dependence of the transition temperature on heating rates suggest the α phase seems to be metastable, the relative stability between the α and the β phases was checked by the isothermal heat treatments: each phase put individually into a separate gold crucible was simultaneously heated below 700°C. The starting β-PdP_2O_6 including a very small quantity of Pd was prepared beforehand by quenching. As a result, for example, the heating at 607°C for 87 hr brought the starting α-PdP_2O_6 into β-PdP_2O_6 completely; however, the starting β-PdP_2O_6 was kept unchanged. The subsequent heating at 637°C for 64 hr led to the same results. Despite of the long heat treatments, we could not detect any weight change in the samples before and after heating. In addition, when only the β-PdP_2O_6 was kept at 503°C for 280 hr, a recognizable change was merely an oxidation of Pd metal impurity. These results indicate that the β phase is more stable than the α phase at lower temperatures than 900°C, and that the reversible transition shown in Fig. 3a may be a seeming character. Thus, we can conclude that β-PdP_2O_6 is a stable phase. On the other hand, from both the present results and the above TG–DTA results, we infer that α-PdP_2O_6 might be a metastable phase.

Not only PdO (*18*) but also some mixed palladium oxides (*10, 11, 19*) show good electrical conductivity at room temperature; they are all semiconductors. Thus, we expect that the present compound, PdP_2O_6, has such a property. However, PdP_2O_6 seems to be an insulator as long as we checked it.

Acknowledgments

One of the authors (A. Watanabe) is grateful to the École Nationale Supérieure de Chimie de Lille and the Arai Science and Technology Foundation for their financial support.

References

1. H. Sabrowsky and R. Hoppe, *Naturwissenschaften* **53,** 501 (1966).
2. H.-D. Wasel-Nielen and R. Hoppe, *Z. Anorg. Allg. Chem.* **375,** 209 (1970).
3. O. Muller and R. Roy, *Adv. Chem. Ser.* **98,** 28 (1971).
4. B. N. Ivanov-Emin, L. P. Petrishcheva, B. E. Zaitsev, V. I. Ivlieva, A. S. Izmailovich, and V. P. Dolganev, *Russ. J. Inorg. Chem.* **29,** 1169 (1984).
5. C. L. McDaniel and S. J. Schneider, *J. Res. Nat. Bur. Stand. Sect. A* **72,** 27 (1968).
6. B. G. Kakhan, V. B. Lazarev, and I. S. Shaplygin, *Russ. J. Inorg. Chem.* **27,** 1180 (1982).
7. R. D. Shannon, D. B. Rogers, and C. T. Prewitt, *Inorg. Chem.* **10,** 713 (1971).
8. C-M. Niu, P. H. Rieger, K. Dwight, and A. Wold, *J. Solid State Chem.* **86** 175 (1990).
9. H. Meyer and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **442,** 26 (1978).
10. V. B. Lazarev and I. S. Shaplygin, *Zh. Neorg. Khim.* **24,** 885 (1979).
11. V. B. Lazarev and I. S. Shaplygin, *Russ. J. Inorg. Chem.* **19,** 1305 (1974).
12. P. Conflant, J.-C. Boivin, and D. Thomas, *Rev. Chim. Miner.* **14,** 249 (1977).
13. K. K. Palkina, S. I. Maksimova, A. V. Lavrov, and N. A. Chalisova, *Sov. Phys. Dokl.* **23,** 691 (1978).
14. J. W. Visser, *J. Appl. Crystallogr.* **2,** 89 (1969).
15. S. Rundqvist and L.-O. Gullman, *Acta Chem. Scand.* **14,** 2246 (1960).
16. L.-O. Gullman, *J. Less-Common Met.* **11,** 157 (1966).
17. A. Watanabe and H. Kodama, *J. Solid State Chem.* **35,** 240 (1980).
18. H. L. Tuller, *in* "Ceramic Materials for Electronics," Chap 8, p. 441, Dekker, New York and Basel (1986).
19. D. B. Rogers, R. D. Shannon, C. T. Prewitt, and J. L. Gillson, *Inorg. Chem.* **10,** 723 (1971).