Phase Relations Between Palladium Oxide and the Rare Earth Sesquioxides in Air

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The equilibrium phase relations were determined in an air environment between PdO and each of the following: La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3. In air PdO dissociates to Pd metal at 800 °C. The dissociation of PdO is apparently a reversible process. The Nd_2O_3-PdO and Sm_2O_3-PdO systems were studied in detail inasmuch as they typified several of the Ln_2O_3-PdO systems. Three compounds, $2Nd_2O_3 \cdot PdO$, metastable $Nd_2O_3 \cdot PdO$, Nd_2O_3 2PdO occur in the Nd_2O_3-PdO system. The 2:1, 1:1, and 1:2 compounds, of unknown symmetry, dissociate or decompose at 1135, 860, and 1085 °C, respectively. The 2:1 compound dissociates to the solid phases, Nd_2O_3 and Pd. No further reactions occur between Nd_2O_3 and Pd up to 1300 °C. Three compounds, 2:1, metastable 1:1, and 1:2 occur in the Sm_2O_3-PdO and Eu_2O_3-PdO systems. Two compounds, 2:1 and 1:2 occur in the La_2O_3-PdO system. Other compounds detected were the 1:1 and 1:2 in the Gd_2O_3-PdO system and the metastable 1:1 in the Dy_2O_3-PdO system. Each of these compounds subsequently dissociated upon heating. No apparent reaction occurred between PdO and either Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, or Lu_2O_3.

Key Words: Dissociation, equilibrium, Ln_2O_3:PdO compounds, Ln_2O_3-PdO systems, phase relations.

1. Introduction

This study is part of a program to determine what effect, if any, various Pt-group metals have upon the metal oxides when heated together in an oxidizing environment. Several of the Pt-group metals have a strong tendency to oxidize when heated in air at moderate temperatures. At higher temperatures in air, these oxides volatilize and dissociate to one solid phase, the metal. Previous work [1, 2] [1] has shown that iridium dioxide reacts with other refractory oxides at moderate temperatures. Considering the fact that several of the Pt-group metals are used as secondary standards on the International Practical Temperature Scale (IPTS)[2] [3] as well as container materials, it is important to better understand the behavior of these metals in an air environment. This work presents the results of an investigation of the phase relations between palladium oxide (PdO) and the rare earth sesquioxides (Ln_2O_3) in air.

The Nd_2O_3-PdO and Sm_2O_3-PdO systems were studied in detail and were found to be quite similar in many respects. The present study was broadened somewhat to include PdO in combination with each of the following sesquioxides: La_2O_3, Eu_2O_3, Gd_2O_3,

Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3. A limited study seemed adequate for these ten systems due to their similarity with the Nd_2O_3-PdO system or to their apparent lack of reaction.

Palladium (Pd) oxidizes to PdO when heated in air at moderate temperatures. Palladium oxide rather than Pd metal was selected as one end member of the system, because the latter oxidizes too slowly in air. By utilizing PdO, an approach to equilibrium could be achieved more readily. The study would still reflect, however, the behavior in air of Pd metal in combination with other oxides.

Palladium has the structure of face-centered cubic copper with $a = 3.8898$ Å [4]. The freezing point of Pd is 1552 °C, a value which is given as a secondary reference point on the International Practical Temperature Scale of 1948. The structure of PdO has been described on the basis of a tetragonal unit cell with $a = 3.0434$ Å and $c = 5.337$ Å [5]. Upon heating, PdO has been reported to dissociate to Pd and a vapor phase at 870 °C in 1 atm oxygen [6].

The stable modification of neodymium sesquioxide (Nd_2O_3) has the hexagonal A type ($a = 3.831$ Å, $c = 5.999$ Å) [7] rare earth oxide structure at the temperatures investigated in this study. Samarium sesquioxide (Sm_2O_3) has been reported to crystallize in the C form at low temperatures and to invert di-

rectly and irreversibly in air to the B type monoclinic structure at about 950 °C [8]. The unit cell dimensions of B type Sm_2O_3 were reported by Roth and Schneider [8] as $a = 14.16$ Å, $b = 3.621$ Å, $c = 8.84$ Å, and $\beta = 100.05°$. The melting points of Nd_2O_3 and Sm_2O_3 have been reported to be over 2000 °C [9].

2. Materials

All starting materials employed in this study had a purity of 99.7 percent or greater. With the exception of PdO and Y_2O_3, the oxides were used in other investigations and their spectrochemical analyses were reported previously [10, 11]. The PdO and Y_2O_3 samples were found by general qualitative spectrochemical analysis [3] to have the following impurities:

PdO: 0.01–0.1%, Fe and Si;

    0.001–0.01% each Al, Ba, Ca, Cu, Mg, Pt, and Sr;

    < 0.001% each Ag, Mn, and Pb

Y_2O_3: 0.01–0.1%, Ca;

    0.001–0.01% each Al, Ho, Tm, and Yb;

    0.0001–0.001% each Cu, Fe, Lu, and Mg.

3. Experimental Procedure

Specimens were prepared from 0.4 g batches of various combinations of PdO and the rare earth oxides. Calculated amounts of each oxide, corrected for ignition loss, were weighed to the nearest milligram. Each batch was thoroughly hand mixed, placed in fused silica tubes (sealed at one end) and fired in a muffle furnace for a minimum of 18 hr at 770 °C and at 780 °C. Succeeding each heat treatment, the materials were thoroughly hand mixed and examined by x-ray diffraction techniques.

Following the preliminary heat treatments, portions of each batch were placed in the open silica tubes and fired in a platinum alloy wire-wound quench furnace at various temperatures for different periods of time. The specimen was air quenched by quickly pulling the tube from the furnace. Equilibrium was assumed to have been achieved when the x-ray pattern showed no change after successive heat treatments or when the data were consistent with the results from a previous set of experiments.

Sealed platinum tubes were employed as specimen containers for the experiments having prolonged heat treatments below the dissociation temperatures. Sealed tubes were utilized in an attempt to maintain composition and to obtain maximum reaction. The use of fused silica tubes instead of platinum was necessary because Pd, frequently found as a decom-

position product, readily reacts with platinum. On the other hand, the silica tube did not appear to influence or react with the various oxide samples.

Temperatures in the quench furnace were measured with a 100 percent Pt versus 90 percent Pt-10 percent Rh thermocouple. All reported temperatures pertaining to quench furnace data are considered accurate to within ±5 °C. The precision of the measurements was ±2 °C.

All specimens were examined by x-ray diffraction at room temperature using a high angle recording Geiger counter diffractometer and Ni-filtered Cu radiation.

4. Results and Discussion

4.1. Nd_2O_3-PdO and Sm_2O_3-PdO Systems in Air

The equilibrium phase diagram for the Nd_2O_3-PdO system in air is given in figure 1. The diagram was constructed from the data listed in table 1. The solid circles indicate the compositions and temperatures of the experiments conducted. It should be emphasized that figure 1 represents a composite of the Nd_2O_3-Pd and Nd_2O_3-PdO systems in the Nd-Pd-Oxygen ternary. At the lower temperatures, the oxygen content of the specimens closely conforms to the compositions represented by the pseudobinary system, Nd_2O_3-PdO. At the higher temperatures, the compositions of the solid phases change by an apparent oxygen loss to those indicated by the Nd_2O_3-Pd join. Figure 1 is a pseudobinary representation of a portion of the ternary system. This method of illustration has been employed by a number of investigators [1, 12].

Palladium oxide was found to dissociate to Pd metal and presumably oxygen at 800 ±5 °C in air at atmospheric pressure. This value compares favorably with the data (870 °C in one atmosphere oxygen) given by Bell et al., in their study of the Pd-oxygen system [6]. The dissociation of PdO is a reversible process. Palladium oxide was first heated above 800 °C, until only Pd was present. The same material was then reheated at 790 °C and the x-ray data indicated only PdO.

Raub [13] reports that palladium takes up appreciable quantities of oxygen into solid solution when the metal is heated in oxygen at 1200 °C. Raub's conclusions were based on weight gain data with no x-ray results given. Chaston [14] concluded the weight gain of Pd observed by Raub was due to the oxidation of base metal impurities. The x-ray diffraction data obtained in the present study show no indication of solid solution of oxygen in Pd, when heated in an air environment.

Three intermediate compounds, 2:1, 1:1, and 1:2 occur in the Nd_2O_3-PdO system. The stable 2:1 and 1:2 compounds dissociate to two solid phases and a vapor phase, presumably oxygen at 1135 and 1085 °C, respectively. The 1:1 phase was found to decompose at about 860 °C to the 2:1 and 1:2 compounds. In order
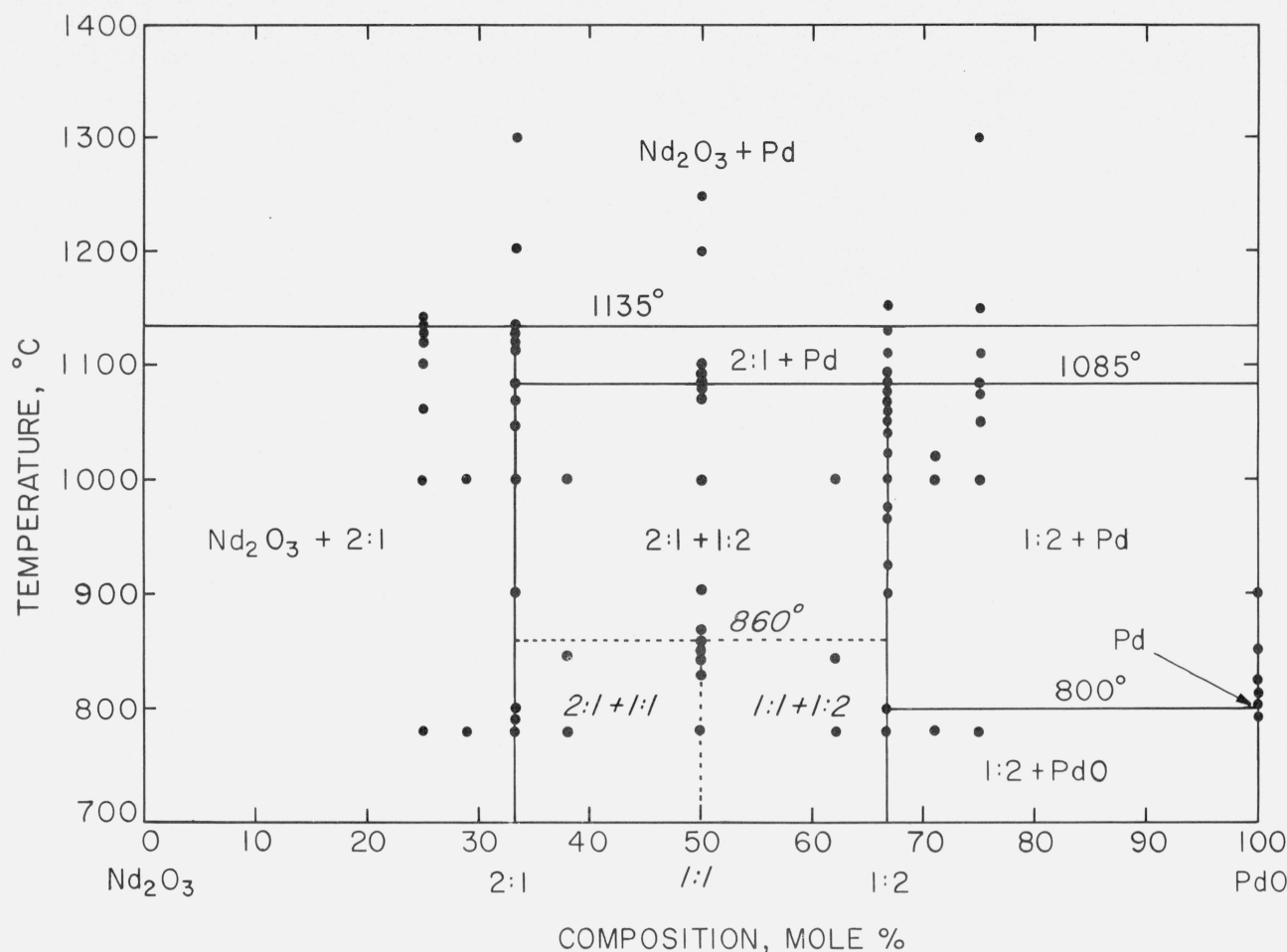
FIGURE 1. *Phase equilibrium diagram for the* Nd_2O_3-PdO *system in air.*
Dotted lines indicate metastable 1:1 compound and decomposition temperature. Italic lettering indicates metastable phase assemblages.
● —compositions and temperatures of experiments conducted.

TABLE 1. *Experimental data for compositions in the* Ln_2O_3-PdO *systems*

System	Composition	Heat treatment[a]		X-ray diffraction analyses[b]	Remarks
		Temp.	Time		
Nd_2O_3-PdO...............	mole % 75:25	°C 780	hr 18	$2:1 + Nd_2O_3 + 1:1$..................	Nonequilibrium.
		[c] 1000	18	$2:1 + Nd_2O_3$	
		[c] 1063	3	$2:1 + Nd_2O_3$	
		[c] 1103	2	$2:1 + Nd_2O_3$..................	Quenched in ice water.
		[d] 1125	2	$2:1 + Nd_2O_3$	
		[c] 1130	62	$2:1 + Nd_2O_3$..................	Quenched in ice water.
		[d] 1130	1.5	$2:1 + Nd_2O_3$	
		[d] 1135	1.5	$2:1 + Nd_2O_3 + Pd$..................	Nonequilibrium.
		[d] 1140	2	$2:1 + Nd_2O_3 + Pd$..................	Nonequilibrium.
	71:29	780	22	$2:1 + Nd_2O_3 + 1:1$..................	Nonequilibrium.
		[c] 1000	78	$2:1 + Nd_2O_3$	
	66.6:33.3	780	18	$2:1 + Nd_2O_3 + 1:1$..................	Nonequilibrium.
		790	18	$2:1 + Nd_2O_3 + 1:1$..................	Nonequilibrium.
		800	20	$2:1 + Nd_2O_3 + 1:1$..................	Nonequilibrium.
		900	71	$2:1 + Nd_2O_3$..................	Nonequilibrium.[e]
		[c] 1000	18	$2:1$	
		[c] 1050	504	$2:1$	
		[c] 1070	2	$2:1$..................	Quenched in ice water.

System	Composition	Heat treatment[a]		X-ray diffraction analyses[b]	Remarks
		Temp.	Time		
	mole %	*°C*	*hr*		
		[c] 1085	2	2:1	
		1115	20	2:1 + Nd_2O_3 + Pd....................	Nonequilibrium; reheat of 1205 °C specimen.
		[d] 1115	2	2:1	
		[d] 1125	2	2:1	
		[d] 1130	2	2:1	
		[d] 1135	2	2:1 + Pd + Nd_2O_3....................	Nonequilibrium.
		1205	1	Nd_2O_3 + Pd	
		1300	1	Nd_2O_3 + Pd	
	62:38	780	18	2:1 + 1:1 + Nd_2O_3....................	Nonequilibrium.
		845	20	2:1 + 1:1	
		[c] 1000	78	2:1 + 1:2	
	50:50	780	18	1:1 + Nd_2O_3 + PdO................	Nonequilibrium.
		[c] 830	20	1:1.....................................	Quenched in ice water.
		842	15	1:1 + Nd_2O_3	Nonequilibrium.[e]
		845	144	2:1 + 1:2.............................	Reheat of 902 °C specimen.
		855	3	1:1	
		860	2	1:1 + 1:2.............................	Nonequilibrium.
		865	2	1:1 + 1:2 + 2:1......................	Nonequilibrium.
		902	18	2:1 + 1:2	
		[c] 1000	18	2:1 + 1:2	
		[c] 1070	78	2:1 + 1:2..............................	Quenched in ice water.
		1080	2	2:1 + 1:2	
		1085	2	2:1 + 1:2 + Pd.......................	Nonequilibrium.
		1090	2	2:1 + 1:2 + Pd.......................	Nonequilibrium.
		1100	4	2:1 + Pd + 1:2.......................	Nonequilibrium.
		1200	18	Nd_2O_3 + Pd	
		1250	2	Nd_2O_3 + Pd	
	38:62	780	21	1:2 + 1:1 + PdO.....................	Nonequilibrium.
		[c] 845	20	1:2 + 1:1.............................	Quenched in ice water.
		[c] 1000	78	1:2 + 2:1	
	33.3:66.6	780	18	1:2 + 1:1 + PdO.....................	Nonequilibrium.
		[c] 800	120	1:2	
		900	2	1:2	
		925	2	1:2	
		970	120	1:2 + Nd_2O_3 + Pd....................	Nonequilibrium; reheat 1150 °C specimen.
		975	2	1:2	
		[c] 1000	18	1:2.....................................	Quenched in ice water.
		[c] 1000	48	1:2	
		1025	2	1:2	
		1040	2	1:2	
		[c] 1050	110	1:2	
		[d] 1060	2	1:2	
		[d] 1070	3	1:2	
		[d] 1080	2	1:2	
		[d] 1085	2	1:2 + Pd + 2:1......................	Nonequilibrium.
		[d] 1090	1.5	1:2 + Pd + 2:1......................	Nonequilibrium.
		1110	18	2:1 + Pd	
		1130	2	2:1 + Pd	
		1150	1	Nd_2O_3 + Pd	
	29:71	780	21	1:2 + 1:1 + PdO.....................	Nonequilibrium.
		1000	3	1:2 + Pd	
		1020	1.5	1:2 + Pd	
	25:75	780	18	1:2 + 1:1 + PdO.....................	Nonequilibrium.
		1000	3	1:2 + Pd	
		1050	1.5	1:2 + Pd	
		1075	2	1:2 + Pd	
		1085	3	Pd + 2:1 + 1:2......................	Nonequilibrium.
		1110	2	Pd + 2:1	
		1150	2	Pd + Nd_2O_3	
		1300	1.5	Pd + Nd_2O_3	
	0:100	780	18	PdO	

See footnotes at end of table, p. 33.

System	Composition	Heat treatment[a]		X-ray diffraction analyses[b]	Remarks
		Temp.	Time		
	mole %	°C	hr		
		795	2	PdO	
		800	2	PdO + Pd............................	Nonequilibrium.
		810	4	Pd	
		825	1.5	Pd	
		850	3	Pd	
		900	3	Pd	
		1200	2	Pd	
Sm_2O_3-PdO..............	75:25	780	18	2:1 + Sm_2O_3 + 1:1................	Nonequilibrium.
		[c] 1103	3	2:1 + Sm_2O_3......................	Quenched in ice water.
		1140	1	2:1 + Sm_2O_3 + Pd................	Nonequilibrium.
	66.6:33.3	780	19	2:1 + Sm_2O_3 + 1:1................	Nonequilibrium.
		790	120	2:1 + Sm_2O_3 + PdO..............	Nonequilibrium; reheat 1200 °C specimen.
		[c] 1000	20	2:1 + Sm_2O_3......................	Nonequilibrium.[e]
		[c] 1000	24	2:1	
		[d] 1100	2.5	2:1	
		[d] 1110	2	2:1	
		[d] 1115	2	2:1 + Pd + Sm_2O_3	Nonequilibrium.
		[d] 1125	1.5	2:1 + Pd + Sm_2O_3	Nonequilibrium.
		1200	2	Sm_2O_3 + Pd	
	50:50	780	21	1:1 + 1:2 + Sm_2O_3	Nonequilibrium.
		800	144	2:1 + 1:2...........................	Reheat of 1000 °C specimen.
		[c] 830	20	1:1...................................	Quenched in ice water.
		830	5	1:1	
		850	2	1:1...................................	Reheat of 830 °C 20 hr specimen.
		880	2.5	1:1...................................	Reheat of 830 °C 20 hr specimen.
		[c] 902	18	1:1...................................	Quenched in ice water.
		915	1.5	1:1...................................	Reheat of 830 °C 20 hr specimen.
		935	2	1:1...................................	Reheat of 830 °C 20 hr specimen.
		940	2	1:1 + 1:2 + 2:1......................	Nonequilibrium; reheat of 830 °C 20 hr specimen.
		1000	20	2:1 + 1:2	
		1100	3	2:1 + Pd + 1:2......................	Nonequilibrium.
		1200	2.5	Sm_2O_3 + Pd	
	33.3:66.6	780	21	1:2 + 1:1 + Sm_2O_3................	Nonequilibrium.
		790	120	1:2 + PdO + Sm_2O_3..............	Nonequilibrium; reheat of 1150 °C specimen.
		[c] 800	54	1:2...................................	Quenched in ice water.
		[c] 1000	20	1:2	
		[d] 1055	2.5	1:2	
		[d] 1060	2	1:2 + Pd............................	Nonequilibrium.
		[d] 1075	2	1:2 + Pd + Sm_2O_3..............	Nonequilibrium.
		1150	1	Sm_2O_3 + Pd	
	25:75	780	21	1:2 + PdO + Sm_2O_3..............	Nonequilibrium.
		1050	1.5	1:2 + Pd............................	Quenched in ice water.
La_2O_3-PdO...............	66.6:33.3	780	20	La_2O_3 + PdO + 1:2..............	Nonequilibrium.
		[c] 1000	18	2:1 + La_2O_3......................	Nonequilibrium.[e]
		[c] 1000	72	2:1 + La_2O_3......................	Nonequilibrium.[e]
		[c] 1070	66	2:1...................................	Quenched in ice water.
		1150	2	2:1...................................	Reheat of 1070 °C specimen.
		1160	3	2:1...................................	Reheat of 1070 °C specimen.
		1185	2	2:1...................................	Reheat of 1070 °C specimen.
		1190	2	2:1 + La_2O_3 + Pd................	Nonequilibrium; reheat of 1070 °C specimen.
	50:50	780	20	La_2O_3 + PdO + 1:2..............	Nonequilibrium.
		850	144	2:1 + 1:2	
		[c] 1000	18	2:1 + 1:2	
		1000	144	2:1 + 1:2 + Pd......................	Nonequilibrium; reheat of 1310 °C specimen.
		1310	2	La_2O_3 + Pd + $La(OH)_3$...........	La_2O_3 commonly hydrates at room temperature.

System	Composition	Heat treatment[a]		X-ray diffraction analyses[b]	Remarks
		Temp.	Time		
	mole %	°C	hr		
	33.3:66.6	780	20	La_2O_3 + PdO + 1:2.................	Nonequilibrium.
		[c]1000	18	1:2.............................	Quenched in ice water.
		[c]1070	66	1:2	
		[d]1085	2	1:2	
		[d]1090	2	1:2	
		[d]1100	2.5	1:2	
		[d]1105	2	1:2 + Pd.................	Nonequilibrium.
		[d]1110	2	1:2 + Pd + 2:1.............	Nonequilibrium.
		[d]1140	2	2:1 + Pd.................	Nonequilibrium.
Eu_2O_3-PdO..............	66.6:33.3	780	18	Eu_2O_3 + PdO + 1:1 + 2:1	Nonequilibrium.[e]
		[c]900	10	2:1 + Eu_2O_3.............	Nonequilibrium.[e]
		[c]950	48	2:1 + Eu_2O_3.............	Nonequlibrium[e]; quenched in ice water.
		[c]1050	36	2:1 + Eu_2O_3.............	Nonequilibrium.[e]
		1085	2	2:1 + Eu_2O_3 + Pd.............	Nonequilibrium[e]; reheat of 1050 °C specimen.
		1090	2	2:1 + Eu_2O_3 + Pd.............	Nonequilibrium[e]; reheat of 1050 °C specimen.
		1095	2	2:1 + Eu_2O_3 + Pd.............	Nonequilibrium[e]; reheat of 1050 °C specimen.
	50:50	780	18	Eu_2O_3 + 1:1 + PdO.............	Nonequilibrium.
		800	144	1:2 + 2:1 + Eu_2O_3.............	Nonequilibrium; reheat of 1000 °C 20 hr specimen.
		[c]850	67	1:1 + Eu_2O_3.............	Nonequilibrium.[e]
		[c]900	168	1:1 + Eu_2O_3.............	Nonequilibrium.[e]
		960	2	1:1 + Eu_2O_3.............	Nonequilibrium[e]; reheat of 900 °C specimen.
		980	2	1:1 + Eu_2O_3.............	Nonequilibrium.[e]
		985	2	1:1 + Eu_2O_3 + 1:2.............	Nonequilibrium.
		990	2	1:1 + Eu_2O_3 + 1:2.............	Nonequilibrium.
		1000	20	1:2 + 2:1 + Eu_2O_3.............	Nonequilibrium.
		1000	144	1:2 + 2:1 + Eu_2O_3.............	Nonequilibrium; reheat of 1250 °C specimen.
		1250	2	Eu_2O_3 + Pd	
	33.3:66.6	780	18	1:2 + PdO + Eu_2O_3 + 1:1	Nonequilibrium.
		[c]900	10	1:2 + Eu_2O_3.............	Nonequilibrium[e]; quenched in ice water.
		[c]950	96	1:2	
		1040	2	1:2.............................	Reheat of 950 °C specimen.
		1045	2	1:2 + Pd + 2:1.............	Nonequilibrium; reheat of 950 °C specimen.
		1050	2	1:2 + Pd + 2:1.............	Nonequilibrium; reheat of 950 °C specimen.
		1055	2	1:2 + Pd + 2:1.............	Nonequilibrium; reheat of 950 °C specimen.
Gd_2O_3-PdO..............	66.6:33.3	780	18	Gd_2O_3 + 1:1 + PdO.............	Nonequilibrium.
		[c]900	144	1:1 + Gd_2O_3	
	50:50	780	18	Gd_2O_3 + 1:1 + PdO.............	Nonequilibrium.[e]
		[c]900	20	1:1 + Gd_2O_3.............	Nonequilibrium.[e]
		900	72	1:2 + Gd_2O_3 + Pd.............	Nonequilibrium; reheat of 1100 °C specimen.
		1000	2.5	1:1 + Gd_2O_3.............	Nonequilibrium[e]; reheat of 900 °C 20 hr specimen.
		1005	2	1:1 + Gd_2O_3 + 1:2.............	Nonequilibrium; reheat of 900 °C 20 hr specimen.
		1010	3	1:1 + Gd_2O_3 + 1:2.............	Nonequilibrium; reheat of 900 °C 20 hr specimen.
		1020	2	1:1 + Gd_2O_3 + 1:2.............	Nonequilibrium; reheat of 900 °C 20 hr specimen.
		1040	2	Gd_2O_3 + Pd + 1:2.............	Nonequilibrium; reheat of 900 °C 20 hr specimen.
		1100	3	Gd_2O_3 + Pd	
	33.3:66.6	780	18	1:1 + 1:2 + Gd_2O_3.............	Nonequilibrium.
		[c]900	144	1:2 + Gd_2O_3.............	Nonequilibrium.[e]

See footnotes at end of table, p. 33.

System	Composition	Heat treatment[a]		X-ray diffraction analyses[b]	Remarks
		Temp.	Time		
	mole %	°C	hr		
		[c]950	28	1:2 + 1:1..............................	Nonequilibrium[e]; quenched in ice water.
		1015	2	1:2 + Gd_2O_3..........................	Nonequilibrium[e]; reheat of 950 °C specimen.
		1020	2	1:2 + Gd_2O_3..........................	Nonequilibrium[e]; reheat of 950 °C specimen.
		1025	2	1:2 + Gd_2O_3 + Pd...................	Nonequilibrium; reheat of 950 °C specimen.
		1030	2	1:2 + Gd_2O_3 + Pd...................	Nonequilibrium; reheat of 950 °C specimen.
		1035	2	1:2 + Gd_2O_3 + Pd...................	Nonequilibrium; reheat of 950 °C specimen.
		1040	2	1:2 + Pd + Gd_2O_3...................	Nonequilibrium; reheat of 950 °C specimen.
Dy_2O_3-PdO................	66.6:33.3	780	18	1:1 + PdO + Dy_2O_3.................	Nonequilibrium.
		850	67	1:1 + Dy_2O_3	
		[c]900	18	1:1 + Dy_2O_3..........................	Quenched in ice water.
		[c]1000	144	1:1 + Dy_2O_3	
	50:50	780	18	1:1 + Dy_2O_3 + PdO................	Nonequilibrium.
		[c]900	68	1:1 + Dy_2O_3..........................	Nonequilibrium.[e]
		790	120	Dy_2O_3 + PdO + Pd.................	Nonequilibrium; reheat of 1250 °C specimen.
		1000	144	Dy_2O_3 + Pd...........................	Reheat of 1250 °C specimen.
		1010	2	1:1 + Dy_2O_3..........................	Reheat of 900 °C specimen.
		1025	2	1:1 + Dy_2O_3..........................	Reheat of 900 °C specimen.
		1030	2	1:1 + Dy_2O_3 + Pd...................	Nonequilibrium; reheat of 900 °C specimen.
		1250	2	Dy_2O_3 + Pd	
	33.3:66.6	780	18	1:1 + PdO + Dy_2O_3.................	Nonequilibrium.
		[c]900	20	1:1 + Pd	
		1050	120	Pd + Dy_2O_3	
Ho_2O_3-PdO................	50:50	780	18	Ho_2O_3 + PdO	
		[c]790	20	Ho_2O_3 + PdO	
		800	2	Ho_2O_3 + PdO + Pd.................	Nonequilibrium.
		900	120	Ho_2O_3 + Pd	
Y_2O_3-PdO................	50:50	780	18	Y_2O_3 + PdO	
		[c]790	20	Y_2O_3 + PdO	
		900	120	Y_2O_3 + Pd	
		1000	144	Y_2O_3 + Pd	
Er_2O_3-PdO................	50:50	780	18	Er_2O_3 + PdO	
		[c]790	20	Er_2O_3 + PdO	
		900	120	Er_2O_3 + Pd	
Tm_2O_3-PdO	50:50	780	18	Tm_2O_3 + PdO	
		[c]790	18	Tm_2O_3 + PdO	
		900	120	Tm_2O_3 + Pd	
		1000	23	Tm_2O_3 + Pd	
Yb_2O_3-PdO	50:50	780	18	Yb_2O_3 + PdO	
		[c]790	18	Yb_2O_3 + PdO	
		900	120	Yb_2O_3 + Pd	
Lu_2O_3-PdO................	50:50	780	21	Lu_2O_3 + PdO	
		[c]790	18	Lu_2O_3 + PdO	
		900	68	Lu_2O_3 + Pd	
		1000	25	Lu_2O_3 + Pd	

[a] All specimens were heat treated at 770 °C, a minimum of 18 hr. Unless otherwise indicated, fused silica tubes (sealed at one end) were used for specimen containers and were air quenched.
[b] The phases identified are given in order of the relative amount present at room temperature.
[c] Sealed platinum tubes were used for specimen containers.
[d] Reheat of 1000 °C specimen.
[e] PdO probably lost by volatilization.

to establish the stability of the three compounds, appropriate mixtures were heated first above and then below their respective decomposition or dissociation temperatures. Only the 2:1 and 1:2 compounds re-formed from their decomposition products. Prolonged heat treatments (up to 6 days) failed to reform the 1:1 compound, indicating perhaps it is metastable phase that forms only on heating.

A literature search did not reveal any compounds structurally similar to the Nd_2O_3-PdO phases. The x-ray powder patterns of the compounds were not similar to those reported by Barry and Roy [15] for the 2:1, 1:1, and 1:2 rare earth oxide-calcium oxide compounds. The unindexed x-ray diffraction powder patterns for the three compounds found in the present study are given in table 2.

At temperatures above 800 °C the system no longer can be represented by the Nd_2O_3-PdO join. The system changes through dissociation and at 1135 °C becomes the true binary Nd_2O_3-Pd. Up to 1300 °C, Nd_2O_3 and Pd do not react in the solid state.

TABLE 2. *X-ray diffraction powder data for* Nd_2O_3-PdO *compounds*

(CuK$_\alpha$ radiation)[a]

$2Nd_2O_3 \cdot PdO$[b]		$Nd_2O_3 \cdot Pd$[c]		$Nd_2O_3 \cdot 2PdO$[b]	
d	I/I_0	d	I/I_0	d	I/I_0
3.2840	15	3.1895	17	4.2387	13
3.0064	100	2.8768	100	3.4568	12
2.8723	45	2.8280	60	3.2733	20
2.8643	81	2.0732	12	2.9303	28
2.8038	45	1.9980	33	2.8228	76
2.1401	21	1.9556	8	2.7792	41
2.0827	20	1.6715	18	2.5924	100
2.0170	8	1.6423	27	2.3178	71
1.9746	19	1.4393	7	2.1372	12
1.9313	12	1.4120	9	2.1185	10
1.7640	8	1.2641	5	2.0732	6
1.7199	9			2.0347	9
1.6888	12			2.0179	54
1.6800	22			1.8192	20
1.6628	4			1.7804	8
1.6137	11			1.7287	11
1.6019	11			1.6634	7
1.5784	10			1.6148	18
1.4342	6			1.5898	11
				1.5732	25
				1.5674	33
				1.5230	21
				1.4669	15
				1.4181	7
				1.3913	11
				1.3807	3
				1.2971	11
				1.2753	8
				1.2281	4
				1.1870	7

[a] d — interplanar spacing, I/I_0 — relative intensity.
[b] X-ray pattern obtained from specimen heat treated at 1000 °C for 18 hr.
[c] X-ray pattern obtained from specimen heat treated at 830 °C for 20 hr.

The equilibrium phase diagram for the Sm_2O_3-PdO system in air is given in figure 2. The pertinent data are listed in table 1. The diagram is similar to the Nd_2O_3-PdO system in many respects in that three intermediate compounds 2:1, metastable 1:1, and 1:2 also occur. These phases dissociate or decompose at 1115, 940, and 1060 °C, respectively.

4.2. Other Ln_2O_3-PdO Systems in Air

Mixtures were prepared from PdO and each of the following sesquioxides: La_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3. The phase equilibrium diagrams for the various Ln_2O_3-PdO systems in air are given in figure 3. The experimental data are tabulated in table 1. It is evident that the Nd_2O_3-PdO system is representative in a general way of the other Ln_2O_3-PdO systems. The La_2O_3-PdO diagram indicates the occurrence of the 2:1 and the 1:2 compounds. The 1:1 compound was not detected. Three compounds, 2:1, metastable 1:1, and 1:2 occur in the Eu_2O_3-PdO system. The 1:2 and metastable 1:1 compounds occur in the Gd_2O_3-PdO system. The $2Gd_2O_3 \cdot PdO$ compound was not detected. In the Dy_2O_3-PdO system, only the metastable 1:1 compound was detected.

The remaining systems of either Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, or Lu_2O_3 with PdO are rather simple and straightforward inasmuch as there was no detectable reaction between end members in the solid state. The diagrams indicate only the dissociation of PdO, the point at which the system reverts to the true Ln_2O_3-Pd system.

Table 3 summarizes the results obtained in this study. Listed are the systems investigated, size of the rare earth cation, and the dissociation temperatures of the Ln_2O_3-PdO compounds. The dissociation temperatures of the 2:1 compounds decrease as the size of the rare earth cation decreases. The 1:2 compounds were found to dissociate in a similar manner. However, the decomposition temperatures of the metastable 1:1 compounds increase as the size of the rare earth cation decreases. As expected, the Ln_2O_3-PdO compounds with the same molecular ratio appear to have similar x-ray patterns. The patterns indicate appropriate shift in d-spacings to account for difference in ionic size of the rare earth cations.

It should be noted that the proposed diagrams pertain only to the phase relations of the systems in an air environment at atmospheric pressure. Any change in oxygen pressure would change the equilibrium diagram. In an air environment, precaution should be taken when utilizing Pd metal in combination with some of the rare earth oxides, since the data indicate the tendency to form new phases.

4.3. Summary

Equilibrium phase diagrams for systems involving PdO and various rare earth oxides were determined in air. Selected mixtures in the systems were studied by x-ray diffraction techniques after various heat treatments. Palladium, in air, oxidizes to PdO at moderate temperatures. The dissociation temperature of PdO in air at atmospheric pressure was established at 800 ± 5 °C. This dissociation was found to be a reversible process. Palladium oxide reacts with a number of oxides to form binary compounds. The pseudobinary system Nd_2O_3-PdO exemplified the typical type of reaction and was studied in detail. Three compounds, $2Nd_2O_3 \cdot PdO$, $Nd_2O_3 \cdot PdO$ (meta-
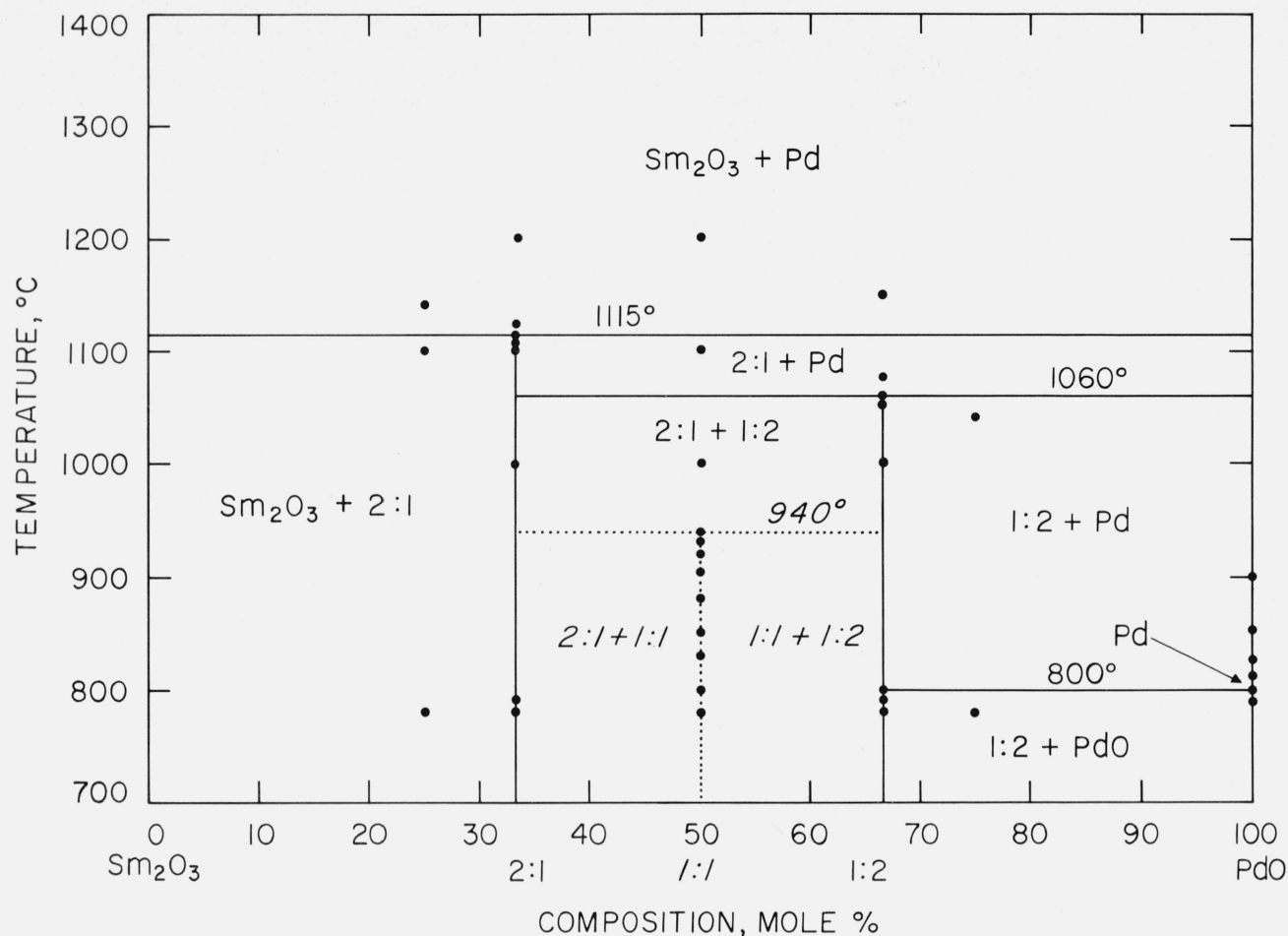
FIGURE 2. *Phase equilibrium diagram for the* Sm_2O_3-PdO *system in air.*
Dotted lines indicate metastable 1:1 compound and decomposition temperature. Italic lettering indicates metastable phase assemblages.
●—compositions and temperatures of experiments conducted.

stable), and $Nd_2O_3 \cdot 2PdO$ occur in the system. The 2:1, 1:1, and 1:2 compounds, of unknown symmetry dissociate or decompose at 1135, 860, and 1085 °C, respectively. Above 1135 °C the system corresponds to the Nd_2O_3-Pd binary system. No further reaction appears to take place between Nd_2O_3 and Pd up to 1300 °C. Similar type compounds were found to exist in other Ln_2O_3-PdO systems.

Three compounds, 2:1, 1:1, and 1:2, occur in the Sm_2O_3-PdO and Eu_2O_3-PdO systems. Two compounds,

2:1 and 1:2, occur in the La_2O_3-PdO system. Other compounds detected were the 1:1 and 1:2 in the Gd_2O_3-PdO system and the 1:1 in the Dy_2O_3-PdO system. Each of these compounds also dissociated upon heating at temperatures above the dissociation temperature of PdO. Mixtures of either Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, or Lu_2O_3 with PdO did not react in the solid state.
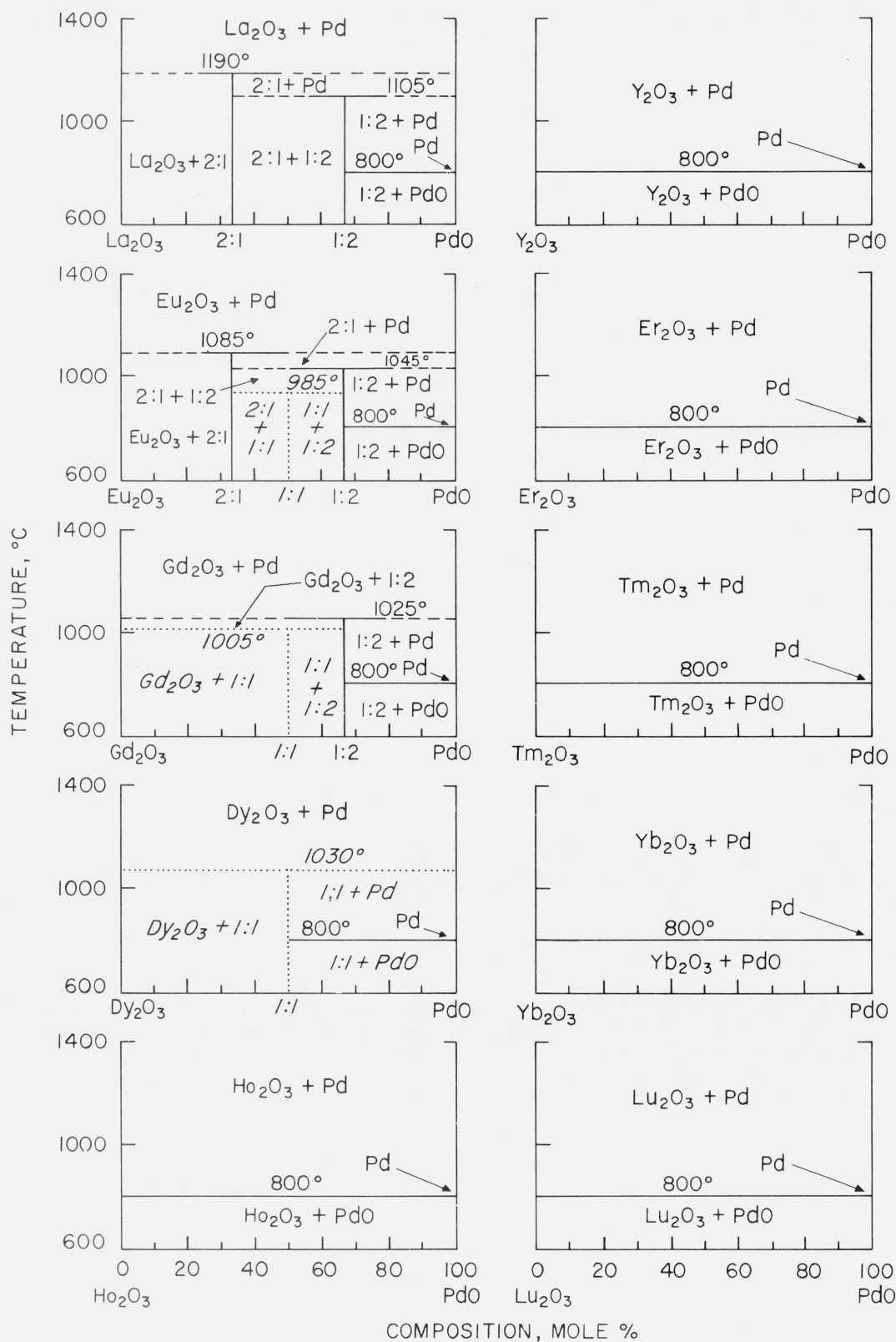
FIGURE 3. *Proposed phase equilibrium diagrams for various* Ln_2O_3-PdO *systems in air.*

For clarity experimental points are not included, see table 1 for exact compositions and temperatures studied. Dotted lines indicate metastable 1:1 compound and decomposition temperature. Italic lettering indicates metastable phase assemblages.

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SYSTEM	RADIUS OF Ln^{+3} Å	DISSOCIATION TEMP. °C		
		$2\,Ln_2O_3 \cdot PdO$	$Ln_2O_3 \cdot PdO$	$Ln_2O_3 \cdot 2\,PdO$
$La_2O_3 - PdO$	1.14	1190	——	1105
$Nd_2O_3 - PdO$	1.04	1135	(860)	1085
$Sm_2O_3 - PdO$	1.00	1115	(940)	1060
$Eu_2O_3 - PdO$	0.98	1085	(985)	1045
$Gd_2O_3 - PdO$	0.97	——	(1005)	1025
$Dy_2O_3 - PdO$	0.92	——	(1030)	——
$Ho_2O_3 - PdO$	0.91	——	——	——
$Y_2O_3 - PdO$	0.91	——	——	——
$Er_2O_3 - PdO$	0.89	——	——	——
$Tm_2O_3 - PdO$	0.87	——	——	——
$Yb_2O_3 - PdO$	0.86	——	——	——
$Lu_2O_3 - PdO$	0.85	——	——	——

TABLE 3. *Dissociation temperatures of* $Ln_2O_3 \cdot PdO$ *compounds.*

All radii of the rare earth cations taken from Arhens [16] with the exception of Y^{+3} which was taken from Roth and Schneider [8]. Parenthesis indicate decomposition temperatures of metastable 1:1 compounds.

5. References

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