JOURNAL OF SOLID STATE CHEMISTRY 95, 224–229 (1991)

LETTERS TO THE EDITOR

A Stabilized Tetragonal Phase of La_2O_3 in the La–Pd–O System*

T. N. GURU ROW, A. K. GANGULI, N. RANGAVITTAL,
RAM SESHADRI, AND C. N. R. RAO†

*Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India*

Communicated by J. M. Honig, July 8, 1991

Based on an X-ray diffraction study, it is shown that the product of the reaction between $PdCl_2$ and La_2O_3 in air or of the thermal decomposition of mixed La and Pd nitrates contains, besides some PdO, a novel tetragonal oxide phase (*P4/mmm*) which is best described as a stabilized tetragonal phase of La_2O_3 containing a small proportion of PdO.

Transition metal oxides of the formula A_2BO_4, possessing the K_2NiF_4 structure (*1*), have gained considerable importance because of superconductivity exhibited by oxygen-excess La_2CuO_4, $La_{2-x}Sr_xCuO_4$, and related cuprates (*2, 3*). Recent studies (*4–6*) have shown that the structural transitions and magnetic properties of La_2NiO_4 are similar to those of La_2CuO_4. Thus, oxygen-excess La_2NiO_4 and La_2CuO_4 are both biphasic, containing an antiferromagnetic stoichiometric phase. Furthermore, there are some indications of superconductivity in La_2NiO_4 and $La_{2-x}Sr_xNiO_4$ as well (*7*). We were interested in investigating the structure and properties of the Pd analog La_2PdO_4, since Pd is in the same group as Ni. An examination of the literature revealed that this compound had not been prepared in pure form. It appears that La_2PdO_4 and the other analogous rare-earth palladates cannot be prepared by the solid state reaction of the rare earth oxide with PdO. Ceramic preparations requiring relatively high temperatures seem inevitably to result in multiphasic mixtures containing La_4PdO_7, $La_2Pd_2O_5$, PdO, etc. (*8, 9*). Although Kakhan *et al.* (*8*) could not prepare pure La_2PdO_4, they listed several reflections from the powder X-ray diffraction pattern of a product mixture which they considered to be due to this palladate. Attfield and Ferey (*10*) have recently fitted these X-ray reflections to a unit cell with $a \simeq 4.12$ Å and $c \simeq 12.6$ Å in the *I4/mmm* space group, with a structure similar to that of Nd_2CuO_4 (*11*). In our efforts to prepare La_2PdO_4, we have obtained a new tetragonal phase in the La–Pd–O system which may be considered to be stabilized tetragonal La_2O_3 containing a small proportion of PdO. We describe this interesting finding in this letter.

---

* Contribution No. 654 from the Solid State and Structural Chemistry Unit.

† To whom correspondence should be addressed.

0022-4596/91 $3.00

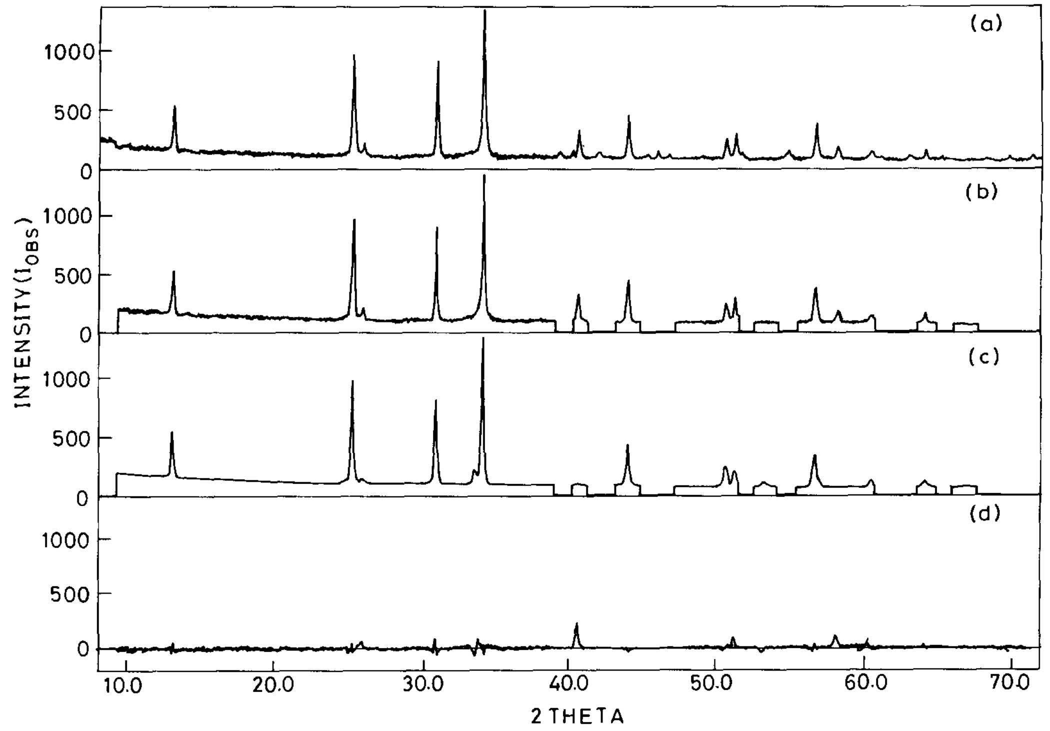

FIG. 1. (a) Powder X-ray diffraction pattern of the product of the $PdCl_2 + La_2O_3$ reaction containing a mixture of a new "palladate" and PdO; (b) X-ray data with PdO lines removed; (c) Calculated X-ray pattern; (d) Difference of (b) and (c).

We attempted to prepare La_2PdO_4 by two methods. The first method involved heating a thoroughly ground stoichiometric mixture of La_2O_3 and $PdCl_2$ at 1050 K in air for a period of 20 hr. The second method involved the thermal decomposition (1050 K, 20 hr) of a homogeneous mixture of metal nitrates obtained by digesting the oxides in concentrated HNO_3. The room temperature X-ray diffraction data were collected on a STOE automatic diffractometer using a linear PSD (2θ, 8–70° in steps of 0.02°). The X-ray diffraction pattern (Fig. 1) contained reflections due to a new oxide phase (which we considered to be due to La_2PdO_4) and impurity lines due to PdO. Neutron diffraction patterns also clearly showed reflections due to a new "palladate" phase and impurity lines due to PdO. The proportion of PdO in the mixture was estimated to be substantial (~30%).

The X-ray diffraction pattern of the "palladate" could be indexed on a primitive tetragonal cell with $a = 4.13$ Å and $c = 6.90$ Å with one formula unit per unit cell. We first considered the structure to be one where the La atoms are at $00z$ with $z = 0.25$ and the Pd atoms are at the origin, leading to one formula unit per unit cell (structure 1 with the space group $P4/mmm$ in Fig. 2). This structure is distinctly different from the K_2NiF_4 structure. The square-planar PdO_4 units are parallel to the ab plane and the La atom has a coordination of eight. The Pd–O and La–O distances are 2.06 and 2.68 Å, respectively. The $P4/mmm$ structure can be related to the $I4/mmm$ structure of La_2PdO_4 of Attfield and Ferey (*10*). In the latter, La

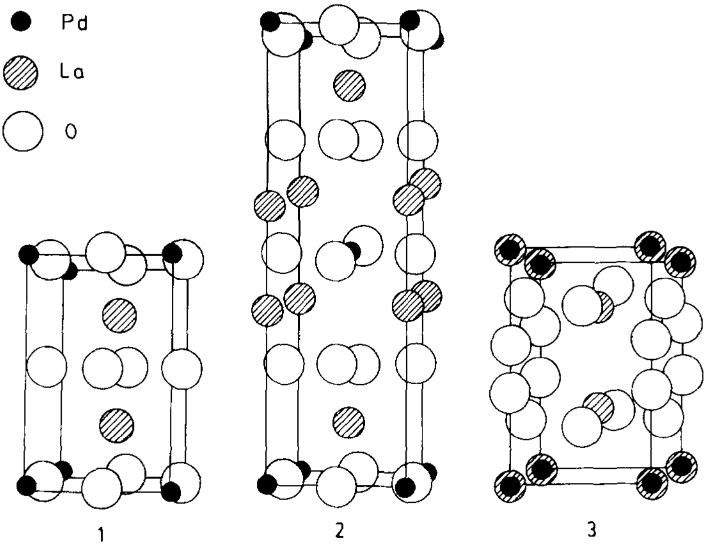

FIG. 2. Crystal structure of lanthanum palladate: (1) $P4/mmm$ of La_2PdO_4; (2) $I4/mmm$, La_2PdO_4; (3) stabilized tetragonal La_2O_3, $P4/mmm$.

atoms are at $z = 0.351$ (structure 2 in Fig. 2) and the unit cell contains two formula units. The two structures are related by the following simple matrix transformation:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1.8 \end{pmatrix}.$$

The observed X-ray diffraction pattern of the "palladate" could not be simulated satisfactorily by the Rietveld method on the basis of structure 1 (Fig. 2). The simulated pattern showed a fairly intense (100) reflection, not present in the observed pattern. The (100) reflection could be completely eliminated only when a large deficiency of La was incorporated (which is unlikely) and when La was also disordered. This seemed unreasonable since what is expected is a deficiency of Pd rather than of La. In light of these observations, it appeared to us rather curious that the tetragonal unit cell dimensions ($a = 4.13$ and $c = 6.89$ Å) found by us are close to the cell dimensions of La_2BeO_4 (β-form of La_2O_3–BeO) as reported

TABLE I

X-RAY DIFFRACTION DATA FOR STABILIZED TETRAGONAL PHASE OF La_2O_3 CONTAINING SOME PdO

h	k	l	M	2θ	FWHM	I_{obs}	I_{calc}
0	0	1	2	12.823	0.195	96.47	91.87
1	0	0	4	21.495	0.204	1.59	1.24
1	0	1	8	25.108	0.210	227.38	226.99
0	0	2	2	25.809	0.211	21.54	10.28
1	1	0	4	30.583	0.219	191.12	195.43
1	1	1	8	33.285	0.225	39.24	27.54
1	0	2	8	33.830	0.226	378.78	348.20
1	1	2	8	40.435	0.241	66.52	3.93
2	0	0	4	43.798	0.250	94.38	110.16
2	1	0	8	49.290	0.265	3.34	0.31
1	1	3	8	50.472	0.269	53.12	53.50
2	1	1	16	51.149	0.271	62.15	41.87
0	0	4	2	53.059	0.277	7.53	14.52
2	1	2	16	56.463	0.289	122.04	97.96
1	0	4	8	57.897	0.294	17.72	0.07
2	0	3	8	60.175	0.302	40.58	22.84
2	2	0	4	63.668	0.315	27.30	21.19

Note. Space group: $P4/mmm$; cell constants: $a = 4.131$ Å, $c = 6.898$ Å.

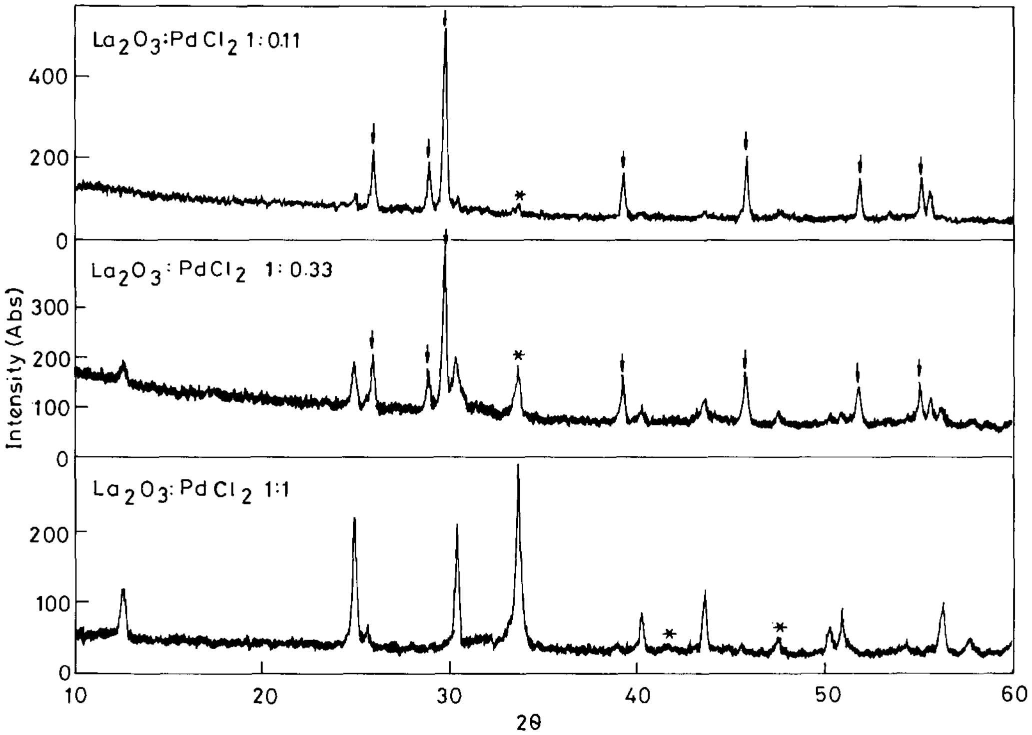

FIG. 3. X-ray diffraction patterns of products of the reaction between La_2O_3 and $PdCl_2$. Arrows indicate unreacted La_2O_3 lines and asterisks indicate PdO lines.

in the literature (*12*). It seemed as if the presence of Be or Pd made no difference to the structure. As a considerable amount of PdO remained in our preparations, it seemed to us that what we had prepared was an unusual stabilized tetragonal form of La_2O_3, in which a small proportion of PdO could be present.

We have examined whether it is possible essentially to account for the observed X-ray diffraction pattern, especially for the absence of the 100 reflection, by a $P4/mmm$ phase of La_2O_3. We could generate such a structure of pure La_2O_3 with respectable R values: $R(p) = 0.126$, $R(wp) = 0.159$, $R(I, hkl) = 0.189$. Refinements were carried out on the X-ray diffraction data of the "palladate" (minus the PdO lines). All the temperature factors (U_{iso}) of the heavy atoms were refined, but constrained to have the same value, while those on the oxygen atoms were held fixed at $U_{iso} = 0.06$ Å^2. The refined occupancies suggest that the second oxygen site O2 is alternately occupied ($n = 0.55$). The overall occupancy of La atoms was constrained to 2.0 and subsequent refinements led to an occupancy of 0.20 on the Pd sites. The agreement was considerably improved by incorporating a small proportion of Pd at one of the La sites (about 20% PdO) as shown in Fig. 1. The composition works out to be roughly $La_2Pd_{0.2}O_{3.2}$; increasing the PdO content to ~50% resulted in poorer fits. This model could be refined to $R(p) = 0.078$, $R(wp) = 0.126$, and $R(I, hkl) = 0.164$ (Table I). This structure has two lanthanum sites, one La at the origin, and another at 000.28. Structure 3 in Fig. 2

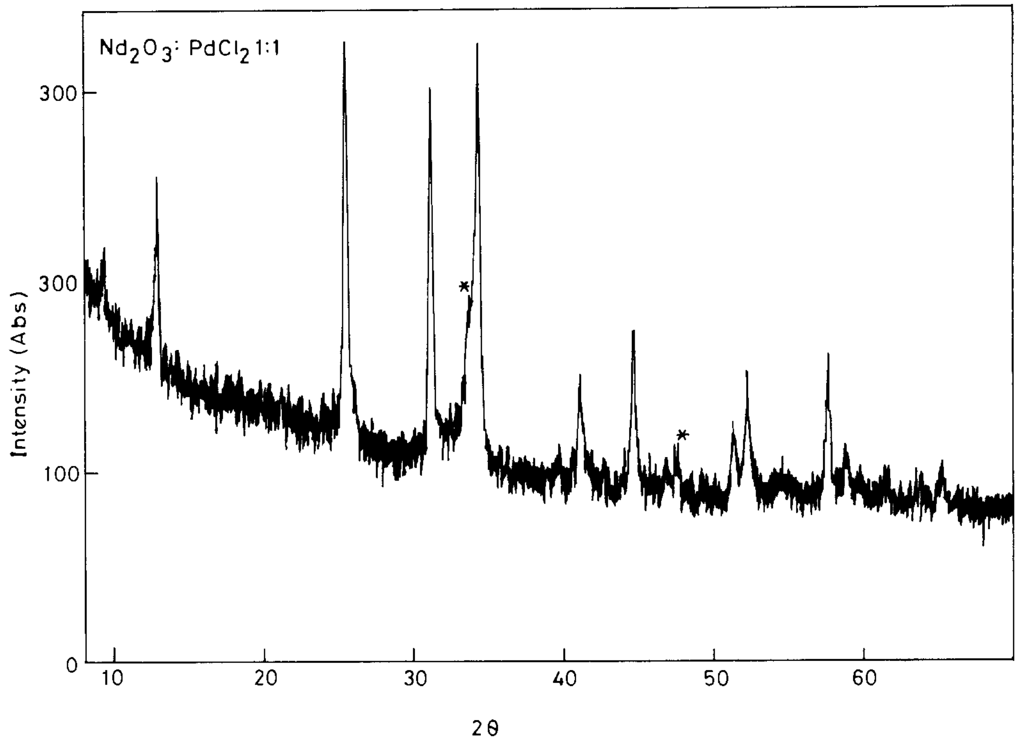

FIG. 4. X-ray diffraction pattern of the product of the reaction between Nd_2O_3 and $PdCl_2$.

shows the unit cell of such a phase. In Table I we list the X-ray reflections with the assignments. Figure 1 shows the difference between the observed and simulated X-ray patterns, which suggests a reasonable fit. We note, however, that for the 112 and 104 reflections, I_{obs}-I_{calc} is somewhat large. It should be possible to get better agreement by further adjustment of stoichiometry and occupancies.

La_2O_3 belongs to a hexagonal cell space group $P321$, with $a = 3.93$ and $c = 6.12$ Å. There are two La atoms, each surrounded by six oxygen neighbors. It appears that on the introduction of some PdO (or BeO) during the reaction, the basic La_2O_3 structure rearranges into a tetragonal cell, space group $P4/mmm$, with $a = 4.13$ and $c = 6.90$ Å (Fig. 2, structure 3). This distortion introduces two types of La–O contacts of lengths 2.08 and 2.66 Å, respectively, as compared to the single La–O distance of 2.30 Å in the parent La_2O_3. The second La atom (with an La–O distance of 2.66 Å) is associated with small amounts of Pd.

It indeed appears that what we have obtained as a "palladate" is a stabilized tetragonal La_2O_3 containing some PdO. It is therefore understandable why, on prolonged heating, the product of the $PdCl_2 + La_2O_3$ reaction (containing a mixture of the "palladate" and PdO) gives rise to the $I4/mmm$ phase of La_2PdO_4 (structure 2, Fig. 2). This is due to the chemical reaction of stabilized La_2O_3, with PdO giving the more stable phase of La_2PdO_4.

In order to ensure that what we have obtained is the stabilized tetragonal phase, we carried out reactions of La_2O_3 with $PdCl_2$ in different molar ratios. The results are shown in Fig. 3 in the form of the X-ray diffraction patterns of the products. We see that there is an increasing proportion of unreacted La_2O_3 with a decrease in the proportion of $PdCl_2$; the maximum yield of the stabilized tetragonal phase is found when the starting $La_2O_3 : PdCl_2$ ratio is 1 : 1. This result indirectly supports the hypothesis that some Pd does get into La_2O_3 to stabilize the tetragonal phase (leaving out the extra PdO). Similar results were obtained from the decomposition of mixed nitrates of La and Pd. It is interesting that the reaction of Nd_2O_3 with $PdCl_2$ in air also gives rise to a tetragonal phase (Fig. 4) with slightly smaller unit cell dimensions (a = 4.04 and c = 6.81 Å) than in the La–Pd–O system. We are pursuing a study of these stabilized phases especially with regard to their structure and properties.

Acknowledgment

Research support from the U.S. National Science Foundation is acknowledged.

References

1. P. Ganguly and C. N. R. Rao, *J. Solid State Chem.* **53,** 193 (1984).
2. J. G. Bednorz and K. A. Müller, *Z. Phys. B.* **64,** 189 (1986).
3. C. N. R. Rao, *J. Solid State Chem.* **74,** 147 (1988); *Acc. Chem. Res.* **22,** 106 (1989) and references cited therein.
4. D. J. Buttrey, J. M. Honig, and C. N. R. Rao, *J. Solid State Chem.* **64,** 287 (1986).
5. G. Aeppli and D. J. Buttrey, *Phys. Rev. Lett.* **61,** 203 (1988).
6. J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards and D. G. Hinks, *Phys. Rev. B* **40,** 2187 (1989).
7. K. S. N. Swamy, A. Lewicki, Z. Kakol, P. Gopalan, P. Metcalf, J. M. Honig, C. N. R. Rao, and J. Spalek, *Physica C* **166,** 361 (1990) and references cited therein.
8. B. G. Kakhan, V. B. Lazarev, and I. S. Shaplygin, *Russian J. Inorg. Chem.* **27,** 1180 (1982).
9. C. L. McDaniel and S. J. Schneider, *J. Res. Natl. Bur. Stand. Sect. A* **72,** 27 (1968).
10. P. A. Attfield and G. Ferey, *J. Solid State Chem.* **80,** 286 (1989).
11. H. R. Müller-Buschbaum, *Angew. Chem. Int. Ed. Engl.* **16,** 674 (1977).
12. M. Foex, *Bull. Chim. Soc. France* 109 (1961).