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Ordering of Pd^{2+} and Pd^{4+} in the Mixed-Valent Palladate KPd_2O_3

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A new potassium palladate KPd_2O_3 was synthesized by the reaction of KO_2 and PdO at elevated oxygen pressure. Its crystal structure was solved from powder X-ray diffraction data in the space group $R\bar{3}m$ (a=6.0730(1) Å, c=18.7770(7) Å, and Z=6). KPd_2O_3 represents a new structure type, consisting of an alternating sequence of K^+ and $Pd_2O_3^-$ layers with ordered Pd^{2+} and Pd^{4+} ions. The presence of palladium ions in di- and tetravalent low-spin states was confirmed by magnetic susceptibility measurements.

Complex oxides, containing palladium in either the +2 or +4 oxidation state, are not numerous. While compounds of divalent palladium, such as Ba_2PdO_3[1] and MPd_3O_4 (M = Sr, Ca),[2] have been prepared by a conventional solid-state reaction or by a hydroxide flux method, a high-pressure technique is generally required to synthesize complex oxides containing palladium in higher oxidation states, such as $Ln_2Pd_2O_7$ (Ln = Gd, Dy, Er, Yb, Sc, Y),[3] $LnPd_2O_4$ (Ln = La, Pr, Nd, Gd, Y),[4,5] $LaPdO_3$,[6] Zn_2PdO_4,[7] and M_4PdO_6 (M = Ca, Sr).[8] From a structural point of view, palladium oxides can be divided into two groups: those containing divalent palladium in planar coordination and those with tri- or tetravalent palladium in octahedral coordination. The planar coordination of palladium remains prevalent in the mixed-valent palladium oxides, where PdO_4 units create a three-dimensional structure by corner-sharing ($LnPd_2O_4$[4,5] with Ln = La, Pr, Nd, Gd, Y and $NaPd_3O_4$[9]) or form PdO_2 staggered strips by connecting via common edges ($K_3Pd_2O_4$[9]). The only compound for which charge disproportionation and both types of palladium coordination were observed is $Ba_2Hg_3Pd_7O_{14}$ with a three-dimensional framework built up of PdO_4 and PdO_6 units sharing common edges and corners.[10]

In this Communication, we report on the synthesis, crystal structure, and magnetic properties of the new KPd_2O_3 phase, containing $Pd_2O_3^-$ layers with ordered Pd^{2+} and Pd^{4+} cations.

KPd_2O_3 was synthesized by a solid-state reaction from a mixture of KO_2 (Aldrich, 95%) and PdO prepared from palladium metal (99.99%). The initial amounts of reagents, partial oxygen pressure, and time and temperature of annealing were varied to produce the pure KPd_2O_3 phase. Some excess of KO_2 was applied to compensate for the loss of alkali metal due to volatilization upon heating, which resulted in the formation of K_2SiO_3 as a white deposit on the inner walls of the silica ampules used for the preparation. Mixtures of reagents ($m \approx 0.1$ g) were intimately ground, pressed into pellets, and placed in corundum crucibles. The synthesis was carried out in silica tubes ($V \approx 20$ cm^3), which were evacuated, then filled with oxygen up to the required pressure, and sealed. The single-phase sample was obtained from a mixture of KO_2 and PdO in a molar ratio of 3:2 by a two-step annealing at 600 °C and then at 650 °C (for 20 h at each step) with a starting oxygen pressure of 0.5 atm. The preparation of the reagent mixtures and sample handling after annealing were carried out in a glovebox (MB 120 B-G, MBraun) under an argon atmosphere. The resulting dark-brown KPd_2O_3 appeared to be very sensitive to moisture and readily transformed to a mixture of $K_2[Pd(OH)_4]$[11] and PdO. Therefore,

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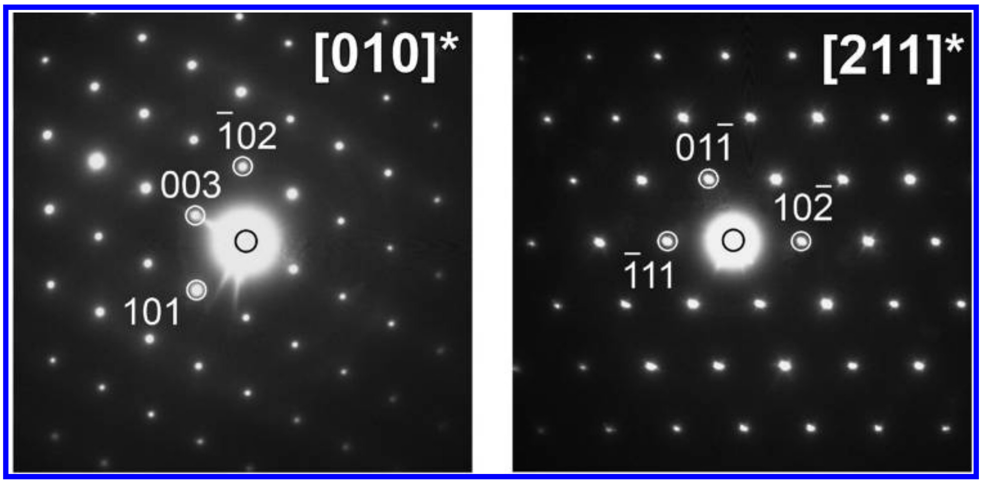

Figure 1. Electron diffraction patterns of KPd_2O_3 along different zone axes.

for X-ray diffraction (XRD), the product was sealed into glass capillaries of 0.3 mm diameter.

The phase composition and lattice parameters were determined by powder XRD using a Huber G670 Guinier camera (Cu Kα_1 radiation, germanium monochromator, and image-plate detector). Powder XRD data for structure refinement were collected on a STOE-STADI P diffractometer (Cu Kα_1 radiation, germanium monochromator, and linear position-sensitive detector) in the range of 12−110° (2θ) at 0.02° intervals. Electron diffraction was carried out with a Philips CM20 transmission electron microscope.

The most intense reflections on the XRD pattern could be indexed on a hexagonal unit cell with $a_{\text{sub}} = 3.0350(7)$ Å and $c_{\text{sub}} = 18.774(3)$ Å, while a complete indexing of the XRD pattern (including four reflections of low intensity) was done in a hexagonal unit cell with $a = 2a_{\text{sub}}$ and $c = c_{\text{sub}}$. For both settings, the reflections obeyed the extinction condition hkl: $-h + k + l \neq 3n$ indicating $R3$, $R\bar{3}$, $R32$, $R3m$, and $R\bar{3}m$ as possible space groups. Electron diffraction (Figure 1) showed the unit cell to be hexagonal ($a \sim 6.07$ Å and $c \sim 18.80$ Å) with the reflection conditions consistent with the XRD observations.

From the close resemblance between the XRD pattern of KPd_2O_3 (subcell setting) and those of β-$Na_{0.6}CoO_2$, a layered structure for the KPd_2O_3 phase was suggested. The initial model for Rietveld refinement was derived from the structure of β-$Na_{0.6}CoO_2$. It consisted of an alternating sequence of CoO_2 and Na layers with cobalt and sodium atoms in octahedral and trigonal-prismatic coordination, respectively.[12] Structure refinement was carried out in the most symmetric space group $R\bar{3}m$ with the program *JANA 2000*.[13] In the initial supercell unit, the PdO_2 layer was modeled by two palladium atoms located in the positions 9e (Pd1) and 3a (Pd2) and two oxygen atoms at sites 18h (O1) and 6c (O2). The position of potassium at (0, 0, z) was determined by difference Fourier synthesis. From subsequent refinements, the O2 site was found to be unoccupied; therefore, this position was omitted from further analysis. Occupation factors for other sites appeared to be close to 1.0 and were fixed at this value at the last stages of the refinement. The final Rietveld refinement plot is shown in Figure 2. The chemical composition estimated from refined structure parameters given in Table 1 corresponds to the formula KPd_2O_3.

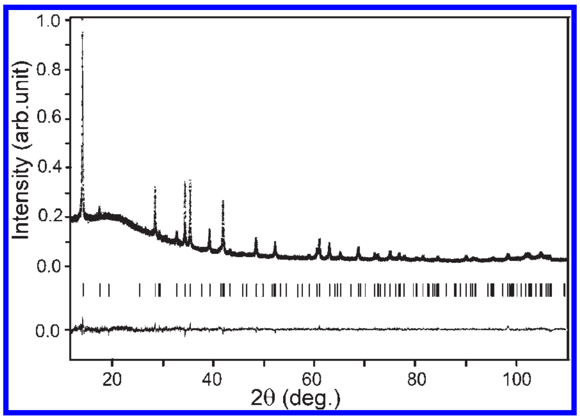

Figure 2. Observed (+) and calculated (solid line) powder XRD patterns and difference (solid line on the bottom) of KPd_2O_3. Vertical bars indicate the positions of the Bragg peaks.

Table 1. Structure Refinement Results on KPd_2O_3[a]

atom	site	x	y	z	U_{iso}/Å^2
Pd1	9e	0	0.5	0	0.006(1)
Pd2	3a	0	0	0	0.019(3)
K1	6c	0	0	0.1686(5)	0.040(3)
O1	18h	−0.173(2)	0.173(2)	0.0501(4)	0.029(3)

[a] Trigonal, space group $R\bar{3}m$ (No. 166), $Z = 6$, $a = 6.0730(1)$ Å, $c = 18.7770(7)$ Å, and $V = 599.75(3)$ Å^3. Refinement parameters $R_1 = 0.062$, $R_p = 0.043$, $R_{wp} = 0.056$, and GOF = 1.11.

Without taking oxygen vacancies into account, this structure can be viewed as an *AABBCC* sequence of close-packed oxygen layers stacked along the c axis, with palladium and potassium atoms occupying respectively all octahedral and one-quarter of the trigonal-prismatic interstitial sites between alternating pairs of oxygen layers. Compared to β-Na_xCoO_2, 25% of the oxygen sites appear to be unoccupied in the KPd_2O_3 structure. An ordering of the oxygen vacancies leads to the doubling of the a parameter and the formation of two distinct palladium sites with planar and octahedral coordination. It is accompanied by ordering of potassium atoms located at the trigonal-prismatic cavities formed by the remaining oxygen atoms (Figure 3a).

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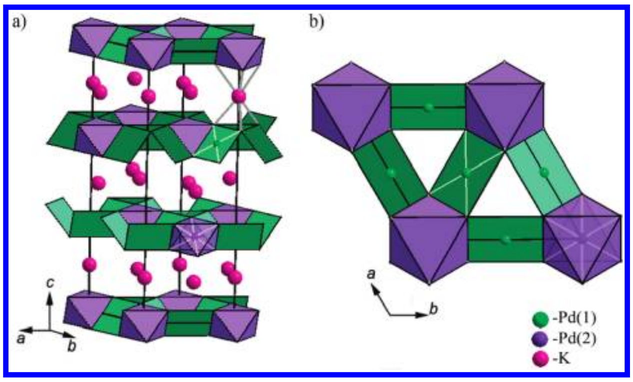

Figure 3. Crystal structure of the KPd_2O_3 phase: (a) alternation of Pd_2O_3 and K layers along the *c* axis; (b) projection of the Pd_2O_3 slab along the *c* axis.

Table 2. Selected Interatomic Distances (Å) in the Crystal Structure of KPd_2O_3

Pd1−O1	4 × 1.963(9)	K1−O1	3 × 2.738(13)
Pd2−O1	6 × 2.044(13)	K1−O1	3 × 2.872(13)
Pd1−Pd2	3.0365(1)		

The most prominent feature of the KPd_2O_3 structure is the alternating sequence of $Pd_2O_3^-$ and K^+ layers along the *c* axis. From the point of view of oxygen packing, the $Pd_2O_3\square^-$ layer can be described as an anion-deficient $CdCl_2$ layer. Ordering of cations or cation vacancies within the $CdCl_2$-type layer was observed in various complex oxides: ordering of different cations within the layer was reported for A_2PdO_3 and A_2PtO_3 (A = Li, Na), while ordering of cation vacancies with the formation of a $B_3\square O_8^{4-}$ slab was observed in $M_2B_3O_8$ oxides (M = Ca, Zn, Cd and B = Pt, Mn, Mo).[9,14−16] An oxygen deficiency, ordered within a $CdCl_2$-type layer, is rather unique, and to our knowledge, this type of ordering in an oxygen sublattice is reported for the first time. An earlier similar arrangement was described for a $Pt_2X_3^-$ layer in platinum chalcogenides $K_2Pt_4X_6$ (X = S, Se), but in contrast to KPd_2O_3, potassium atoms in these compounds are tetrahedrally coordinated.[17]

In the KPd_2O_3 structure, the palladium atoms are present in two different environments: the $Pd_2O_3^-$ layer is built up of PdO_4 and PdO_6 polyhedra connected via common edges (Figure 3b). Selected interatomic distances of KPd_2O_3 are given in Table 2. Both the Pd1−O and Pd2−O distances are shorter than the bond lengths usually observed for other complex oxides containing Pd^{2+} or Pd^{4+} (e.g., 2.033 Å in $CaPd_3O_4$[2] and 2.063 Å in Ca_4PdO_6[8], respectively). They are consistent with the interatomic distances found for $Ba_2Hg_3Pd_7O_{14}$, in which charge diproportionation takes place, and Pd^{2+} and Pd^{4+} ions are located at different sites (~2.00 and ~2.02 Å, respectively). The bond valence sum (BVS)[18,19] of Pd1 is found to be 2.43, while the BVS calculation for Pd2, with the r_0 estimated using data of $Ba_2Hg_3Pd_7O_{14}$ obtained from a single-crystal experiment,[10] yields the value of 3.56. This finding allows us to suggest a charge-distribution model for palladium atoms with Pd^{2+} and Pd^{4+} in planar and octahedral sites, respectively. The average oxidation state of +2.5 for palladium in KPd_2O_3 is consistent with the proposed distribution of the Pd^{2+} and Pd^{4+} cations over the crystallographic positions, which results in a formal Pd^{2+}/Pd^{4+} ratio = 3:1. The magnetic susceptibility data (see Figure S1 in the Supporting Information) reveal this phase to be diamagnetic; this observation is in agreement with the presence of palladium ions in divalent and tetravalent low-spin states with the ground-state d^8 configuration for the Pd^{2+} cation in the square-planar environment and the ground-state t_{2g}^6 configuration for the octahedral Pd^{4+} cation.

KPd_2O_3 appears to be the second example of complex palladium oxides in which charge disproportionation takes place. The average oxidation state of palladium in KPd_2O_3 of +2.5 is the same as that in the $K_3Pd_2O_4$ and $LnPd_2O_4$ (Ln = La, Pr, Nd, Gd, Y) phases. However, in contrast to KPd_2O_3, where palladium adopts both types of coordination polyhedra, for $K_3Pd_2O_4$ and $LnPd_2O_4$, the planar coordination of palladium remains preferable.[4,5,9]

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Supporting Information Available: Crystallographic information (CIF) file and temperature dependence of the magnetic susceptibility of KPd_2O_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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