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$LaPdO_3$: The First Pd^{III} Oxide with the Perovskite Structure

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Perovskite-type oxides containing transition-metal ions with degenerated electron configurations have attracted a considerable interest due to their specific physical properties[1] including colossal negative magnetoresistance [high-spin Mn^{3+} ($3d^4$)], charge disproportionation [high-spin Fe^{IV} ($3d^4$)], metal−insulator transition [low-spin Ni^{III} ($3d^2$)], and high-T_c superconductity [Cu^{2+} ($3d^9$)]. Although Pd^{III} (d^7) may also represent promising candidates in these fields, the main investigations have been carried out within fluorides[2] and halogen-bridged salts[3] systems, owing to a configurational instability of Pd^{III} (d^7) and a strong tendency to disproportionate into Pd^{II} and Pd^{IV}. In early works, Pd_2F_6 with the $LiSbF_6$-type structure have been characterized by a cationic ordering with the formulation $Pd^{II}Pd^{IV}F_6$.[4] Under high-pressure Pd_2F_6 has shown a pronounced decrease of the resistivity, which suggests the charge redistribution ($Pd^{II} + Pd^{IV} \rightarrow 2Pd^{III}$).[5] The stabilization of Pd^{III} as single valent form has been achieved in $NaPdF_4$ and K_2NaPdF_6, and EPR measurements confirm the electronic configuration $(t_{2g}^6 d_{z^2}^1)^2$. The oxides containing Pd^{III} are quite rare. Recently the series of APd_2O_4 (A = rare earth) have been prepared under high pressure where the Pd with mixed valence of +2.5 is coordinated by four oxygen atoms forming approximately square planar PdO_4 group.[6] The aim of this work is to stabilize Pd^{III} in an oxygen lattice through the high-pressure techniques for which we select perovskite structure, very stable under the pressure conditions.

Stoichiometric amounts of La_2O_3 and PdO in the ratio 1:2 were mixed together and then fired at 1040−1070 °C for 2 weeks. The product was composed of mainly $La_2Pd_2O_5$ and small amount of La_4PdO_7 and Pd metal. To help the oxidation of Pd metal, the previous product was treated under oxygen pressure (100 MPa) at 800 °C for 1 day. The resultant product was mixed with $KClO_3$ as oxygen source and treated under vacuum at 120 °C to eliminate water contamination. The mixture was encapsulated in a platinum tube, pressurized under 5 GPa using a *Belt*-type apparatus, and heated at 1100−1150 °C for 10 min. After being quenched to room temperature, the sample was washed with distilled water to remove KCl and subsequently dried at 120 °C for 2 h. The composition of final black powder was determined as $LaPdO_{2.98\pm0.02}$ with chemical titration and microprobe analysis.[7] The compound was stable to 500 °C at which it started to decompose to $La_2Pd_2O_5 + 0.5O_2$.

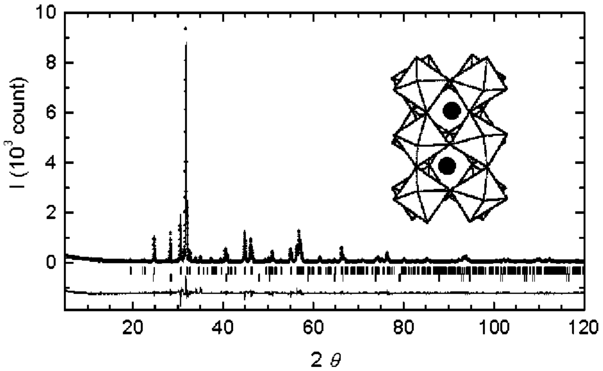

Figure 1. X-ray powder diffraction patterns, Rietweld refinement (upper and lower tick marks represent the Bragg positions for $LaPdO_3$ and KCl, respectively), and schematic presentation of crystal structure for $LaPdO_3$.

X-ray diffraction profile (Figure 1) for the final black powder could be indexed using a primitive orthorhombic unit cell implying that $LaPdO_3$ would adopt the $GdFeO_3$-type structure (space group *Pbnm*) with unit cell parameters $a = 5.5898(3)$ Å, $b = 5.8502(3)$ Å, $c = 7.8666(4)$ Å. Significant Jahn−Teller effect was not observed although $c/\sqrt{2}a$ ratio(0.995) is smaller than 1.[8] Considering the difference ($\Delta r = 0.07$ Å) between the radii of oxide and fluoride ions, the average Pd^{III}−O bond distance (2.08 Å) is compatible with the average Pd^{III}−F bond distance (2.00 Å) estimated from recent EXAFS study on K_2NaPdF_6 with the elpasolite-type structure where the (PdF_6) octahedra exhibit a Jahn−Teller distortion.[9]

To confirm the oxidation state of Pd, an X-ray absorption spectroscopic study was performed at the Pd L_3 edge (3173 eV).[10] Two Pd oxides were used as references ($Pd^{II}O$ and $Zn_2Pd^{IV}O_4$[11]). The Pd L_3-edge XANES spectra (Figure 2) for all compounds are characterized by one main peak which primarily corresponds to the electric dipole-allowed transition from 2p states to 4d ones.

Since no multiplets effect was detected in the Pd L_3 XANES spectra of fluorides,[9] it can be assessed that multiplet transitions are also absent from the spectra of the oxides, due to a higher covalency of the Pd−O bond compared to that of the Pd−F bond. Therefore the Pd L_3 edge spectra of these oxides is directly relevant of the empty electronic states of the 4d orbitals.[12] A shift of the peak to higher energies is clearly observed while moving from $Pd^{II}O$ to $Zn_2Pd^{IV}O_4$. The peak in the Pd L_3 XANES of

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(7) After dissolving the sample in HCl solution containing Br^-, Br_2 liberated from the re-dox reaction of Pd^{III} and Br^- was titrated with hydrazine sulfate standard solution. The end point was determined by bi-amperometry. Microprobe analysis revealed that K, Cl, and Pt were not contained in the final sample (<0.5%).

(8) $c/\sqrt{2}a$ ratio does not work in some trivalent nickelates (d^7), $PrNiO_3$ (0.994) and $NdNiO_3$ (0.998) where no static Jahn−Teller effect has been observed.

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(10) The XANES spectra of Pd L_3-edge were measured at room temperature in transmission mode using a Si(111) double-crystal monochromator on station D44 in LURE (Orsay-France). The spectra were calibrated in energy with the presence of argon traces in the ionization chamber (Ar K-edge: 3202 eV). The spectra were normalized at 3185 eV.

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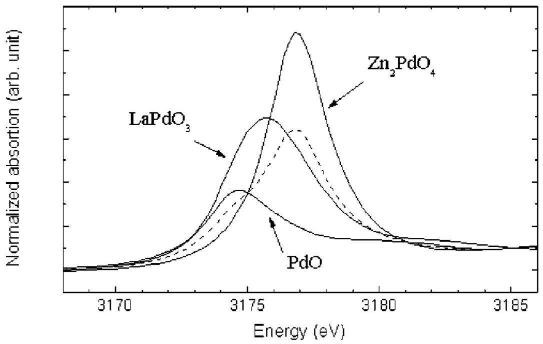

Figure 2. Normalized Pd L_3-edge XAS spectra of $Pd^{II}O$, $LaPd^{III}O_3$, and $Zn_2Pd^{IV}O_3$ at room temperature. The dotted line represents the average spectrum of $Pd^{II}O$ and $Zn_2Pd^{IV}O_3$.

$LaPdO_3$ (3175.7 eV) is exactly located at the middle position of two peaks for Pd^{II} (3174.6 eV) and Pd^{IV} (3176.8 eV) references. The shift induced by the difference in oxidation state is less predominant in such oxides compared to the fluorides (only 2.2 eV between the Pd^{II} and Pd^{IV} oxides compared to 4 eV in the fluorides[9]), owing to the lower ionicity of Pd−O bond of than Pd−F one. The peak intensity for $LaPdO_3$ is also between them, which is correlated with d-band vacancies. Additionally, the spectrum of $LaPdO_3$ can clearly be distinguished from the average of the Pd L_3 spectra of Pd^{II} and Pd^{IV} oxides. Therefore, the formal oxidation state of Pd in $LaPdO_3$ is close to III rather than II + IV. However, the peak for $LaPdO_3$ is broader than those for $Pd^{II}O$ and $Zn_2Pd^{IV}O_4$. Such broadening may be attributed from strong covalency due to the high degree of hybridization of Pd 4d and O 2p orbitals.[13] A similar effect has been observed in comparing the Cu L_3-edge of metallic cuprate with the insulating one.[14]

The local structure of Pd^{III} was estimated by the EXAFS analysis on Pd K-edge.[15] The first shell (1.1 Å < R < 2.1 Å) in R space (phase shift: uncorrected), which seems to be nearly isotropic, corresponds to the nearest neighbors of Pd ion, that is, (Pd−O) shells (Figure 3a). For this shell the radial distance (R), the edge position (E_0) and the Debye−Waller factor (σ^2) were refined. Due to the strong correlation between σ^2 and the coordination number (CN), the CN was fixed to 6. A good fit accuracy is obtained for this shell by considering standard harmonic pair distribution, which suggests the absence of a large distortion of (PdO_6) octahedra in $LaPdO_3$ (Figure 3b). The average Pd−O bond distance is estimated to be 2.06 Å, which is well consistent with XRD results mentioned above.

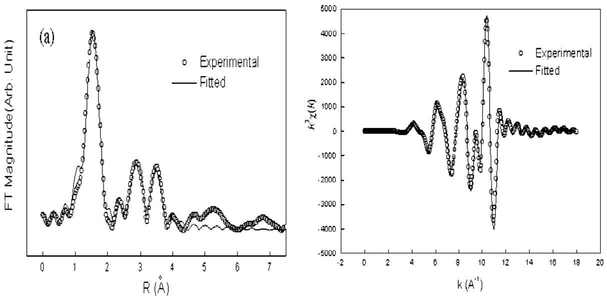

Figure 3. (a) Fourier transform of k^3-weighted Pd K-egde for $LaPdO_3$ (b) k^3-weighted Fourier-filtered EXAFS functions of Pd K-edge for $LaPdO_3$.

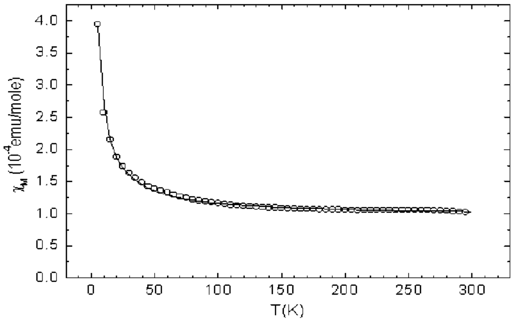

Figure 4. Temperature dependence of the molar magnetic susceptibility of $LaPdO_3$ after correction of the core diamagnetic term.

The molar magnetic susceptibility taken at H = 10 kOe for 5 K ≤ T ≤ 300 K can be fitted to the formula,[16]

$$\chi = \chi(0) - aT^2 + C/T$$

with $\chi(0) = 1.0 \times 10^{-4}$ emu/mol, $a = 1.1 \times 10^{-10}$ emu/K^2 mol, and $C = 1.5 \times 10^{-3}$ emu K/mol (Figure 4). The first and second terms are Pauli paramagnetic susceptibility and its small temperature dependency, respectively. The last term represents a small Curie component. We cannot rule out a trace of impurities as sources of the Curie term. Such a magnetic behavior is consistent with the metallic electron configuration ($t_{2g}^6\sigma^{*1}$) for Pd^{III} which is deduced from the XANES/EXAFS analyses. The absence of large enhancement of the Pauli susceptibility observed in $LaNiO_3$ (5.1×10^{-4} emu/mol) is probably due to weak electron-correlation effect in the 4d compared to the 3d system.[17]

From these physicochemical characterizations $LaPdO_3$ appears the first oxygen-perovskite containing Pd^{III}.

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Supporting Information Available: The results of Rietveld refinemet on powder XRD patterns and the fitted structural parameters in EXAFS analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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