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The Crystal Structure of $CaPd_3O_4$

Introduction

This paper describes experiments to determine the crystal structure of a new oxide of calcium and palladium, $CaPd_3O_4$. This compound was obtained during the course of efforts to prepare alkaline earth palladates. In this process excess $CaCO_3$ was heated with PdO in air to about 800° to 900°C. At intervals the reaction mixture was removed from the furnace, thoroughly remixed and then reheated. After several cycles, the reaction products were examined by x-ray powder diffraction methods and were found to contain CaO, $CaCO_3$, small amounts of Pd and PdO plus one or more unidentified phases. The CaO and $CaCO_3$ were readily removed by washing with aqueous NH_4Cl solution. Small amounts of Pd and PdO remaining in the mixture were removed by boiling with aqua regia, which appeared to have no significant effect on the unknown phase or phases.

All the lines of x-ray powder patterns of the latter (a black powder with a greenish cast), were indexed on the basis of a cubic unit cell with $a = 5.746 \pm 0.001$A. The volume of one unit cell$_3$ is approximately 189A. Estimates based on the volumes per oxygen atom in PdO and CaO indicated that the unit cell of the new phase contained 8 oxygen ions (i.e., ~23A per oxygen ion$_3$). If the valences of the ions in the new phase are assumed to correspond to those manifested in PdO and CaO, the formula of the phase could be written as $Ca_xPd_{8-x}O_8$.

Initial searches of the literature revealed no likely isostructural phases, and a determination of the crystal structure was therefore undertaken.

Crystal structure determination

X-ray powder data were obtained with a diffractometer using filtered CuK radiation in conjunction with pulse amplitude discrimination. The diffraction peaks were scanned at 1/4°(2θ) per minute: integrated intensities were obtained by subtracting background intensities from totals for each peak. Three specimens were examined in this way. No statistically significant differences among the sets of intensities were detected. The values of structure factors, F_{obs}, in Table 1 are based on intensity data averaged over the three runs.

The indexing of the cubic unit cell indicated that the lattice is primitive; also, reflections of the type *hhl* with 1 odd were systematically absent. The two possible space groups are P43n and Pm3n. A few trial calculations quickly indicated that good agreement between F_{obs} and F_{calc} at least for low angle reflections, could be obtained by placing 2Ca, 6Pd, and 8O in the following positions in Pm3n:

oxygen ions in 8*c*: 1/4, 1/4, 1/4, etc.
palladium ions in 6*d*: 1/4, 0, 1/2, etc.
calcium ions in 2*a*: 0, 0, 0; 1/2, 1/2, 1/2.

All position parameters in this structure are fixed. There are only four variable parameters: the scale factor and the three individual atomic temperature factors, *B*. These were refined by the method of least squares. Best agreement between F_{obs} and F_{calc} was obtained with:

$B_{Pd} = 0.40 \pm 0.05$

$B_{Ca} = 0.40 \pm 0.05$

$B_O = 0.85 \pm 0.20$.

These parameters correspond to root mean square amplitudes of thermal motion of 0.07A for palladium and calcium and 0.10A for oxygen. In these calculations corrections for dispersion were applied to the atomic scattering factors of palladium and calcium using a computer program written by Dr. James Ibers of the Brookhaven National Laboratory. It is worth noting that it was not possible to obtain satisfactory agreement between F_{obs} and F_{calc} for the (220) reflection without dispersion corrections. The real part of F_{calc} for this reflection is only 3.9, as compared with 5.4 for the imaginary part.

Structure factors calculated for all reflections are listed in Table 1. The good agreement between observed and calculated values of the structure factors, as indicated by

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Eq. (1), appears to establish the crystal structure and chemical formula beyond serious doubt.

$$R = \frac{\sum_{hkl} ||F_{obs}| - |F_{calc}||}{\sum_{hkl} |F_{calc}|} = 2.5 \text{ percent.} \quad (1)$$

Chemical analysis of the material showed 9.24 percent Ca and 75.76 percent Pd: the formula $CaPd_3O_4$ would correspond to 9.47 percent Ca and 75.41 percent Pd.

Shortly after this work was completed, a reference to the crystal structure of $Na_xPt_3O_4$ was located[1]. Waser and McClanahan[2] had described a sodium platinate ($NaPt_3O_4$) whose unit cell was cubic: $a = 5.69$A, space group Pm3n. The published powder pattern of $NaPt_3O_4$ is very similar to the $CaPd_3O_4$ pattern. However, in a note published shortly after the appearance of Waser and McClanahan's paper, Galloni and Busch[3] criticized the conclusions drawn concerning the sodium platinate. They asserted that they had prepared platinum oxides, which contained no detectable sodium, but whose powder patterns were essentially identical with the "$NaPt_3O_4$" pattern of Waser and McClanahan. Galloni and Busch concluded that the "$NaPt_3O_4$" was actually a simple oxide of platinum. Subsequently Waser[4] pointed out that spectrographic analysis of his specimen revealed appreciable amounts of sodium. Waser suggested the possibility of a continuous range of sodium content, i.e., $Na_xPt_3O_4$ with $0 \leq x \leq 1$. In view of the isostructural relationship between calcium palladate and sodium platinate, it appears likely that the original Waser-McClanahan formula is the correct one, and that additional double oxides of this type may exist.

Table 1 **Observed and calculated structure factors for $CaPd_3O_4$.**

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
200	61.7	57.3	630	73.7	74.4
400	209.5	212.0	440	163.0	160.7
600	39.7	41.3	640	33.5	35.6
110	48.5	49.0	211	97.6	97.0
210	145.6	144.6	611	53.1	53.9
310	38.9	39.7	321	79.3	78.8
510	32.7	31.0	421	101.7	102.1
610	81.5	81.6	521	59.2	59.9
710	23.9	23.6	631	46.3	49.4
220	7.3	6.6	541	23.3	25.3
320	117.4	118.2	222	189.1	189.0
420	52.5	48.4	422	22.2	13.4
520	90.8	90.6	622	114.4	112.3
720	67.2	68.8	332	66.3	67.6
330	30.7	34.8	444	136.4	132.0
530	24.2	28.0			

Discussion

Waser and McClanahan[2] have described the crystal structure of $NaPt_3O_4$ and the reader is referred to that paper for drawings and details. The structure may be visualized conveniently in terms of cubic subcells, 2.87A on edge, with oxygen ions at all corners. The calcium ions are located at the centers of two of the eight subcells in each unit cell; each Ca ion is surrounded by eight oxygen ions at a distance of 2.49A. Each palladium ion is surrounded by 4 oxygen ions in square planar array: Pd-O = 2.03A. This arrangement is very similar to that found[5] in PdO where Pd ions lie at the centers of rectangles, with oxygen ions at each corner, and with Pd-O = 2.02A.

Preliminary electrical measurements made on a sintered pellet of $CaPd_3O_4$ gave room temperature resistivities of about 0.2 ohm-cm. The pellet, 2.5 mm diameter and 1 mm thick, was pressed at about 10^5 psi and fired at 900°C for 3 hours. The resistivity was measured by the van der Pauw technique,[6] using silver electrodes.

The resistivity decreased with increasing temperature, apparently with a higher activation energy for conduction in the range from 200° to 400°K than in the range from 77° to 200°K. This energy in the higher temperature range was of the order of 0.1 ev. The resistivity at liquid nitrogen temperature was about 3 ohm-cm.

The thermoelectric effect indicated qualitatively that the current carriers are positive. No Hall effect could be detected at room or liquid nitrogen temperature with a magnetic field of 15 kilogauss. A Hall coefficient of 0.3 cm^3/coulomb or greater would have been detectable with the available equipment.

These preliminary electrical measurements indicate that the new compound is a *p*-type semiconductor.

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