

Neutron Powder Diffraction Study of Two Sodium Platinum Oxides: $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ and $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$

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Abstract

Neutron powder diffraction profile analysis has been used to confirm the structures of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ and $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$. Both compositions are cubic in space group $Pm\bar{3}n$ with $Z = 2$. The structure of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$, with $a = 5.6868$ (2) Å as determined by X-ray powder diffraction, was refined to a final discrepancy factor for the weighted profile of $R_{wp} = 0.120$ for 30 peaks representing 39 reflections. The structure of $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$, a poorly crystallized compound with $a = 5.675$ (1) Å, was refined to $R_{wp} = 0.212$ for 31 peaks representing 40 reflections. Reliable thermal parameters were determined for lighter atoms in this platinum-dominated structure. The refined values of the sodium occupancy factor in both cases confirm the chemical analysis. Sodium occupancy values are also consistent with the linear relationship of unit-cell measurements *vs* sodium content for these compounds. The short Pt–Pt distance of 2.843 Å in the structure of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ is consistent with its electrical properties. The metallic resistivity of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ ($\rho = 9 \times 10^{-7}$ Ωm at 293 K) and the presence of a single Pt site with formal valence $\frac{7}{3}$ places $\text{Na}_x\text{Pt}_3\text{O}_4$ compositions in class III-B of the Robin & Day mixed-valence classification [Robin & Day (1967), *Adv. Inorg. Chem. Radiochem.* **10**, 247–422].

1. Introduction

$\text{Na}_x\text{Pt}_3\text{O}_4$ is the most widely studied phase in this family of noble-metal oxides. The general formula,

$M_x\text{Pt}_3\text{O}_4$, contains platinum (or palladium) in square-planar coordination and has been synthesized with a variety of alkali, alkaline-earth and transition metals as the counterion (Scheer, van Arkel & Heyding, 1955; Scheer, 1956; Bergner & Kohlhaas, 1973; Cahen, Ibers & Wagner, 1974; Lazarev & Shaplygin, 1978*a*). The M site need not be totally occupied. In fact, the value of x is found to vary widely between zero (Pt_3O_4) (Muller & Roy, 1968; Sukhotin, Gankin, Kondvashov, Omel'chenko & Shal'man, 1971) and unity (*e.g.* stoichiometric $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$).

Cahen & Ibers (1973) demonstrated that $\text{Na}_x\text{Pt}_3\text{O}_4$ is the active component in Adam's catalyst, a mixture of Pt, α - PtO_2 , and $\text{Na}_x\text{Pt}_3\text{O}_4$ that is used in the reduction of organic compounds. Whereas both α - PtO_2 and $\text{Na}_x\text{Pt}_3\text{O}_4$ are active hydrogenating agents, $\text{Na}_x\text{Pt}_3\text{O}_4$ is the only constituent of the mixture that does not decompose during the process. More recently, $M_x\text{Pt}_3\text{O}_4$ compositions have been used as chlor-alkali anodes (Thiele, Zöllner & Koziol, 1973; Fukunda & Asai, 1975; Koziol, Siekerer & Ruthjen, 1976; Thiele, Zöllner & Koziol, 1976; Zöllner, Zöllner & Koziol, 1976*a,b*).

The structure of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$, characterized by isolated Pt–Pt chains parallel to the three cubic axes (Cahen, Ibers & Shannon, 1972), was first determined by Waser & McClanahan (1951) with X-ray powder diffraction techniques. It was not necessary to refine atom positional parameters, as Na, Pt, and O are in special positions 2(*a*), 6(*c*) and 8(*e*), respectively, of the space group $Pm\bar{3}n$ and are thus totally constrained by symmetry. They determined the space group and indexed 42 reflections on a simple cubic lattice with a unit-cell edge of 5.69 Å, based on extrapolation to $\theta =$

* Contribution No. 2884.

90°. No correction was made for thermal motion and the final discrepancy factor was $\sum |F_o| - |F_c| / \sum |F_o| = 0.061$.

The first single-crystal X-ray diffraction refinement of a platinum oxide with this general formula was reported by Cahen, Ibers & Shannon (1972) for $\text{Ni}_{0.25}\text{Pt}_3\text{O}_4$. Reasonable temperature factors for Ni and O could not be obtained ($B = 2.0 \pm 4.0 \text{ \AA}^2$ and $3.2 \pm 3.4 \text{ \AA}^2$, respectively) because of the overwhelming scattering power of Pt in this platinum-dominated structure. It was noted that the isotropic temperature factor for Ni was strongly correlated with Ni occupancy when both parameters were refined. The unweighted and weighted discrepancy factors were $R_F = \sum |F_o| - |F_c| / \sum |F_o| = 0.056$ and $wR_F = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.063$ with $w = 1/\sigma^2$ for a refinement performed in space group $Pm\bar{3}n$. A subsequent examination (Cahen, Ibers & Mueller, 1974) of $\text{Cd}_{0.3}\text{Pt}_3\text{O}_4$ by X-ray and neutron powder diffraction resulted in a temperature factor for oxygen of $B = 1.9 \pm 0.1 \text{ \AA}^2$, with discrepancy factors in $Pm\bar{3}n$ of $R = \sum |I_o - I_c| / \sum I_o = 0.098$, and $R_w = [\sum w(I_o - I_c)^2 / \sum wI_o^2]^{1/2} = 0.114$, where $w = 1/\sigma^2 = 1/I_o$, for the neutron powder diffraction data set. Recently, a reasonable oxygen temperature factor was obtained by refinement of neutron powder diffraction data for TlPd_3O_4 (Müllner, Thiele & Zöllner, 1978). This cardinal-red cubic compound, space group $Fm\bar{3}m$, contains square-planar PdO_4 units with cubic and rhombicuboctahedral voids occupied by Tl^{3+} and Tl^+ cations, respectively. It is formulated as a mixed-valency thallium(III) thallium(I) oxopalladate(II) (Zöllner, Thiele & Müllner, 1978).

2. Experimental

Stoichiometric $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ was synthesized by a hydrothermal technique. In a typical experiment, a mixture of 0.5 g $\alpha\text{-PtO}_2$ (0.0022 mol), 0.2 g NaOH (0.0050 mol), 0.25 g KClO_3 (0.0020 mol), and 2 ml H_2O was sealed in a platinum tube 125 mm long with an outer diameter of 9.5 mm. This capsule was heated at 973 K and ~ 0.3 GPa for 24 h and cooled to room temperature in several minutes by cutting power to the furnace. The product, a fine-grained black powder, was treated in hot *aqua regia*. This procedure was scaled up by a factor of fifteen to produce material for neutron powder diffraction data collection. Atomic absorption analysis showed the sample to be stoichiometric with 1.0 cations of sodium per formula unit. Emission spectroscopic analysis showed no significant cation impurities.

The sample of $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ for neutron powder diffraction was synthesized by the reaction of 1.2 g of $\text{Na}_2\text{Pt}(\text{OH})_6$ (0.0035 mol) and 8.8 g of PtO_2 (0.0039 mol) (containing a trace of $\text{Na}_x\text{Pt}_3\text{O}_4$). This reaction mixture in pellet form was heated slowly to 983 K in an

oxygen atmosphere for 15 h. The pellet was ground and reheated in oxygen for an additional 20 h. X-ray powder diffraction analysis of this product showed the presence of a cubic $\text{Na}_x\text{Pt}_3\text{O}_4$ phase and elemental platinum. Treatment of the product with hot *aqua regia* yielded 6 g of a Pt-free powder with the $\text{Na}_x\text{Pt}_3\text{O}_4$ structure. Sodium analysis by atomic absorption gave a sodium content $x = 0.73$ (2) cations per formula unit.

X-ray powder diffraction patterns were obtained for $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ and $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ with a Guinier-Hägg focusing camera having a radius of 40 mm. The radiation was monochromatic $\text{Cu } K\alpha_1$ ($\lambda = 1.54051 \text{ \AA}$) and KCl ($a = 6.2931 \text{ \AA}$) was used as an internal standard. Line positions on the film were determined to $\pm 5 \mu\text{m}$ with a Mann film recorder. Cell dimensions determined by least-squares refinement were $a = 5.6868$ (2) and $a = 5.675$ (1) \AA for $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ and $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$, respectively.

Crystals of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ were grown in a similar fashion. A mixture of 0.40 g PtCl_2 (0.0015 mol), 0.60 g NaOH (0.0015 mol), 0.5 g KClO_3 (0.0041 mol), and 1 ml H_2O was sealed in a platinum tube, soaked for 24 h at 973 K and ~ 0.3 GPa, and then cooled slowly to room temperature. Clusters of crystals were found adhering to the walls of the tube.

Neutron diffraction measurements were made at room temperature on a powder diffractometer at the High-Flux-Beam Reactor of Brookhaven National Laboratory. Powder samples of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ and $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ were placed in cylindrical vanadium cells 4.76 mm in diameter for data collection. A germanium monochromator (111) and a pyrolytic graphite analyzer (004) were used. The wavelength was 1.30 \AA . $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ data were collected by step scanning from $2\theta = 12.01$ to 110.00° with a step width of $0.1^\circ 2\theta$ and a counting time of 80 s per step. The data for $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ were collected from $2\theta = 6.01$ to 115.00° with a step width of $0.05^\circ 2\theta$ and a counting time of 92.3 s per step.

Refinement of the data was performed using the method of profile analysis with the program *PROFILE* written by Rietveld (1969a,b) and modified by Hewat (1973). The neutron scattering amplitudes were $b(\text{Na}) = 3.6 \text{ fm}$, $b(\text{Pt}) = 9.5 \text{ fm}$, and $b(\text{O}) = 5.8 \text{ fm}$ (Bacon, 1978). The parameters refined during each cycle were: scale factor, unit-cell parameter (a), zero point of the profile, and half-width parameters. The half-width parameters U , V and W were related to the full width of a single reflection at half height (H) in degrees 2θ by:

$$H^2 = U \tan^2 \theta + V \tan \theta + W.$$

The initial value of the unit-cell parameter was taken from Waser & McClanahan (1951). The only structural parameters varied during the refinements were the temperature factors and site occupancies. Preliminary B 's for $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ and $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ were obtained by holding the occupancy to the chemically analyzed

value. Anisotropic temperature-factor coefficients (β_{ij}) were eventually used for all atoms in $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$. Site occupancies were then refined with these anisotropic values. Finally, all parameters were refined simultaneously until convergence was obtained.

3. Results

3.1. Neutron data refinement of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$

The final structural parameters for stoichiometric $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ are given in Table 1.* The discrepancy factors are R_I , which corresponds to the conventional discrepancy factor for integrated intensities, R_E and R_{wp} , representing respectively, the EXPECTED and weighted profile discrepancy factors based upon individual data points as defined by Rietveld (1969b).

* Lists of intensities for both oxides have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36320 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for $\text{Na}_x\text{Pt}_3\text{O}_4$ (cubic, $Pm\bar{3}n$)

	x	y	z		
Na	2(a)	0	0	0	$\beta_{11} = \beta_{22} = \beta_{33}$
Pt	6(c)	$\frac{1}{2}$	0	$\frac{1}{2}$	$\beta_{11} \neq \beta_{22} = \beta_{33}$
O	8(e)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\beta_{11} = \beta_{22} = \beta_{33}$
					$\beta_{12} = \beta_{13} = \beta_{23} = 0$
					$\beta_{12} = \beta_{13} = \beta_{23} = 0$
					$\beta_{12} = \beta_{13} = \beta_{23}$
				$x = 1.0$	$x = 0.73$
Occupancy: Na				0.99 (3)*	0.78 (3)
Occupancy: Pt				2.98 (3)	2.92 (3)
$\beta_{11} \ddagger$: Na				0.005 (1)	—
$\beta_{11} \ddagger$: Pt				0.0010 (6)	—
$\beta_{22} \ddagger$: Pt				0.0009 (4)	—
$\beta_{11} \ddagger$: O				0.0036 (4)	—
$\beta_{12} \ddagger$: O				0.0017 (3)	—
$B_{11} \ddagger$: O				0.46 (5)	—
$B_{12} \ddagger$: O				0.22 (4)	—
B: Na				0.63 (9)§	0.4 (2)¶
B: Pt				0.12 (4)	0.06 (3)
B: O				0.47 (3)	0.51 (6)
R_I				0.021	0.050
R_E				0.102	0.168
R_{wp}				0.120	0.212

$$R_I = \sum |I_o - I_c| / \sum I_o$$

$$R_E = [(N - P + C) / \sum w(Y_o)^2]^{1/2}$$

$$R_{wp} = [\sum w|Y_o - Y_c|^2 / \sum (Y_o)^2]^{1/2} \text{ where } Y = \text{counts per step};$$

$$w = 1/\sigma^2 = 1/Y.$$

* Errors in parentheses.

† Anisotropic temperature-factor coefficients of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

‡ Elements of the mean-square displacement matrix \mathbf{B} , where $B_{ij} = 8\pi^2\langle\mu^2\rangle$, $\langle\mu^2\rangle$ being the mean-square displacement from equilibrium position in \AA^2 .

§ Equivalent isotropic temperature factor in \AA^2 calculated from anisotropic temperature-factor coefficients.

¶ Equivalent isotropic temperature factor in \AA^2 as refined.

Explicit expressions are given in Table 1. The oxygen site is believed to be fully occupied because in initial refinements the oxygen occupancy parameter refined to a value of 4.00 (4). This parameter was not refined in succeeding stages. Sodium and platinum occupancy refinements confirm the stoichiometric nature of this sample with no statistically significant vacancies in either cation site.

Thermal parameters are given in terms of: B_{ij} , the elements of the mean-square displacement matrix; β_{ij} , the anisotropic temperature-factor coefficients; and B , the equivalent isotropic temperature factor (Cruickshank, 1965; Willis & Pryor, 1975). The values obtained appear to be physically reasonable. Sodium, a light cation coordinated by eight oxygen anions, has a root-mean-square (r.m.s.) displacement of 0.09 \AA , much larger than the heavier platinum r.m.s. displacement of 0.04 \AA . The oxygen thermal ellipsoid is oriented along [111], directed towards the Na atoms. The r.m.s. amplitudes are 0.11 \AA parallel to [111] and 0.06 \AA perpendicular to [111]. The oxygen temperature factor shows a strong, inverse correlation with platinum occupancy, demonstrated by a correlation coefficient of -72. The sodium occupancy and temperature factor also show a strong correlation with a value of 73 for the correlation coefficient. The final discrepancy factors for this refinement are $R_I = 0.021$, and $R_{wp} = 0.120$, with $R_E = 0.102$.

Bond distances for $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ are based on the unit-cell dimension $a = 5.6868$ (2) \AA determined by X-ray powder diffraction. The Pt-O distance of 2.0106 (1) \AA is in good agreement with that found in $[\text{Cu}(\text{C}_2\text{H}_3\text{N}_2)_2][\text{Pt}(\text{C}_2\text{O}_4)_2]$ by Bekaroglu (1976). The Na-O distance of 2.4625 (1) \AA is considerably less than the distance of 2.57 \AA predicted from crystal radii (Shannon, 1976). The Pt-Pt distance, 2.8434 (1) \AA , is significant in its relation to the electrical resistivity of the material. This relationship will be discussed later.

3.2. Neutron data refinement of $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$

The refinement of $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ is of particular interest because of the non-stoichiometric nature of the sample. The final structural parameters are given in Table 1.* As in the case of stoichiometric $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$, the oxygen site was presumed to be fully occupied and the occupancy factor was not refined. The occupancy parameter for the sodium site was refined to a value of 0.78 (3) cations per formula unit. When the sodium content was constrained to be equal to the chemically analyzed value, 0.73 (2), platinum and oxygen occupancies were refined to 2.74 (10) and 3.76 (14) cations per formula unit, respectively. Correlation coefficients between occupancy and temperature factor for sodium and platinum are comparable to those

* See previous footnote.

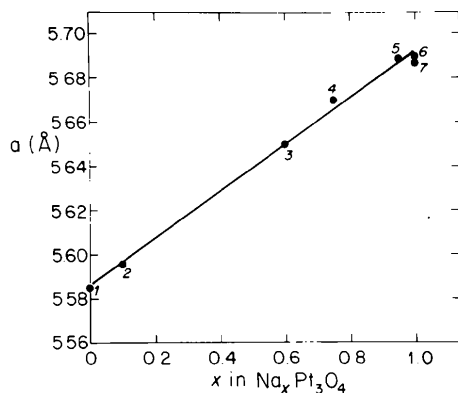


Fig. 1. Unit-cell dimension a (Å) as a function of sodium content x for $\text{Na}_x\text{Pt}_3\text{O}_4$ ($0 < x < 1$). The straight line represents a first-order least-squares fit to the experimental data with the equation a (Å) = $0.11x + 5.59$ (after Brown & Banks, 1954). From: (1) Muller & Roy (1968); (2) Cahen, Ibers & Wagner (1974); (3) Lazarev & Shaplygin (1978a); (4) present work; (5) Scheer (1956) and Scheer, van Arkel & Heyding (1955), as cited in Cahen, Ibers & Wagner (1974); (6) Waser & McClanahan (1951); (7) present work.

discussed above for $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$. The sodium site is the only source of significant deviation from stoichiometry.

The unit-cell parameter is also indicative of the decreased sodium content in $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$. A plot of all available unit-cell data *vs* sodium content for $\text{Na}_x\text{Pt}_3\text{O}_4$ compositions, shown in Fig. 1, demonstrates the linear relationship of these two parameters. The equation of the line is a (Å) = $0.11x + 5.59$. This yields a value of $x = 0.77$ (5) sodium cations per formula unit based on the unit cell of $a = 5.675$ (1) Å given previously.

Bond distances for $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ are shorter than the corresponding distances in $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ because of unit-cell contraction. The Na—O and Pt—O distances are 2.4574 (4) and 2.0064 (4) Å, respectively. The Pt—Pt distance is 2.8375 (5) Å.

The $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ sample is considered to be poorly crystallized relative to the stoichiometric $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ sample. This conclusion is based upon peak widths, which are 30–50% broader in $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$ than in $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$. The poor crystallinity leads to lower peak-to-background ratios and more serious overlapping of closely spaced peaks, especially at higher angles. This situation is reflected in the higher discrepancy factors for this refinement as compared to $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$, with $R_{wp} = 0.212$ and $R_E = 0.168$.

3.3. Electrical resistivity

The hydrothermally grown cluster of crystals ($0.6 \times 1.3 \times 2.7$ mm) of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ was used to make four-probe electrical resistivity measurements from 4.2 to 298 K. The technique is described by Bither, Gillson & Young (1966). As shown in Fig. 2, $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ exhibits typical metallic conductivity, with

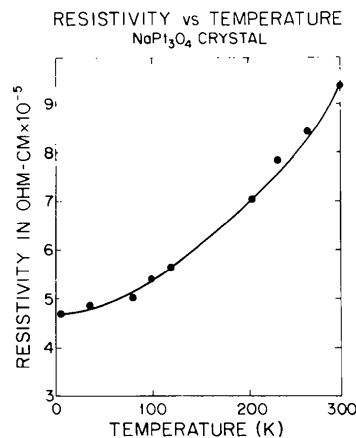


Fig. 2. Electrical resistivity of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$.

resistance increasing as a function of temperature. This type of behavior, with $\rho(293 \text{ K}) = 9 \times 10^{-7} \Omega\text{m}$, results from interaction along the chains of closely spaced Pt atoms.

Shannon (1969) reports metallic conductivity in a crystal chip of $\text{Na}_x\text{Pt}_3\text{O}_4$ where the value of x is not ascertained. The room-temperature resistivity is given as $\rho(293 \text{ K}) = 6 \times 10^{-6} \Omega\text{m}$. Measurements on a polycrystalline pellet of $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ by Cahen, Ibers & Wagner (1974) yield a value for room-temperature resistivity of $\rho(293 \text{ K}) = 3 \times 10^{-4} \Omega\text{m}$. Because the present results are obtained on single crystals, they are probably the most representative measurements of the inherent electrical resistivity of any well-characterized $\text{Na}_x\text{Pt}_3\text{O}_4$ sample.

The electrical properties for $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$ determined in the present study, as well as the results cited above, are at variance with the work of Lazarev & Shaplygin (1978a,b,c). They report semiconductor behavior for $\text{Na}_x\text{Pt}_3\text{O}_4$ and other $M_x\text{Pt}_3\text{O}_4$ phases with $M = \text{Mg, Ca, Ba, Zn, Cd, Ni, Co, and Cu}$. However, Lazarev & Shaplygin perform their measurements on polycrystalline specimens, and as such their results cannot be considered as reliable as the present study.

4. Discussion

The method of profile analysis of neutron powder diffraction data yields a satisfactory structure refinement for stoichiometric $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$. The agreement between chemical analysis and occupancy parameter, the values of thermal parameters for sodium and oxygen, and the discrepancy factors all attest to the relatively high quality of this sample and the suitability of this method for structure refinement. The data for $\text{Na}_{0.73}\text{Pt}_3\text{O}_4$, though impaired by relatively broad and weak diffraction peaks, are also able to produce an acceptable refinement. The agreement on sodium content obtained from the structure refinements, atomic

absorption analyses, and interpolation of unit-cell dimensions provide a basis for future studies of crystal chemistry in non-stoichiometric $M_xPt_3O_4$ compounds. A neutron powder diffraction study of $Li_xPt_3O_4$, $Co_xNa_yPt_3O_4$, and $Ni_xNa_yPt_3O_4$ is now in progress (Schwartz, Parise, Prewitt & Shannon, 1981).

Some of the physical characteristics of $Na_xPt_3O_4$ can be explained by examination of its structure. In particular, structural considerations are essential for explaining electrical properties of $M_xPt_3O_4$ compounds. As shown in Fig. 3, $Na_{1.0}Pt_3O_4$ consists of infinite stacks of square-planar PtO_4 groups extending along all three crystallographic axes. These groups are parallel to each other and separated by edges of other PtO_4 groups, allowing for strong Pt–Pt interactions. The Pt–Pt distance in the structure is 2.843 Å, only slightly longer than the 2.775 Å Pt–Pt distance found in platinum metal. This metal–metal distance is considerably shorter than the critical internuclear separation, R_c , that Goodenough (1963) defines as the maximum internuclear separation such that outer electrons are best described as high-mobility collective (MO) electrons. Based on semi-empirical physical arguments, Goodenough (1963) calculates a value of $R_c = 4.2$ Å for platinum in oxide structures. This number, though approximate, provides a guide for prediction of electrical conductivity in metallic oxides. The strong cation–cation interaction resulting from this small Pt–Pt separation involves the delocalization of d electrons, and the platinum substructure can be thought of as the major path for the transport of these collective electrons (Cahen, Ibers & Wagner, 1974). Thus, $Na_xPt_3O_4$ is probably a class I metallic oxide (Goodenough, 1971) where, in the absence of bridging oxygen anions, a small cation–cation separation, in itself a consequence of the $Na_xPt_3O_4$ structure, is responsible for the presence of delocalized d electrons and the concomitant metallic conductivity.

The non-stoichiometric nature of many $M_xPt_3O_4$ derivatives including $Na_{0.73}Pt_3O_4$ is believed to be another manifestation of the presence of delocalized

conduction electrons within the platinum substructure. Conduction electrons can vary in concentration relative to the sodium content of a particular sample. This variation allows for charge compensation regardless of the total charge contribution of the counterion and enables the diversity of counterion content and valence states seen in compounds with the $Na_xPt_3O_4$ structure.

The observed conductivity of $Na_{1.0}Pt_3O_4$ can also be used to confirm the characterization, by Robin & Day (1967), of $Na_xPt_3O_4$ as a class III-B mixed-valence compound. This assignment, based primarily on the presence of a single Pt site with a formal valence of $\frac{2}{3}$, is also made for $Ni_{0.25}Pt_3O_4$ (Cahen, Ibers & Shannon, 1972) and is perhaps valid for other $M_xPt_3O_4$ compositions. Compounds of class III-B are described by Robin & Day as having indistinguishable metal ions in exactly equivalent sites with associated delocalized electrons. In an approach similar to that of Goodenough described above, Robin & Day require a molecular-orbital scheme to describe the ground state of the delocalized electrons of such a system. In both cases, the application of the MO approach results in a band model for the collective electrons (Goodenough, 1963). This type of description is consistent with our present understanding of $Na_xPt_3O_4$. Future studies on $Na_xPt_3O_4$ and other compositions with this general structure should further elucidate the relationship between the structure and physical properties of these compounds.

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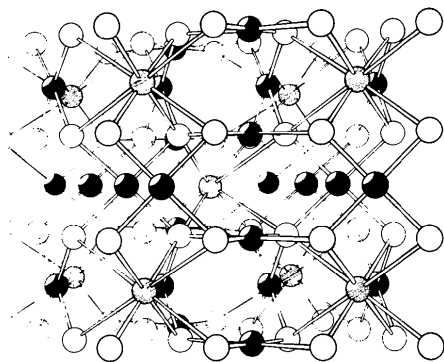


Fig. 3. The structure of $Na_{1.0}Pt_3O_4$. The filled circles are platinum in square-planar coordination. The shaded circles are eight-coordinated sodium and the open circles are oxygen.

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Compounds with Perovskite-Type Slabs. V. A High-Temperature Modification of $\text{La}_2\text{Ti}_2\text{O}_7$

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Abstract

$\text{La}_2\text{Ti}_2\text{O}_7$ with the monoclinic space group $P2_1$ transforms its structure into one with the orthorhombic space group $Cmc2_1$ at approximately 1053 K. The orthorhombic structure at 1173 ± 10 K with $a = 3.954$ (2), $b = 25.952$ (8) and $c = 5.607$ (2) Å and $Z = 4$ has been determined from three-dimensional X-ray diffraction data and refined to a conventional R value of 0.066 for 766 observed reflexions. The crystal is essentially isostructural with that of $\text{Sr}_2\text{Nb}_2\text{O}_7$, in which

all atoms are on the mirror plane at $x = 0$ or 0.5 and the corner-shared BO_6 octahedra and A atoms with twelve coordination form perovskite-type slabs. The structural change between the orthorhombic and monoclinic modifications is characterized by displacements of La atoms taking place within the respective planes perpendicular to the a axis on which the relevant La atoms lie, and by rotations of TiO_6 octahedra around axes parallel to the b axis and running through the respective Ti atoms. No significant displacement of the Ti positions occurs. Half of the mirror planes in the orthorhombic modification are lost on the phase transition and the remaining half survive as local mirror

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