JOURNAL OF SOLID STATE CHEMISTRY **21**, 277–282 (1977)

# Synthesis and Structure of $BaPtO_3$

P. K. GALLAGHER, D. W. JOHNSON, JR., E. M. VOGEL, G. K. WERTHEIM,
AND F. J. SCHNETTLER

*Bell Laboratories, Murray Hill, New Jersey 07974*

Received October 28, 1976; in final form February 14, 1977

$BaPtO_3$ was prepared by the reaction of $BaO_2 + PtO_2$ at high $O_2$ pressures and by the thermal decomposition of $BaPt(OH)_6$ at 500–700°C in $O_2$ at 1 atm. The powder pattern can be indexed based on a hexagonal cell with $a = 5.64$, $c = 27.44$ Å, corresponding to a 12-layer perovskite structure. The Oxygen content of $BaPtO_{3-x}$ materials was determined by firing the samples in $H_2$ to form $Ba(OH)_2 + Pt$ and calculating $x$ from the weight loss.

## Introduction

In recent years a variety of transition metal ions in oxides having the perovskite structure have received considerable attention as catalysts for the oxidation of CO and hydrocarbons and for the reduction of $NO_x$ (*1–7*). Platinum or other noble metals have sometimes been deliberately added to these materials in order to enhance their activity as oxidation catalysts in the presence of $SO_2$ or they may also have become incorporated in these materials as an impurity during processing or crystal growth in platinum containers (*8*, *9*).

Recent work has shown that Pt in $La_{0.7}Pb_{0.3}MnO_3$ is present as the dissolved tetravalent ion (*9*). It was also shown that $Pt^{4+}$ in this structure enhanced the activity for CO oxidation by an amount disproportionally large compared to the amount present. This could be explained if $Pt^{4+}$ were more active than the normally used metal or if the Pt were concentrated near the surface. To test the first hypothesis, a compound not unlike the simple perovskite containing a known even distribution of $Pt^{4+}$ was needed. This then served as the initial motivation for synthesizing $BaPtO_3$ which had been previously shown to exist by Schneider and McDaniel (*10*). The successful synthesis of this compound has led to studies (*9*) showing that $Pt^{4+}$ in $BaPtO_3$ is about twice as catalytically active for CO oxidation as is Pt metal.

Two general approaches were taken. The first involves the more common technique of mixing the appropriate oxides in the proper amounts and then firing to achieve a complete reaction. It was recognized that, because of the tendency of platinum(IV) toward reduction, this would require a high pressure of oxygen at the elevated temperatures. The second approach was to seek a suitable precursor compound of the proper stoichiometry which would readily decompose and subsequently react at such a sufficiently low temperature that high-pressure facilities would not be needed. Both approaches proved successful.

## Experimental Procedures

For high-pressure synthesis, equimolar amounts of $BaO_2$ (Fisher Scientific Co.) and $PtO_2$ (Alpha Inorganics) were mixed and lightly pressed into pellets. These pellets were wrapped with Pt foil, placed in a Pt tube which was then partially filled with an equimolar mixture of $BaO_2$ and $TiO_2$ (to provide an $O_2$ atmosphere upon reaction), and sealed under vacuum by electron beam welding.

ISSN 0022-4596

This tube was placed in a hot isostatic press and fired at 1000°C for 2hr in He at 28,000 psi. The surface area of the product was 1.3 $m^2/g$.

In the precursor approach, $BaPt(OH)_6$ was chosen as the candidate material. It was prepared as described by Tromel and Lupprich (*11*). Thermogravimetric (TG) experiments were performed using a Perkin–Elmer TGS-1 balance which has been modified to give a digital output (*12*, *13*). Experiments were performed in $O_2$, Ar, or $H_2$ at 40 $cm^3$ $min^{-1}$ with a heating rate of 10°C $min^{-1}$. Differential thermal analysis (DTA) of $BaPt(OH)_6$ was done using the DuPont 900 thermoanalyzer at a heating rate of 10°C $min^{-1}$ in either $O_2$ or $N_2$ at 500 $cm^3/min^{-1}$. Evolved gas analysis (EGA) was performed by heating the sample at 6°C $min^{-1}$ under vacuum ($\sim 10^{-7}$) and repeatedly scanning selected mass peaks using a quadrupole mass spectrometer (UTI Co., Model 100C).

X-ray diffraction patterns of the product from the hot isostatic press and from samples of $BaPt(OH)_6$ calcined at various conditions were made using both an automated Diano XRD 8000 system and a Guinier camera with Cu*Kα* radiation. Atomic absorption spectroscopy established that the Ba to Pt ratio was 1.0 for both products.

X-ray photoelectron spectra (XPS) were made of samples prepared by mounting powdered material with conducting epoxy cement. The data were taken in an HP5950A spectrometer using monochromatized Al*Kα* radiation. In order to overcome a strong tendency of the sample surface to acquire a positive charge the samples were flooded with low-energy electrons from a hot filament. The electron current was adjusted to optimize the lineshape. Because of this the binding energy scale is not absolute, a common problem in XPS spectra of insulators.

## Results and Discussion

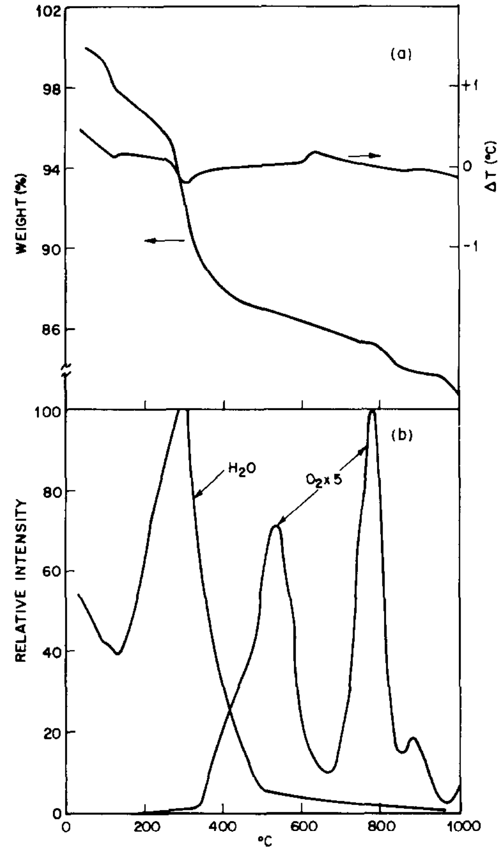

FIG. 1. Thermal analytical curves for the decomposition of $BaPt(OH)_6 \cdot 0.5H_2O$. (a) TG and DTA, in $O_2$ at 10°/min. (b) EGA, under vacuum at 6°/min.

Figure 1 shows the TG and DTA curves for $BaPt(OH)_6$ heated in $O_2$ and the EGA curve. Differences in thermal and atmospheric environments make direct correspondence between temperature scales impractical. The loss of water is evident in two stages with the major amount occurring in the second stage around 250–400°C. The exothermic peak near 600° may be due to crystallization of the poorly formed $BaPtO_3$ or possibly to the reaction of separate products from the decomposition of the hydroxide to form $BaPtO_3$. Evidence given later, however, suggests the former explanation. Oxygen is evolved in steps to form $BaPtO_{3-x}$ as subsequently described.

The weight loss agrees well with the decomposition scheme indicated below.

$$BaPt(OH)_6 \cdot 0.5H_2O \xrightarrow[-2.0\,wt\%]{\sim 100^\circ} BaPt(OH)_6 + 0.5H_2O \quad (1)$$

$$BaPt(OH)_6 \xrightarrow[-12.2\,wt\%]{\sim 300^\circ} BaPtO_3 + 3H_2O \quad (2)$$

$$BaPtO_3 \xrightarrow{>650^\circ} BaPtO_{3-x} + x/2\ O_2 \quad (3)$$

Equation (3) may take place in steps with the possible formation of new structures and intermediates. A more detailed analysis of the oxygen loss is deferred until after the X-ray diffraction and XPS spectra have been presented.

X-ray diffraction results based on a Guiner photograph taken with $CuK\alpha$, radiation for the HP preparation are given in Table I. The relatively poor pattern of broad lines can be fitted to a hexagonal unit cell with $a = 5.64$ and $c = 27.44$ Å. This suggests a 12-layer perovskite structure with 12 formulas per unit cell and a calculated density of 10.03 g $cm^{-3}$. This same X-ray pattern was obtained from $BaPt(OH)_6$ when heated to 600 or 700°C in $O_2$. At 500°C in $O_2$ a very weak diffuse pattern appeared which correlated well with this pattern.

It must be emphasized that this assignment of structure is far from unequivocal because of the poorly crystaline sample and the lack of a single crystal. The hexagonal cell proposed does fit the data in Table I slightly better than the orthorhombic cell proposed by Schneider and McDaniel (*10*). Both of these cells and the others tried in this study which gave reasonable fits to the data are all large and the ratio of lines observed to those calculated is small. However, the layered perovskite structure has been observed for $BaRuO_3$ (*14*) and it seems reasonable to expect a layered perovskite in this system because of the similarities in the size, charge, and nature of $Ru^{4+}$ and $Pt^{4+}$ ions. Both the oxygen stoichiometry and the Ba/Pt ratio are factors considering the wide range of solid solution toward the Pt-rich material proposed by Schneider and McDaniel (*10*).

TABLE I

POWDER DIFFRACTION DATA FOR $BaPtO_3$

| $h$ | $k$ | $l$ | $d_{calc}$ | $d_{obs}$ | $I$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 4.884 | 4.885 | S |
| 1 | 0 | 5 | 3.648 | 3.650 | S |
| 1 | 1 | 0 | 2.820 | 2.821 | VS |
| 1 | 1 | 1 | 2.805 | | |
| 1 | 1 | 2 | 2.762 | 2.758 | W |
| 1 | 1 | 4 | 2.608 | 2.615 | W |
| 2 | 0 | 0 | 2.442 | 2.443 | W |
| 2 | 0 | 2 | 2.404 | | |
| 1 | 1 | 6 | 2.400 | 2.399 | W |
| 2 | 0 | 5 | 2.321 | 2.234 | M |
| 1 | 1 | 10 | 1.966 | 1.964 | W |
| 2 | 1 | 0 | 1.846 | 1.841 | W |
| 2 | 1 | 1 | 1.842 | | |
| 2 | 1 | 2 | 1.829 | | |
| 2 | 1 | 5 | 1.749 | 1.750 | W |
| 0 | 0 | 16 | 1.715 | 1.717 | W |
| 3 | 0 | 0 | 1.628 | 1.628 | M |
| 2 | 2 | 1 | 1.408 | 1.408 | W |
| 3 | 1 | 4 | 1.329 | 1.329 | W |
| 2 | 2 | 7 | | | |

At 800°C and above in $O_2$ another pattern occurred along with that of $BaPtO_3$. This grew in intensity, predominating at 900 and 1000°C in $O_2$, and was particularly strong for material quenched from 1000°C in $O_2$. The pattern for metallic Pt also appeared at the higher temperature. Table II summarizes the X-ray diffraction pattern, after subtraction of the lines due to Pt, for the oxygen-deficient material obtained by heating to 1000°C in $O_2$ and quenching. Attempts to index this pattern were unsuccessful.

The XPS spectrum of $BaPtO_3$, prepared from $BaPt(OH)_6$, in the Ba 4*d* and Pt 4*f* regions is shown in Fig. 2. The upper spectrum has been shifted to align the Ba doublet. Both electrons show the expected spin–orbit splitting, with intensity rations approaching the theoretical 2:3 and 3:4, respectively. The

TABLE II

POWDER DIFFRACTION DATA FOR GROSSLY OXYGEN-DEFICIENT $BaPtO_{3-x} (x \approx 1)$

| $d_{obs}$ | $I$ |
|---|---|
| 5.027 | S |
| 3.356 | M |
| 3.290 | M |
| 2.899 | VS |
| 2.404 | W |
| 2.178 | M |
| 2.151 | M |
| 1.746 | W |
| 1.672 | M |
| 1.445 | M |

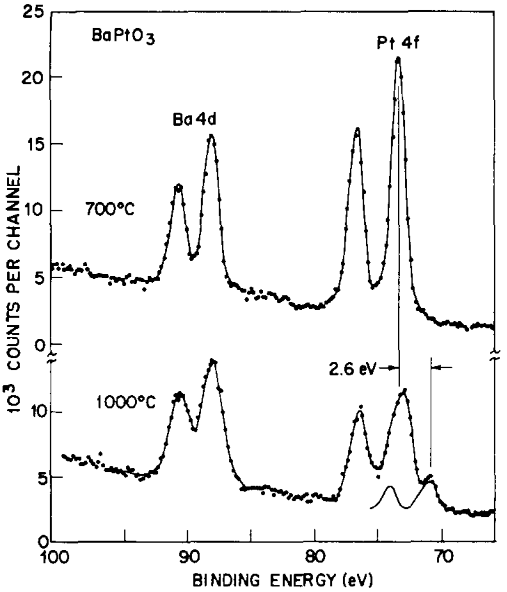

FIG. 2. X-ray photoelectron spectra of $BaPtO_{3-x}$ prepared by heating $BaPt(OH)_6 \cdot 0.5H_2O$ to the indicated temperatures in $O_2$ and quenching.

hot-pressed (HP) sample exhibited a similar spectrum. The coprecipitated material which had been heated to 1000°C and quenched shows an additional line at the low-energy side of the Pt 4*f* spectrum, which must be due to metallic Pt. This was confirmed by measurements of Pt metal deposited on $BaTiO_3$ by the decomposition of chloroplatinic acid in $H_2$ at 400°C. It is therefore one line of a spin–orbit doublet as sketched in Fig. 2. This is in accord with other information regarding decomposition on heating to 1000°C. The valence is inferred from the spacing of the doublets, since an absolute binding energy scale could not be established. The shift from metallic Pt to PtO is 1.2 eV, while that from Pt to $PtO_2$ is 3.0 eV (*15,16*). The shift of the Pt 4*f* spectrum in the 700°C spectrum is 2.6 eV relative to the metallic Pt. Although this is smaller than the shift from Pt to $PtO_2$ it is sufficiently large to exclude $Pt^{2+}$. The broadening of the Pt 4*f* lines in the 1000°C material is indicative of a mixture of $Pt^{2+}$ and $Pt^{4+}$. Because of the breadth of the lines for the higher-temperature material they are unresolved in Fig. 2. The presence of both valences is compatible with the assignment to the $BaPtO_{3-x}$ phase.

More exact data regarding the oxygen stoichiometry can be derived from the weight loss data. Figure 3 presents TG curves in Ar for $BaPtO_3$ prepared by each technique. Differences in surface area and porosity lead to substantially different rates of oxygen loss, e.g., the surface area of the HP material is 1.3 as compared to 8.1 $m^2/g$ for a sample of $BaPt(OH)_6$ decomposed at 700°C. The loss of an atom of oxygen from pure $BaPtO_3$ would correspond to a loss of 4.21 wt%. The material derived from the hydroxide is close to that level at 1000°C and the X-ray diffraction pattern of this sample corresponds well with that given in Table II. This, however, does not offer any sound basis for calculation of the oxygen loss.

In an effort to establish a well-defined weight–stoichiometry relationship at a readily accessible temperature, TG experiments were performed in flowing $H_2$. Figure 4 shows a typical curve. There is a well-defined plateau in the TG curve in the range 200–500°C which examination by X-ray diffraction revealed to be associated with $Ba(OH)_2 + Pt$. This is entirely reasonable based upon the reversibility and the high temperature of the thermal decomposition of $Ba(OH)_2$. Actual oxygen content was determined for many of the samples based upon this method and the results are summarized in Table III.

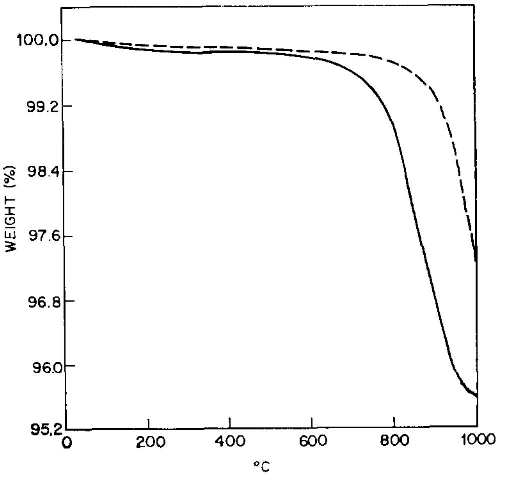

FIG. 3. TG curves for $BaPtO_3$ in Ar, 10°C/min. Solid line, $BaPtO_3$, prepared from $BaPt(OH)_6$ at 600°C. Dashed line, $BaPtO_3$, HP sample.

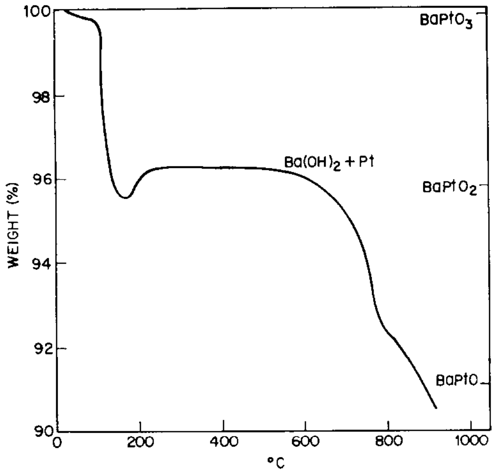

FIG. 4. TG curve of $BaPtO_3$ (HP) in $H_2$ at 10°/min.

TABLE III

OXYGEN STOICHIOMETRY OF VARIOUS $BaPtO_x$ MATERIALS

| Sample | Formula |
|---|---|
| High pressure | $BaPtO_{3.02}$ |
| $BaPt(OH)_6$ (500°C) Q[a] | $BaPtO_{2.99}$ |
| $BaPt(OH)_6$ (600°C) Q | $BaPtO_{2.99}$ |
| $BaPt(OH)_6$ (700°C) Q | $BaPtO_{2.95}$ |
| $BaPt(OH)_6$ (800°C) Q | $BaPtO_{2.84}$ |
| $BaPt(OH)_6$ (900°C) Q | $BaPtO_{2.72}$ |
| $BaPt(OH)_6$ (1000°C) Q | $BaPtO_{2.38}$ |
| $BaPt(OH)_6$ (1000°C) SC | $BaPtO_{2.60}$ |

[a] Temperature to which material has been heated for 30 min in $O_2$ and either quenched (Q) or allowed to cool slowly with the furnace (SC).

The values indicated in Table III are self-consistent. The wide variation between the slowly cooled sample and the quenched material indicates the difficulty of preparing a sample of specified nonstoichiometry. The stoichiometry of the sample quenched from 1000°C in $O_2$ does not agree well with the assignment of the X-ray pattern in Table II to nearly stoichiometric $BaPtO_{2.0}$. This is consistent with the ESCA results which also indicate incomplete reduction to $BaPtO_2$. The close correspondence of the weight loss in Fig. 3 results from the formation of some Pt.

## Conclusions

1. $BaPtO_{3.0}$ can be prepared by the reaction of $BaO_2 + PtO_2$ at high oxygen pressures or by the thermal decomposition of $BaPt(OH)_6$ in the temperature range of 500–700°C.

2. The relatively poor X-ray diffraction pattern of $BaPtO_3$ can be fit to a hexagonal layered perovskite with $a = 5.64$ and $c = 27.44$ Å.

3. The oxygen content of $BaPtO_{3-x}$ materials can be determined based on weight change upon heating the samples to ~300° in $H_2$ to form $Ba(OH)_2$ + Pt.

## Acknowledgments

The authors are grateful to Mr. S. C. Abrahams and R. L. Barns for assistance on interpretation of the X-ray data, to Mr. J. L. Bernstein for assistance in preparing the Guinier photography, to Mr. W. W. Rhodes for assistance in the high-pressure synthesis, to Mr. F. Schrey for measurements of surface area, to Mr. D. N. E. Buchanan for experimental assistance in the measurements of the XPS, and to Mr. T. Y. Kometani for the chemical analysis.

## References

1. G. PARRAVANO, *J. Amer. Chem. Soc.* **75**, 1497 (1953).
2. D. B. MEADOWCRAFT, *Nature*, **226**, 847 (1970).
3. R. J. H. VOORHOEVE, J. P. REMEIKA, P. E. FREELAND, AND B. T. MATHIAS, *Science* **177**, 353 (1972).
4. R. J. H. VOORHOEVE, J. P. REMEIKA, AND D. W. JOHNSON, JR., *Science* **180**, 62 (1973).
5. P. K. GALLAGHER, D. W. JOHNSON, JR., J. P. REMEIKA, F. SCHREY, L. E. TRIMBLE, E. M. VOGEL, AND R. J. H. VOORHOEVE, *Mater. Res. Bull.* **10**, 529 (1972).
6. S. KATZ, J. J. CROAT, AND J. V. LAUKONIS, *Ind. Eng. Chem. Prod. Res. Develop.* **14**, 274 (1975).
7. Y. Y. YAO, *J. Catal.* **36**, 266 (1975).
8. P. K. GALLAGHER, D. W. JOHNSON, JR., E. M. VOGEL, AND F. SCHREY, *Mater. Res. Bull.* **10**, 623 (1975).
9. D. W. JOHNSON, JR., P. K. GALLAGHER, G. K. WERTHEIM, AND E. M. VOGEL, *J. Catal.*, in press.

*10.* S. J. Schneider and C. L. McDaniel, *J. Amer. Ceram. Soc.* **52**, 518 (1969).

*11.* M. Tromel and E. Lupprich, *Z. Anorg. Allg. Chem.* **414**, 169 (1975).

*12.* P. K. Gallagher and F. Schrey, *Thermochim. Acta* **1**, 465 (1970).

*13.* P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta.* **4**, 283 (1972).

*14.* P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.* **4**, 306 (1965).

*15.* G. M. Bancroft, I. Adams, H. L. Coatsworth, C. G. Bennewitz, J. D. Brown, and W. D. Westwood, *Anal. Chem.* **47**, 586 (1975).

*16.* G. C. Allen, P. M. Tucker, A. Capon, and R. Parsons, *J. Electrochem.* **50**, 335 (1974), and the discussion of the earlier literature therein.