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REDUCTION CHEMISTRY OF PLATINUM GROUP METAL PEROVSKITES

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ABSTRACT

The reduction chemistry of the perovskite and perovskite-related compounds, $CaRuO_3$, $SrRuO_3$, $BaRuO_3$, $SrIrO_3$, and $BaIrO_3$, was examined. Samples were reduced at low temperatures (≤ 600°C) by direct reduction with hydrogen gas and by a method that utilized zirconium metal as an oxygen getter. No evidence for oxygen deficient perovskites was observed. In almost all cases, the mixed metal oxide was reduced to form the zero valent platinum group metal and the binary oxide or hydroxide (AO or $A(OH)_2$). One exception was seen in the reduction of $SrIrO_3$ via the getter method where the intermediate Sr_4IrO_6 was found.

MATERIALS INDEX: ruthenium, iridium, oxides, perovskites

Introduction

Numerous examples of oxygen deficient perovskites (ABO_{3-x}) with first row transition metals on the B-site have been reported. It is not known whether many of the compounds with second and third row transition metals can also support a variable oxygen stoichiometry while maintaining the perovskite structure. The purpose of this study is to investigate the redox chemistry of alkaline earth ruthenium and iridium compounds and determine if they can support such defect structures.

Many alkaline earth ruthenium and iridium compounds with perovskite and polytypic layered perovskite structures (ABO_3, where A = Ca, Sr, or Ba and B = Ru or Ir) are known. In the ruthenium system, $CaRuO_3$, (1-6) and $SrRuO_3$,(1-10) are orthorhombic perovskites while the barium compound has a nine-layered hexagonal structure, 9H-$BaRuO_3$ (1,2,4,6-8,11-13). The chemistry of the iridium system is much more complex. The $CaIrO_3$ perovskite is not easily synthesized (14-17) while a nonpolytypic layered polymorph that contains edge and corner sharing IrO_6 octahedra is readily prepared (14,18). $SrIrO_3$ occurs as a six-layered polytype (6H) under ambient conditions (19,20) and has an orthorhombic perovskite structure at high pressure (40 kbar) (19). In the Ba-Ir-O system, $BaIrO_3$ has been reported as several different polymorphs (7,11,13,18). These reports include descriptions of polycrystalline four- and nine-layered polytypes and single crystals of an eighteen-layered polytype. The polycrystalline samples could not be prepared as single phase materials

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nor could structural details be obtained from the single crystals.

The redox behavior of these compounds has not been thoroughly investigated. Randall and Ward (1) proposed that $SrRuO_3$ was oxygen deficient, but this was not substantiated by later reports (2-10). One study on the uptake of hydrogen in $BaRuO_3$ described its reduction with no mention of oxygen deficiency (12). Longo et al. found that $SrIrO_3$ formed Sr_2IrO_4 and Ir metal on reduction in hydrogen up to 400°C (19). Reller has provided the most recent investigation of any of these systems (21). When specifically looking for oxygen deficient ruthenates, he found that $CaRuO_3$ and $SrTi_{0.95}Ru_{0.05}O_3$ on reduction both resulted in the formation of elemental ruthenium.

Experimental

Preparation of Polycrystalline Samples

$CaRuO_3$ and $SrRuO_3$. $CaRuO_3$ and $SrRuO_3$ were prepared from Ru metal (Alfa 99.9%, -80 mesh) and $CaCO_3$ (Aldrich, reagent) and $SrCO_3$ (Aldrich, reagent), respectively (1). The carbonates were found to be > 99.9% by thermogravimetric analysis. Ruthenium metal and the appropriate carbonate were thoroughly mixed with a mortar and pestle, placed in an alumina crucible, and heated at 1000°C for ten days. Samples were ground daily. $CaRuO_3$ is dark grey-black and $SrRuO_3$ is black.

$BaRuO_3$. $BaRuO_3$ was prepared from ruthenium metal and anhydrous BaO_2 (Alfa) (11). Commercially available BaO_2 typically comes as a mixture of BaO_2 and $BaCO_3$. X-ray powder diffraction showed the presence of BaO_2 and infrared spectroscopy, obtained from KBr pellets, verified the presence of $BaCO_3$; IR bands characteristic of carbonates were observed at 1440 (vs, broad), 860 (s), 700 (s), and 300 cm^{-1} (s, broad) (22). Thermogravimetric analysis was performed in air and CO_2. The weight loss in air was attributed to the decomposition of BaO_2 and $BaCO_3$ to BaO. In CO_2, the weight gain was ascribed to the formation of $BaCO_3$ from BaO_2. Values for the percent BaO_2 in the sample were calculated from both analyses and were within 0.2 percent. The "BaO_2" sample contained 95.8% BaO_2 and 4.2% $BaCO_3$. Ru metal and "BaO_2" were thoroughly mixed, heated to 1000°C for ten days, and ground daily. $BaRuO_3$ is black in color.

$CaIrO_3$. It has been reported that the perovskite polymorph of $CaIrO_3$ is metastable and pure samples cannot be made by conventional solid state techniques (14). Synthetic efforts here support this observation. $CaCO_3$ and Ir metal (Æsar, 99.95%) were heated at 800°C for several days. After reacting for one day, samples were found to contain the $CaIrO_3$ nonperovskite polymorph and a small fraction of $CaIrO_3$ perovskite. With additional reaction time the perovskite phase disappeared. When the reaction temperature was increased, the $CaIrO_3$ nonperovskite was replaced by Ca_2IrO_4 and iridium metal. Overall these results were consistent with the phase diagram reported by McDaniel and Schneider (14) with the exception that the upper temperature limit of the nonperovskite polymorph was at least 50°C lower.

Sarkozy et al. have reported a precursor method for the synthesis of pure $CaIrO_3$ perovskite (15-17). This method involves the precipitation of an amorphous precursor $CaIr(OH)_6$ from an aqueous solution at high pH (> 12). An aqueous solution of $Ca(NO_3)_2$ (prepared by the dissolution of $CaCO_3$ in dilute nitric acid) and K_2IrCl_6 (Aldrich, reagent) was made basic by the slow addition of a dilute KOH solution. The pH was monitored with an Orion Research model SA250 portable pH meter equipped with an Orion combination pH electrode. The basic mixture was allowed to sit at room temperature for three days before the resultant off-white precipitate was isolated by filtration and fired in a box furnace at 650°C. Powder diffraction of the products showed the presence of the perovskite $CaIrO_3$ but it was always accompanied by a large amount of Ca_2IrO_4 ($CaIrO_3$:Ca_2IrO_4 ca. 1:2). Even after several attempts at the method outlined by Sarkozy, a single phase material could not be prepared. Modifications of this method, i.e. lower pH and/or different reaction times, were also unsuccessful.

$SrIrO_3$. $SrIrO_3$ was readily prepared from a mixture of $SrCO_3$ and Ir metal by the method of Longo et al. (19). The sample was heated at 900°C for three days and ground daily. The resulting sample was black.

$BaIrO_3$. "BaO_2" and Ir metal were combined and heated to 1000°C for two weeks with intermittent grindings. In this work a sample consisting of a single polymorph could not be prepared. The $BaIrO_3$ mixture is a black color.

Reduction Studies

The five compounds, $CaRuO_3$, $SrRuO_3$, $BaRuO_3$, $SrIrO_3$, and $BaIrO_3$, were examined to determine if they could support oxygen deficiency. Two synthetic techniques were used. The first involved the use of a gaseous reducing agent, dilute hydrogen, at low temperatures. In the second, oxygen was scavenged indirectly from the mixed metal oxides by means of an oxygen getter. Both techniques have been found to be effective in the synthesis of oxygen deficient perovskites (23-26).

Direct Reduction. Reactions were carried out on a thermogravimetric analysis instrument (TGA) in flowing dilute hydrogen (8.5% in helium, Matheson). Samples were heated isothermally at a temperature just below the onset of reduction. This temperature was determined from reduction profiles of the samples previously obtained to 1000°C. Additionally, a minimum reduction temperature was determined by slowly heating the sample until a significant rate of reduction was observed. Typical reduction rates were less than 0.005%/min.

Reduction with Zirconium. Zirconium metal will scavenge oxygen at an appreciable rate near 580°C. Perovskites can reversibly release oxygen at elevated temperatures. When perovskite samples and zirconium metal are heated together in sealed evacuated glass tubes, the degree to which the perovskite is reduced can be regulated by simply controlling the perovskite to zirconium metal ratio. Initially, stoichiometric amounts of mixed metal oxide (ca. 0.5 g) and zirconium metal (-20 to +60 mesh, Alfa 99.9%) were weighed out separately into small dry fused silica vials (7 mm o.d.) on an analytical balance. The vials were placed into a dry 12 mm o.d. fused silica tube that was then sealed under vacuum ($< 10^{-4}$ torr). Samples were slowly heated over two days to 600°C. A chromel-alumel thermocouple was placed within a few millimeters of the reaction end of the sealed tube to monitor the temperature. Typical reaction times were ten days, with the completion of the reaction judged by the conversion of the dark grey coarse grained zirconium metal to an off-white fine ZrO_2 powder. Samples were reweighed after the fused silica tubes were opened to verify that complete reaction had occurred. Because some oxygen deficient perovskites are known to be sensitive to oxidation when exposed to air (26), sealed tubes were routinely opened under a nitrogen atmosphere in a dry box.

Some oxygen deficient perovskites are not stable at elevated temperatures (26) and therefore, cannot be heated to the temperature required for the oxidation of zirconium metal (580°C). In this case, temperature gradients would be effective in the synthesis of thermally sensitive compounds. In a nonisothermal approach, zirconium metal was heated to 600°C or above, while the mixed metal oxide was held at a lower temperature. To determine the minimum temperature required for reduction, the temperature of the oxide was raised until oxidation of the zirconium was observed. A two-zone furnace was employed.

Characterization

X-ray Diffraction. Polycrystalline samples were characterized by X-ray powder diffraction (XRD). A Rigaku Geigerflex diffractometer, equipped with Cu Kα radiation ($\lambda = 1.54178$ Å) and a Ni filter, was used to obtain data at room temperature. Typical powder patterns were obtained in the range $5° \leq 2\theta \leq 80°$ in increments of 0.02° with 10 sec. count times. Silicon (NIST) was used as an internal standard. A fitting program, XRAY-FIT (27), was used to determine peak position and intensity. The program LAZY-PULVERIX (28) was used to generate powder patterns of known structures. Lattice parameters were refined with the program POLSQ (29).

Thermogravimetric Analysis. Thermogravimetric measurements were performed on a Du Pont 9900 thermal analysis system. Oxygen contents were determined by reduction of the mixed metal oxides in dilute hydrogen. Generally flow rates of 25 cc./min. were used with heating rates of 10°C/min. Weight losses were attributed to the reduction of Ru(IV) or Ir(IV) to Ru(0) and Ir(0), respectively. The formation of the zero valent metals was verified by the examination of the products with XRD. The weight percents of oxygen calculated from the reductions of $CaRuO_3$, $SrRuO_3$, $BaRuO_3$, $SrIrO_3$, and $BaIrO_3$ were all within 0.1% of the theoretical values.

Results

$CaRuO_3$. The X-ray powder diffraction pattern of $CaRuO_3$ can be indexed on an orthorhombic unit cell (a = 5.364(2), b = 5.536(2), and c = 7.673(4) Å). Calculated and observed reflections are listed in Table 1. Refined lattice parameters are consistent with those reported in the literature (1,5). The powder diffraction pattern, however, does not match the one reported by Van Loan (4). Some reflections seen by Van Loan were not observed in the present study. Though these additional peaks could correspond to a polymorph of $CaRuO_3$, it is more likely that they are due to a completely different phase. The Ca-Ru-O phase diagram is not known but additional compounds, such as Ca_2RuO_4, may exist. It should be noted that the two reflections at d = 3.17 and 2.55 Å in the pattern reported by Van Loan correspond to the two most intense reflections of RuO_2 (30). The $CaRuO_3$ XRD pattern was also found to contain reflections not observed by Van Loan (Table 1). These were of relatively low intensity and could be indexed on the same unit cell.

TABLE 1

X-ray Powder Diffraction Data for $CaRuO_3$.

hkl	d_{obs}	d^{a}_{calc}	d^{b}_{lit}	$(I/I_1)^{c}$
110	3.849	3.852	3.85	68.0
111	3.444	3.443	3.45	2.3
102[d]	---	---	3.17	---
020	2.769	2.768	2.77	20.2
112	2.719	2.718	2.72	100.0
200	2.682	2.682	2.68	36.5
021[e]	2.606	2.604	---	0.4
003[d]	---	---	2.56	---
210	2.414	2.414	2.41	1.0
121[e]	2.343	2.342	---	0.3
211	2.305	2.302	2.304	5.0
022	2.245	2.245	2.243	1.4
202	2.198	2.198	2.201	2.6
113	2.131	2.131	2.127	2.3
122[e]	2.071	2.071	---	1.3
220	1.923	1.926	1.926	53.9
023[e]	1.879	1.879	---	1.0
221	1.869	1.868	1.870	1.8
104[d]	---	---	1.814	---
130	1.746	1.745	1.746	7.7
222	1.720	1.721	1.719	21.4
310	1.702	1.701	1.704	7.4
132	1.589	1.588	---	14.0
024	1.577	1.577	---	10.7
312	1.557	1.555	---	47.0
133	1.440	1.441	---	3.0
040	1.385	1.384	---	2.7
224	1.359	1.359	---	16.7
400	1.341	1.341	---	5.5
410	1.303	1.303	---	2.3
134	1.291	1.291	---	7.7
314	1.270	1.273	---	8.1
240	1.231	1.230	---	2.7
241	1.214	1.214	---	25.9

[a] Data was refined on an orthorhombic unit cell where a = 5.364(2), b = 5.536(2), and c = 7.673(4) Å.

[b] Data from reference 4. Only reflections up to 50°2θ were reported.

[c] Relative intensity times 100.

[d] Reflections observed in reference 4 not observed in this work.

[e] Minor reflections not reported in reference 4.

TGA showed that the reduction of $CaRuO_3$ in dilute hydrogen occurred in a single step. The onset was at ca. 425°C with a midpoint at 500°C. Complete reduction to CaO and Ru(0) required an isotherm at 1000°C for 60 min. The TGA scan did not show an obvious inflection that could be associated with an oxygen deficient perovskite (23). Initially, to examine whether $CaRuO_3$ could support oxygen deficiency, reductions in hydrogen were carried out at temperatures just below the onset. Isotherms at 400°C and 375°C resulted in the reduction of $CaRuO_3$ directly to ruthenium metal (eqn. 1).

$$CaRuO_3 + 2\ H_2 \rightarrow CaO + Ru + 2\ H_2O \qquad \text{(eqn. 1)}$$

Subsequently, the minimum temperature required for reduction was found to be ca. 300°C. Even at this temperature $CaRuO_3$ was reduced to ruthenium metal.

Reductions via a zirconium getter produced similar results (eqn. 2).

$$CaRuO_3 + (Zr) \rightarrow CaO + Ru + (ZrO_2) \qquad \text{(eqn. 2)}$$

Reactions investigated at 600°C by a single zone method with compositions set to x = 0.5 and x = 0.25 for ABO_{3-x}, resulted in the formation of ruthenium metal. Subsequent reductions with a two-zone approach at 375°C (x = 0.20) again produced Ru(0). Reductions below 375°C did not proceed at an appreciable rate. (Note: The parentheses around Zr and ZrO_2 in eqns. 2, 4 and 5 are to indicate that these materials are isolated from the rest of the sample.)

In general, reduced samples were found by XRD to contain unreacted starting material and the zero valent platinum group metal. The XRD pattern of the product mixture from a reduction of $CaRuO_3$ at 400°C in hydrogen is shown in Figure 1. It is typical for reductions done at lower temperatures. The ruthenium metal peaks at 38.4°, 42.2°, and 44.0°2θ (40%, 35%, and 100% reported relative intensities (31), respectively), are quite broad due to a lack of crystallinity. Samples reduced at higher temperatures had much sharper peaks.

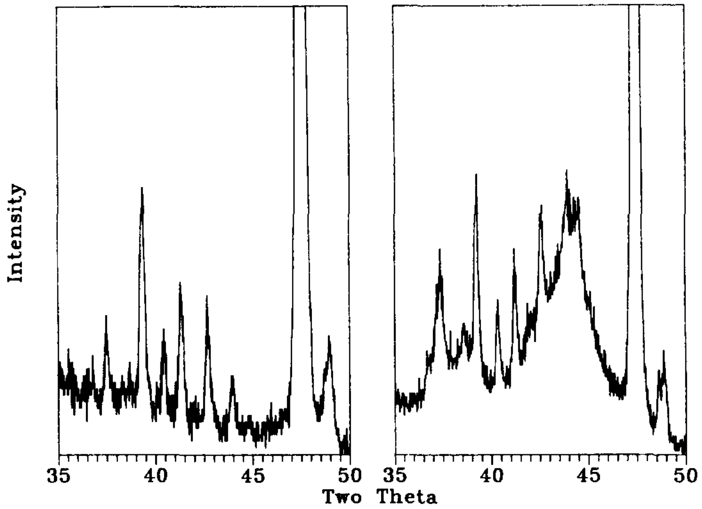

FIG. 1

Comparison of X-ray powder diffraction patterns of $CaRuO_3$ before (left) and after (right) reduction.

Though the alkaline earth oxide is the assumed reduction by-product with the platinum group metal, the corresponding reflections were often not observed even for samples completely reduced in hydrogen at over 1000°C. This was especially true for samples exposed to air. The formation of an amorphous hydroxide is expected to readily occur on exposure to moisture in the atmosphere.

$\underline{SrRuO_3}$. The X-ray powder diffraction data for $SrRuO_3$ varies slightly from that calculated from the recent structure determination (neutron powder diffraction) of Jones et al (10). When three minor reflections (d = 3.074, 2.208, and 1.775 Å; I/I_1 = 0.7, 0.2, and 0.3, respectively) are ignored, the data are in good agreement with their values. The extra reflections may, however, be significant. Because they don't appear to belong to any of the known phases in the Sr-Ru-O system, the possibility that they may be attributed to superstructure was examined. It was found that when the a-axis is doubled, these extra reflections could be indexed on the supercell a = 11.12(2), b = 5.536(9), and c = 7.82(2) Å.

Van Loan also reported an XRD pattern of $SrRuO_3$ (4). Again it contained additional reflections (d = 3.18 and 2.55 Å). These were not observed here or by Jones et al. (10) and strongly indicate that Van Loan's preparations contained excess RuO_2.

The redox behavior of $SrRuO_3$ is very similar to $CaRuO_3$. On heating in dilute hydrogen, the compound was reduced to SrO and Ru metal in a single step. Again, to look for oxygen deficient perovskites, samples were heated isothermally on the TGA. The minimal temperature necessary for reaction was ca. 350°C. Reductions resulted in the formation of zero valent ruthenium metal and $Sr(OH)_2$ (eqn. 3), with no indication of intermediates.

$$SrRuO_3 + 2\ H_2 \rightarrow Sr(OH)_2 + Ru + H_2O \qquad \text{(eqn. 3)}$$

Reductions conducted with zirconium metal also produced Ru metal. Two-zone reactions were carried out at 450°C for x = 0.5 (in ABO_{3-x}) and 375°C at x = 0.2.

$\underline{BaRuO_3}$. The X-ray powder diffraction data of $BaRuO_3$ is in good agreement with the literature (1,11).

The reduction behavior of $BaRuO_3$ observed on the TGA differs from that of $CaRuO_3$ and $SrRuO_3$ but is consistent with the literature (12). The thermogram shows two intermediate steps centered at 580°C and 720°C. Both steps are beyond the composition range typical for oxygen deficient perovskites ($0 \le x \le 0.5$, for ABO_{3-x}). An isotherm at 450°C for one hour resulted in a continuous weight loss. XRD showed that this sample contained unreacted $BaRuO_3$ and a substantial amount of ruthenium metal. In another experiment, the minimal temperature necessary for reduction was found to be approximately 350°C. An isotherm at this temperature also reduced the sample to ruthenium metal. $Ba(OH)_2$ was initially detected by XRD, but after a thirty minute exposure to the air, reflections from this material could no longer be observed. No indication of the presence of an oxygen deficient perovskite was found at either temperature.

$BaRuO_3$ was reduced by Zr at 425°C (x = 0.50) and 375°C (x = 0.20). The sample at 425°C resulted in ruthenium metal and unreacted starting material. Reaction at 375°C did not occur even after several months.

$\underline{SrIrO_3}$. The XRD pattern obtained for $SrIrO_3$ agrees with data reported by Longo et al. (19).

The TGA of $SrIrO_3$ in hydrogen indicated that this compound began to be significantly reduced at low temperature (< 200°C). The first step in the reduction has a midpoint at ca. 230°C. If an oxygen deficient perovskite were present, the first plateau would correspond to a composition of $SrIrO_{2.73}$. Many oxygen deficient perovskites, like $CaMnO_3$ and $YBa_2Cu_3O_7$, (32,33) are known to release oxygen at elevated temperatures in air. When $SrIrO_3$ was heated in air above 1000°C, it showed no weight loss. An isotherm at 200°C in hydrogen was employed to reduce this material. Reduction resulted in the formation of iridium metal. An XRD pattern of the reduced sample showed unreacted $SrIrO_3$ along with an extremely broad iridium metal reflection (width > 5°2θ) centered around 40°2θ and $Sr(OH)_2$. No evidence for additional phases was seen.

Reduction with Zr metal was investigated at 375°C for a composition of x = 0.2 in $SrIrO_{3-x}$ by a two-zone approach. Longo et al. (19) had reported that the reduction of $SrIrO_3$ in hydrogen proceeded through an Sr_2IrO_4 intermediate. The reaction done here resulted in the formation of Sr_4IrO_6: no Sr_2IrO_4 was observed. Sr_4IrO_6 was accompanied by unreacted $SrIrO_3$ and Ir metal. The reaction appears to proceed as in eqn. 4.

$$4SrIrO_3 + 3(Zr) \rightarrow Sr_4IrO_6 + 3Ir + 3(ZrO_2) \qquad \text{(eqn. 4)}$$

An indirect formation of Sr_4IrO_6 from SrO and $SrIrO_3$ (eqns. 5-6) is

$$SrIrO_3 + (Zr) \rightarrow SrO + Ir + (ZrO_2) \quad \text{(eqn. 5)}$$

$$3SrO + SrIrO_3 \rightarrow Sr_4IrO_6 \quad \text{(eqn. 6)}$$

also plausible, but eqn. 6 would be surprising when one considers the low temperature of 375°C.

$\underline{BaIrO_3}$. Initially, Rodi and Babel (18) reported the growth of $BaIrO_3$ single crystals with a rhombohedral unit cell (a = 5.76 and c = 44.5 Å) and had suggested that the structure was 18-layered. Around the same time, Donohue et al. (7,11) reported the synthesis of both polycrystalline and single crystals of $BaIrO_3$. Part of the XRD pattern of the polycrystalline material (not reported) could be indexed on a hexagonal unit cell (a = 5.76 and c = 22.2 Å) that indicated a 9-layer structure. To carry out this indexing, however, several reflections had to be ignored. Single crystal data, like Rodi and Babel's, showed a doubled c-axis (44.4 Å). A complete structure determination was not obtained. A high resolution electron microscopy study (HREM) by Gai et al. (13) found that polycrystalline samples contained both the 9-layer and a 4-layer stacking sequence. No evidence for an 18-layer structure was observed. Other samples were prepared at a higher temperature (1400°C) and showed an orthorhombic superlattice, a = 11.8, b = 20.4, and c = 21.2 Å. It is not particularly surprising, considering the size of the unit cell, that the diffraction pattern for this sample was successfully indexed. Details of the XRD pattern were not presented.

Synthetic efforts here also didn't produce a single phase material. Though not rigorously indexed, the sample appeared to primarily contain the 9-layered polytype. Other reflections could be assigned to the 4-layered, the 18-layered, and the large cell reported by Gai et al., as well. If all of these common reflections are in fact significant, then the polytypism of this compound is extremely complex. None of the known binary phases in the Ba-Ir-O system (BaO, Ir_2O_3, and IrO_2) were observed. Other ternary phases in the Ba-Ir-O system have not been reported.

Though a single phase material could not be obtained, attempts to synthesize oxygen deficient $BaIrO_3$ were still undertaken. It is known that in some systems specific polytypes occur for specific oxygen compositions (e.g. $SrMnO_{3-x}$ and $BaMnO_{3-x}$) (34,35). This allows for the possibility that a single phase oxygen deficient material might be accessible. The TGA of the $BaIrO_3$ mixture to 1000°C in hydrogen was very similar to that of $BaRuO_3$. Reductions with hydrogen at 200°C and zirconium at 400°C (x =0.25) still resulted in the formation of Ir metal.

Summary. A summary of the reduction conditions for all the above experiments are presented in Tables 2 and 3. No evidence for oxygen deficient phases was seen on the reduction of any of these compounds. Except for the case of $SrIrO_3$, that showed the intermediate Sr_4IrO_6, all reactions resulted in the direct formation of zero valent platinum group metal from the parent oxide.

None of the reactions listed in Tables 2 and 3 showed the presence of an alkaline earth oxide by XRD. As stated above, when samples were reduced above 1000°C, the oxide could sometimes be observed. At these lower temperatures the only form of the Group 2 metal found was the hydroxide and this was only possible for reactions in hydrogen. When the alkaline earth oxide does form in these reactions, it would appear that it is amorphous.

Discussion

The inability to readily synthesize oxygen deficient perovskites ABO_{3-x} with the second and third row transition metals, Ru and Ir, is in marked contrast to what is observed for analogous first row transition metal systems. Compounds with first row transition metals from the same families (Fe and Co), for instance, can lose oxygen over a wide compositional range and still maintain perovskite related structures (36). In these systems the B-cation is known to direct the vacancy orderings of the oxygen deficient perovskites through its coordination preferences. It is therefore not surprising that the B-cation also plays a crucial role in the accessibility and stability of oxygen deficient perovskites that contain second and third row transitions metals.

Consider the formation of an oxygen deficient perovskite (ABO_{3-x}) from the corresponding parent oxide (ABO_3). This event requires that the B-cation must be able to achieve and maintain both a lower formal valence and lower

TABLE 2

Summary of Results for Isothermal Reductions with Dilute Hydrogen.

Compound	Temperature	Product(s)[a]
$CaRuO_3$	400	Ru
	375	Ru
	300[b]	Ru
$SrRuO_3$	350[b]	Ru, $Sr(OH)_2$
$BaRuO_3$	450	Ru
	350[b]	Ru, $(Ba(OH)_2)$[c]
$SrIrO_3$	250	Ir, $Sr(OH)_2$
	200[b]	Ir
$BaIrO_3$	200[b]	Ir

[a] Products observable by XRD.
[b] Approximate minimum temperature required for reduction.
[c] Reflections due to $Ba(OH)_2$ disappeared after exposure to air.

TABLE 3

Summary of Results for Reductions with Zirconium.

Compound	Temperature	Composition	Product(s)[a]
$CaRuO_3$	600	0.50	Ru
	600	0.25	Ru
	375	0.20	Ru
$SrRuO_3$	425	0.50	Ru
	375	0.20	Ru
$BaRuO_3$	425	0.50	Ru
	375[b]	0.20	--
$SrIrO_3$	375	0.20	Ir, Sr_4IrO_6
$BaIrO_3$	400	0.25	Ir

[a] Products observed by XRD.
[b] No reduction occurred at this temperature.

coordination number. On reduction the cation is converted from tetravalent to trivalent with the stability of the reduced compound strongly influenced by the stability of the lower oxidation state with respect to further reduction or disproportionation. For those compounds that contain first row transition metals, accessibility and stability is not a problem and consequently the trivalent oxidation state is common in these oxides. In the case of Ru and Ir, however, there is an inherent thermodynamic instability with respect to reduction that is common to late second and third row transition metals. For example, the free energy values for the formation of their binary oxides are considerably closer to zero than those of first row transition metals (37,38). There may be further instability specifically associated with Ru^{3+} and Ir^{3+}. In the binary oxides, compounds of the tetravalent metals are very stable (RuO_2 and IrO_2) while those of the trivalent metals are not; Ru_2O_3 does not exist (39) and Ir_2O_3, although known, is only stable to 400°C where it disproportionates to iridium metal and IrO_2 (37).

Though it is believed that the above thermodynamic considerations greatly influence the stability of oxygen deficient perovskites, these points should be considered along with the affect coordination number has on these compounds. The reduction of the parent oxide ABO_3 requires that the B-cation reduce its coordination number by at least one. Again this is not a problem for oxides with first row elements in a trivalent oxidation state where square pyramidal, tetrahedral, and square planar coordinations are common. For oxides of Ru and Ir in this same oxidation state, however, there are no examples where these cations assume a coordination number lower than six. It is therefore thought that the these lower coordination requirements are destabilizing and that this combined with thermodynamic instabilities prevents the formation of oxygen deficient perovskites of Ru and Ir.

Conclusions

The inability of alkaline earth oxides of ruthenium and iridium to form oxygen deficient perovskites is in contrast to what is seen for analogous first row transition metal compounds. This is believed to be due to both an inherent thermodynamic instability common to late second and third row transition metals and the inability of this low valent metals to assume lower coordination. One would expect based on these arguments that many other late second and third row transition metals should not form oxygen deficient perovskites. Some exceptions might include compounds of Pd, Pt, Ag or Au where even though the metals are easily reduced, lower coordination numbers are exhibited.

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