

The Structural Interrelationship between the Three Polymorphs of Rh_2O_3 and Rh_2S_3 , Rh_2Se_3 , and Ir_2S_3

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The syntheses of each of the three modifications of rhodium sesquioxide are reviewed and their infrared spectra are described. Models of each of these structures were constructed and manipulated using interactive molecular graphics. Their interrelationship is clearly described and used both to explain the similar features observed in their respective infrared spectra and to predict the occurrence of other discrete structures in the Rh_2O_3 system. Rhodium sesquisulfide, Rh_2S_3 , is shown to be isostructural with the high pressure modification, II- Rh_2O_3 . © 1985 Academic Press, Inc.

Introduction

For those transition metal oxides that are polymorphic, an appreciation of the interrelationship between the polymorphs provides the basis for an understanding of their macroscopic properties, such as their reactivity or catalytic behavior. Rhodium sesquioxide, Rh_2O_3 , is unique among those sesquioxides which adopt the common rhombohedral structure (1, 2) of $\alpha\text{-Al}_2\text{O}_3$ (corundum) in that it also forms two additional polymorphs with structures related to that of corundum. This corundum, or low-temperature, form of rhodium sesquioxide (I- Rh_2O_3), has been prepared by oxidation of the metal and by the decomposition of a variety of rhodium compounds, including the chloride (3), hydroxide, nitrate, and sulfate (4). It irreversibly converts to the high-temperature phase (III- Rh_2O_3) above 750°C in air (5). At 65 Kbar

and 1200°C the high pressure phase (II- Rh_2O_3) has been prepared (6). We have also recently succeeded in preparing the high pressure phase (7) under the very different circumstances of chemical vapor transport with gaseous HCl as the transporting agent. Although the low- and high-temperature forms are the modifications of Rh_2O_3 generally encountered (8, 9), the structures of all three forms are closely related.

The diffraction results of Coey on I- Rh_2O_3 (2), Shannon and Prewitt on II- Rh_2O_3 (6), and Biesterbos and Hornstra on III- Rh_2O_3 (10) demonstrate that each is comprised of sheets of face-shared pairs of RhO_6 octahedra, as is discussed in more detail below.

In the present report we describe the infrared spectrum of each of these modifications. Further, in order to better understand the structural interrelationships that are manifested in the infrared spectra, we have used interactive molecular graphics to model each of the three modifications. We have also considered the structure of the

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sulfide, Rh_2S_3 , and show that it, along with Rh_2Se_3 , $\text{Rh}_2\text{S}_2\text{Se}$, Rh_2SSe_2 , and Ir_2Se_3 (11), is isomorphous with the high pressure modification of rhodium oxide, II- Rh_2O_3 .

Experimental

Sample Preparation

Polycrystalline rhodium sesquioxide (corundum structure), I- Rh_2O_3 , was prepared by the thermal decomposition of $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (Alfa Products) in air at 700°C . The high-temperature, III- Rh_2O_3 , and high pressure, II- Rh_2O_3 , modifications were prepared by charging 300 mg of the corundum modification into a vycor tube ca. 12 mm o.d. \times 15 cm., which was then evacuated, backfilled with electronic grade HCl to 10 Torr, and sealed. In a dual control, two-zone furnace, a temperature gradient was maintained along the vycor tube such that the charge of I- Rh_2O_3 was at 1000°C and the opposite end was at 850°C . During the 4 days that the gradient was maintained, red-black crystals grew in the 850°C zone. The crystals grown by chemical vapor transport were identified by powder and single crystal X-ray diffraction as the high pressure modification, II- Rh_2O_3 (7). The Rh_2O_3 that remained in the hot zone was identified by powder X-ray diffraction as the high-temperature form, III- Rh_2O_3 .

Infrared Study

With the identity of each Rh_2O_3 polymorph established by X-ray diffraction, each sample was ground with KBr and pressed into discs. Infrared spectra were recorded in the region $3800\text{--}450\text{ cm}^{-1}$ on a Digilab FTS-14 spectrometer. Their spectra are shown in Fig. 1. The main peak assignments are given in Table I.

Representations of the Structures

Although Shannon and Prewitt (6) and Biesterbos and Hornstra (10) did con-

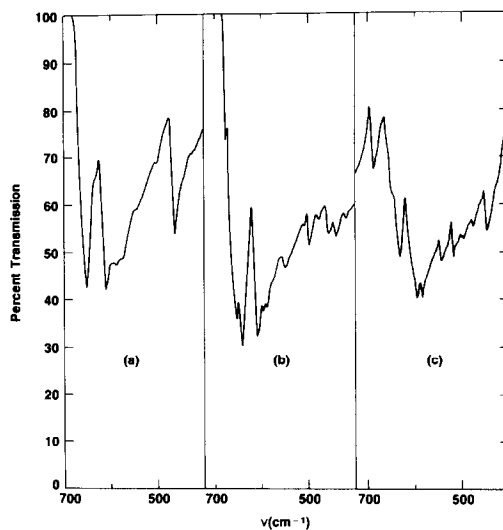


FIG. 1. Infrared spectra of (a) I- Rh_2O_3 , (b) III- Rh_2O_3 , and (c) II- Rh_2O_3 .

sider similarities between the individual oxide structures, we have redrawn the complete structures of I- Rh_2O_3 , II- Rh_2O_3 , and III- Rh_2O_3 , and that of the sulfide, Rh_2S_3 , in ways which emphasize their relationships. The details of each of these representations are provided below. Each of the models was constructed and manipulated, interactively, using CHEMGRAF (12). The drawing radii used for Figs. 2–5 were 0.39, 0.26, and 0.32 \AA for rhodium, oxygen, and sulfur, respectively.

A. The Corundum Form, I- Rh_2O_3

The corundum form of Rh_2O_3 has space group symmetry $R\bar{3}c$, with hexagonal lattice constants $a = 5.127\text{ \AA}$ and $c = 13.853\text{ \AA}$. Rhodium occupies the $12c$ positions; $0, 0, z$ with $z = 0.348$, and oxygen is located on the $18e$ sites; $x, 0, \frac{1}{4}$ with $x = 0.295$ (2). Unfortunately, when viewed with reference to this true, rhombohedral unit cell, the relationship between the structure and those of the other rhodium oxide polymorphs is not obvious. It is then more convenient to transform the unit cell to one which does enable a direct comparison with the other

TABLE I
MAIN FEATURES (cm⁻¹) OF INFRARED SPECTRA

I-Rh ₂ O ₃ (low temperature)	III-Rh ₂ O ₃ (high temperature)	II-Rh ₂ O ₃ (high pressure)
	675	685
650	652	645 shoulder
	640	630
608	608	
	595	593
585	587	583
	549	543
	498	
459	459	
	441	446

modifications. Thus, if we apply the transformation matrix

$$\begin{pmatrix} \frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} \\ 1 & 1 & 0 \\ \frac{2}{3} & -\frac{2}{3} & \frac{1}{3} \end{pmatrix}$$

to the hexagonal unit cell, we derive a monoclinic cell with lattice constants $a = 5.485$, $b = 5.127$, and $c = 7.508$ Å, with $\beta = 95.29^\circ$. The corresponding matrix (see, for example, "International Tables for X-Ray Crystallography," Vol. I, pp. 15, 16) for transforming the atomic coordinates is

$$\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & -2 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix}$$

After this transformation, the structure can be described in space group $I2/m$ (No. 12), with the origin at $0, 0, \frac{1}{4}$ from the center $2/m$. The equivalent positions are $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + x y z, \bar{x} y \frac{1}{2}-z, \bar{x} \bar{y} \bar{z}$ and $z \bar{y} \frac{1}{2}+z$, and the atomic coordinates are:

	x	y	z
Rh1	0.304	0	0.348
O1	0.3525	0.1475	0.1025
O2	0.5	0.705	0.25

The structure is drawn referenced to this monoclinic unit cell and viewed along b in Fig. 2. Although this representation is most useful for the present purposes, we note that $I2/m$ is a nonstandard space group. The more conventional space group would be $C2/m$ (No. 12) for which the transformation matrices from the hexagonal parent are:

$$\begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \text{ unit cell;}$$

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 1 & 0 & 3 \end{pmatrix} \text{ atomic coordinates.}$$

The unit cell constants would then be $a = 8.880$, $b = 5.127$, $c = 5.485$ Å and $\beta = 122.66^\circ$, with atomic coordinates, referenced to the standard origin, of:

		x	y	z
Rh1	4i	0.598	0	0.294
O1	8j	0.3525	0.1475	0
O2	4g	0.5	0.705	0

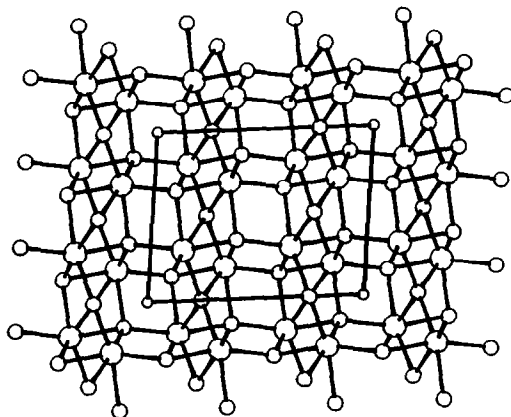


FIG. 2. The corundum structure of I-Rh₂O₃ represented in a monoclinic unit cell with $a = 5.485$ Å, $b = 5.12$ Å, $c = 7.508$ Å, $\beta = 95.3^\circ$ (see text). The drawing radii are rhodium—0.39 Å; oxygen—0.26 Å.

B. The High-Temperature Modification, III- Rh_2O_3

Atomic coordinates were taken from Biesterbos and Hornstra (10) and used without modification. The structure shown in Fig. 3 is projected along the a direction.

C. The High-Pressure Modification, II- Rh_2O_3

The space group of the high pressure modification, II- Rh_2O_3 given by Shannon and Prewitt (6) is $Pbna$. Although this a nonstandard setting of $Pbcn$ (No. 60), for consistency the structure is drawn referenced to this unit cell. Figure 4 shows the structure viewed along the a direction.

D. Rhodium Sulfide, Rh_2S_3

The structures of the isostructural Rh_2S_3 , Rh_2Se_3 , and Ir_2S_3 were described in space group $Pbcn$ (No. 60) by Parthe, Hohnke, and Hulliger in 1967 (11). On transforming the structure to the nonstandard $Pbna$, and labeling the negative x direction as positive, according to

$$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$$

for both unit cell and coordinates, the atomic coordinates become very similar to

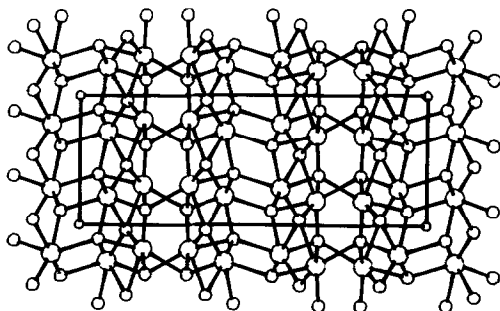


FIG. 3. The high-temperature form, III- Rh_2O_3 , viewed along the a axis of the orthorhombic unit cell that has $a = 5.148 \text{ \AA}$, $b = 5.443 \text{ \AA}$, and $c = 14.698 \text{ \AA}$.

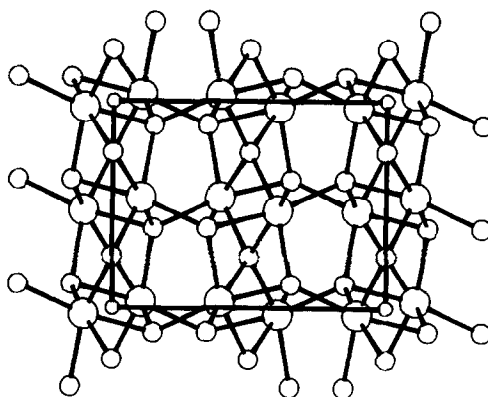


FIG. 4. The high pressure Rh_2O_3 form, II- Rh_2O_3 , viewed along the a axis of the orthorhombic unit cell that has $a = 5.169 \text{ \AA}$, $b = 5.381 \text{ \AA}$ and $c = 7.243 \text{ \AA}$.

those of II- Rh_2O_3 . The sulfide and the high pressure form of the oxide are isomorphous. This is shown graphically in Fig. 5 which is a view of the transformed sulfide structure along the a direction. Figure 5 is almost indistinguishable from Fig. 4. This correspondence is unusual in that in all but a few special cases, the structure of a given metal sulfide does not resemble that of the corresponding oxide (13). Wells has observed (14) that Rh_2S_3 had "obvious resemblances" to the corundum structure.

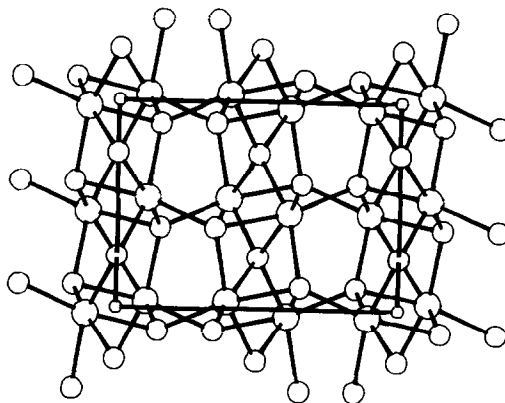


FIG. 5. Representation of the Rh_2S_3 structure drawn in the same orientation as II- Rh_2O_3 in Fig. 4 (see text). The drawing radii are rhodium— 0.39 \AA ; sulfur— 0.32 \AA .

Discussion

In Figs. 2–5 the structures of the three modifications of rhodium oxide are seen to consist of sheets of face-shared RhO_6 octahedra with the viewing directions parallel to the planes of the sheets. There are two ways in which these sheets can be interlinked. In the corundum form, I- Rh_2O_3 , adjacent sheets are separated by a simple translation of $c/2$, or 3.75 \AA along the monoclinic c direction (see Fig. 2). In the high pressure form, II- Rh_2O_3 , in addition to a translation, adjacent sheets are rotated by 180° so that the inter-sheet connections are not parallel but crossed (see Fig. 4). The separation, ($c/2$), between the sheets is now 3.62 \AA . The high-temperature form, III- Rh_2O_3 , is in some sense the intermediate, for it consists of an alteration of the two types of linkage (see Fig. 3). The c axis of III- Rh_2O_3 , 14.70 \AA , is close to that calculated for two occurrences of each type of linkage ($2 \times 3.75 \text{ \AA} + 2 \times 3.62 = 14.74 \text{ \AA}$). The facility with which both types of linkages are accommodated in the same structure suggests the possible occurrence of other stacking sequences in which sheets of the corundum structure are not separated by alternating parallel and crosslinkages. These possible sequences would contain two or three or four, etc., crosslinks between each pair of opposite parallel linkages. Note that such structures require pairs of opposite parallel linkages, because in I- Rh_2O_3 the direction of the translation that brings one sheet into correspondence with its second neighbor sheet is at an angle of $\beta = 95.29^\circ$, not 90° , to the plane of the sheets. Although this new family of structures has not yet been observed, Herrero-Fernandez and Alario-Franco (15) have recently detected remnants of the low-temperature phase, I- Rh_2O_3 , intergrown with the high temperature phase, III- Rh_2O_3 , by electron microscopy.

In qualitative terms, the relationships between the structures also provide an expla-

nation for the appearance of the vibrational spectrum of III- Rh_2O_3 . In the region $400\text{--}700 \text{ cm}^{-1}$, two features at ca. 650 and 585 cm^{-1} are common to both I- and II- Rh_2O_3 , and these presumably then derive from the face-shared manner in which the octahedra are joined within the sheets. None of the other five features from the II- Rh_2O_3 spectrum coincide with either of the additional two features found in the spectrum of I- Rh_2O_3 . However, the infrared spectrum of the high-temperature modification, III- Rh_2O_3 , provides features that coincide with all peaks from both I- Rh_2O_3 and II- Rh_2O_3 . The observed spectrum is indeed similar to that which would be expected for a mixture of equal amounts of the I- and II- Rh_2O_3 phases. The methods detailed above that were used to construct the rhodium oxide structures shown in Figs. 2–4 can provide the basis for a thorough group-theoretical analysis of their vibrational spectra. An earlier study (16) was in error because of the incorrect assumption that the high-temperature form of Rh_2O_3 had the gadolinium orthoferrite structure (GdFeO_3).

The application of interactive molecular graphics to inorganic structures is relatively recent, and there is considerable scope for further development, particularly in using such routines for computing interaction energies. In the present case, the simple construction and representation of the rhodium sesquioxide structures provides an appreciation of their interrelationship and also led us to identify a group of known chalcogenide compounds (11) that are isostructural with II- Rh_2O_3 . The octahedral coordination of rhodium, the strong distortion of their octahedra, and their pairing in a face-shared manner are all features common to the structures of Ir_2S_3 , Rh_2S_3 , and Rh_2Se_3 , and, presumably, the mixed anion phases $\text{Rh}_2\text{S}_2\text{Se}$ and Rh_2SSe_2 . These collective results suggest that the high pressure rhodium sesquioxide and oxysulfides may exist

under preparative conditions before believed improbable.

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