JOURNAL OF SOLID STATE CHEMISTRY **139,** 416–421 (1998)
ARTICLE NO. SC987877

Synthesis and Characterization of New Rh(III) Compounds with the K_4CdCl_6 Structure-Type: Sr_3MRhO_6 (M = Y, Sc, In)

Ralph C. Layland, Shalawn L. Kirkland, Pedro Núñez, and Hans-Conrad zur Loye[1]

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received March 25, 1998; accepted April 27, 1998

The compounds Sr_3MRhO_6 (M = Y, Sc, In) have been synthesized and structurally characterized by Rietveld refinement of powder X-ray diffraction data in the space group $R\bar{3}c$; $Z = 6$. The lattice parameters for the series were found to be $a = 9.7598(1)$ Å and $c = 11.3152(1)$ Å, $a = 9.6833(1)$ Å and $c = 11.0478(2)$ Å, and $a = 9.6473(1)$ Å and $c = 11.3597(1)$ Å, for Sr_3YRhO_6, Sr_3ScRhO_6, and Sr_3InRhO_6, respectively. Thermogravimetric analysis indicates that these phases are stoichiometric rhodium(III) oxides. The oxygen content was determined to be 6.00(2), 6.05(2), and 5.99(2), for Sr_3MRhO_6 (M = Y, Sc, In), respectively. These compounds are isostructural with K_4CdCl_6. The structure consists of infinite one-dimensional chains of alternating face-shared RhO_6 octahedra and MO_6 trigonal prisms (M = Y, Sc, In). The strontium cations are located in a distorted square antiprismatic environment.

INTRODUCTION

Oxides of Ir, Ru, Rh, and Pt, which are isostructural with K_4CdCl_6, are being studied extensively because of their structural and magnetic properties (1–4). These, and related oxides having the general formula $A_3BB'O_6$ (5), can be described as consisting of infinite chains of alternating face-shared trigonal prisms [BO_6] [B = Na, Mg, Ca, Sr, Ba, Cu, Ni, Co, Zn, Cd] and octahedra [$B'O_6$] [B' = Pt, Ir, Rh, Nb, Ta, Bi], where A = alkali or alkaline-earth cation. This structure type is extremely versatile and receptive to a large number of possible cationic substitutions and can also be thought of as resulting from the stacking of BA_3O_6 layers with filling of the octahedral site by the B' cation. In addition to this sequence, many other stacking sequences using A_3O_9 and BA_3O_6 are possible, resulting in structurally related chain compounds. Often, the oxidation states for the B and B' cations are +2 and +4, respectively (6). In addition, numerous compounds with oxidation states of +1 and +5 such as Sr_3NaRuO_6 (3), Ba_3LiBiO_6 (7), Ba_3NaBiO_6 (7), Ba_3NaNbO_6 (8), Ba_3NaTaO_6 (8), Ca_3NaRuO_6 (9), and Ca_3NaIrO_6 (9), are known, while only relatively few compounds with both cations in the +3 oxidation state occupying both the octahedral and trigonal prismatic sites have been prepared. Compounds of this type include Sr_3YbNiO_6 (10), Sr_3MNiO_6 (M = Sc, In, Tm, Yb, Lu) (11), and $Ca_3Co_2O_6$ (12). Recently, we reported the synthesis of the first examples of a Rh(III) compound with this structure type, Sr_3GdRhO_6, with both B and B' cations in the +3 oxidation state (13).

In this paper we describe the further syntheses and structural characterizations of Rh(III) oxides with the general formula Sr_3MRhO_6, where M = Y, Sc, In. These are three new examples of compounds with the K_4CdCl_6 structure type with two cations in the +3 oxidation state.

EXPERIMENTAL

Sample Preparation

Polycrystalline samples of Sr_3MRhO_6 (where M = Y, Sc, In) were prepared by firing stoichiometric quantities of strontium carbonate (Alfa, 99.99%), yttrium oxide (REacton, 99.99%), scandium oxide (Aran Isles Chemicals, 99.9%), indium(III) oxide (Alfa, 99.99%), and rhodium metal powder (Engelhard, 99.95%) at 1150°C. For the Sr_3YRhO_6 sample, the yttrium oxide was first dissolved in approximately 100 ml of concentrated nitric acid in a Pyrex beaker. The strontium carbonate and rhodium metal were added to the mixture at this point. The reaction mixture was heated and stirred until dryness. The dried reaction mixture was initially heated in air overnight at 400°C in the Pyrex beaker. Subsequently, the sample was ground under acetone and transferred to an alumina crucible. Attempts to synthesize Sr_3ScRhO_6 and Sr_3InRhO_6 by the nitrate preparation failed to produce single-phase products. Therefore, the Sr_3ScRhO_6 and Sr_3InRhO_6 samples were prepared by solid state routes in alumina crucibles. For all samples, the alumina crucibles were heated at a rate of 25°C/min to 850°C, held at this temperature for 10 h, and then heated at 10°C/min to 1150°C for 14 days with intermittent grinding.

[1]To whom correspondence should be addressed. E-mail: hanno@psc.sc.edu.

0022-4596/98 $25.00

When the samples are prepared at 1150°C the materials are light brown. One final heating at 1350°C for 18 h was done in order to increase the crystallinity of the samples. However, long thermal treatments at $\geq$ 1300°C led to decomposition of the phase.

Crystal Structure Determination

The X-ray powder diffraction data were collected on a Rigaku D\Max-2200 powder X-ray diffractometer using a Bragg–Brentano geometry with Cu$K\alpha$ radiation. The step-scan covered the angular range 15–135° 2θ in steps of 0.02° 2θ.

Structure refinements of Sr_3MRhO_6 (M = Y, Sc, In) were carried out in the space group $R\bar{3}c$ (No. 167), using the structure of Sr_4PtO_6 (14, 15) as the starting model. On the basis of our recent experience with the structurally related compound Sr_3GdRhO_6, the rhodium atom was placed in the octahedral site 6*b*, the yttrium, scandium, or indium atom was placed in the trigonal prismatic site 6*a*, and the strontium atom was placed in the 18*e* site. Structure refinements were performed using the Rietveld method (16) implemented in the computer program GSAS (17). The profile of the diffraction peaks of Sr_3MRhO_6 was described by a pseudo-Voigt function. Refinements of the peak asymmetry were allowed, and the background was described by a polynomial function with six refinable coefficients. Refinement of Sr_3YRhO_6 converged at values of $R_p = 7.45\%$ and $R_{wp} = 10.84\%$; refinement of Sr_3ScRhO_6 converged at values of $R_p = 7.78\%$ and $R_{wp} = 11.48\%$; and refinement of Sr_3InRhO_6 converged at values of $R_p = 7.74\%$ and $R_{wp} = 10.78\%$. Minor amounts of Y_2O_3 were found in the Sr_3YRhO_6 sample, and consequently a two-phase refinement was done. No impurities were observed in either the Sr_3ScRhO_6 or the Sr_3InRhO_6 samples. We performed various refinements to check for antisite disorder and for partial substitution of Al(III) for Rh(III). The best refinement is obtained with yttrium, scandium, or indium in the 6*a* site and rhodium in the 6*b* site with full occupancy for both metals.

Thermogravimetric Analysis

The oxygen content of the samples was determined by thermogravimetric analyses (TGA), using either a Cahn TG121 system or a TA Instruments SDT 2960 simultaneous TGA-DTA. Thermogravimetric analyses was carried out on $\approx$ 80 mg of Sr_3MRhO_6 (M = Y, In) using the Cahn TGA and $\approx$ 20 mg of Sr_3ScRhO_6 using the TA Instruments DTA-TGA. The samples were reduced under 5% H_2/95% N_2 (flow rate of 60 ml/min). Sr_3YRhO_6 was heated over a temperataure range of 50 to 950°C at a heating rate of 5°C/min, Sr_3ScRhO_6 over a temperature range of 50 to 1150°C at a heating rate of 5°C/min, and Sr_3InRhO_6 over a temperature range of 50 to 900°C at a heating rate of 5°C/min.

TABLE 1
Summary of Crystallographic Data and Least-Squares Refinement Results for Sr_3MRhO_6 (M = Y, Sc, In)

Compound	Sr_3YRhO_6	Sr_3ScRhO_6	Sr_3InRhO_6
Space group	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$
a (Å)	9.7598(1)	9.6833(1)	9.6473(1)
c (Å)	11.3152(1)	11.0478(2)	11.3597(1)
V (Å^3)	933.42(2)	897.13(3)	915.60(2)
No. of observations	844	382	386
No. of refined parameters	24	24	24
No. of profile parameters	5	5	5
χ^2	3.363	3.727	3.144
R_p[a] (%)	7.45	7.78	7.74
R_{wp}[a] (%)	10.84	11.48	10.78
R_{exp}[a] (%)	5.92	5.96	6.09
R_{Bragg}[a] (%)	4.46	3.36	4.83

[a] Reliability factors were calculated as follows:
$R_p = [\sum|I_o - I_c|/\sum I_o]$,
$R_{wp} = [\sum w(I_o - I_c)^2/\sum wI_o^2]^{1/2}$,
$R_{exp} = R_{wp}/[(\chi^2)^{1/2}]$,
$R_{Bragg} = [\sum|I_{k(obs)} - I_{k(calc)}|/\sum I_{k(obs)}]$,
where I_o and I_c are the observed and calculated integrated intensities, respectively, and w is the weight derived from an error propagation scheme during the least-squares refinement process. I_k is the Bragg intensity.

RESULTS AND DISCUSSION

Crystallographic data and further details of the Rietveld refinement of Sr_3MRhO_6 (M = Y, Sc, In) are given in Table 1. The best agreement obtained between the calculated and the observed profiles for Sr_3MRhO_6 (M = Y, Sc, In) is shown in Figs. 1, 2, and 3, respectively. The atomic positions and thermal parameters for Sr_3MRhO_6 (M = Y, Sc, In) can be found in Table 2. Selected inter-

TABLE 2
Atomic Positions and Isotropic Thermal Parameters with E.s.d.'s (in Parentheses) for Sr_3MRhO_6 (M = Y, Sc, In)

Compound	Atom	Site	x	y	z	U_{iso} (Å^2)
Sr_3YRhO_6	Rh	6*b*	0	0	0	0.0015(2)
	Sr	18*e*	0.3693(1)	0	$\frac{1}{4}$	0.0041(2)
	Y	6*a*	0	0	$\frac{1}{4}$	0.0014(3)
	O	36*f*	0.1809(4)	0.0215(4)	0.1138(3)	0.0034(9)
Sr_3ScRhO_6	Rh	6*b*	0	0	0	0.0018(3)
	Sr	18*e*	0.3693(1)	0	$\frac{1}{4}$	0.0053(2)
	Sc	6*a*	0	0	$\frac{1}{4}$	0.0022(3)
	O	36*f*	0.1757(4)	0.0227(4)	0.1188(3)	0.0058(9)
Sr_3InRhO_6	Rh	6*b*	0	0	0	0.0012(3)
	Sr	18*e*	0.3690(1)	0	$\frac{1}{4}$	0.0026(2)
	In	6*a*	0	0	$\frac{1}{4}$	0.0031(3)
	O	36*f*	0.1753(4)	0.0199(5)	0.1165(3)	0.0089(9)

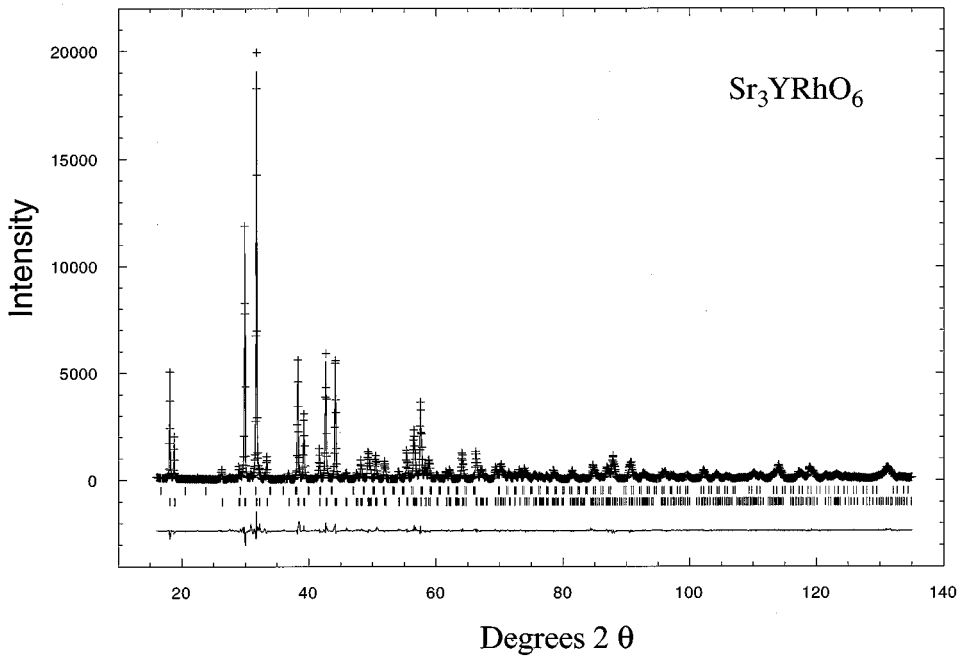

FIG. 1. Observed (cross) and calculated (solid line) X-ray diffraction pattern for Sr_3YRhO_6. Tick marks indicate the positions of allowed Bragg reflections for Y_2O_3 (top) and Sr_3YRhO_6 (bottom). The difference line, observed minus calculated, is located at the bottom of the figure.

atomic bond distances and angles for Sr_3MRhO_6 (M = Y, Sc, In) can be found in Tables 3, 4, and 5, respectively. Sr_3MRhO_6 (M = Y, Sc, In) are isostructural with the rhombohedral structure type K_4CdCl_6, as was expected on the basis of the fairly large number of compounds that have been synthesized with this structure type. The rhombohedral structure can be described as consisting of slightly bent chains of face-connected trigonal prisms and octahedra,

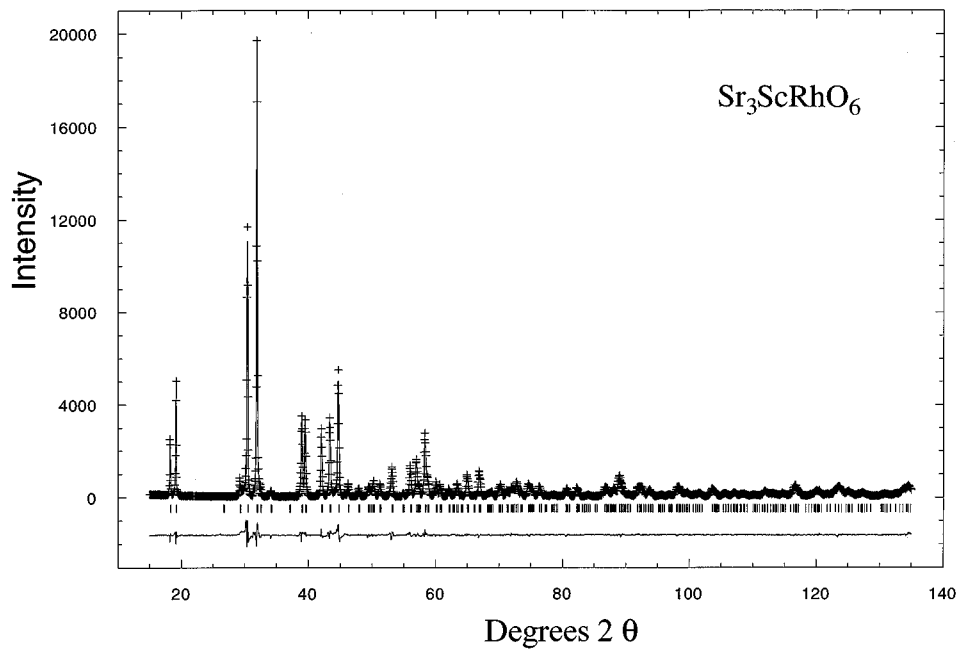

FIG. 2. Observed (cross) and calculated (solid line) X-ray diffraction pattern of Sr_3ScRhO_6. Tick marks indicate the positions of allowed Bragg reflections. The difference line, observed minus calculated, is located at the bottom of the figure.

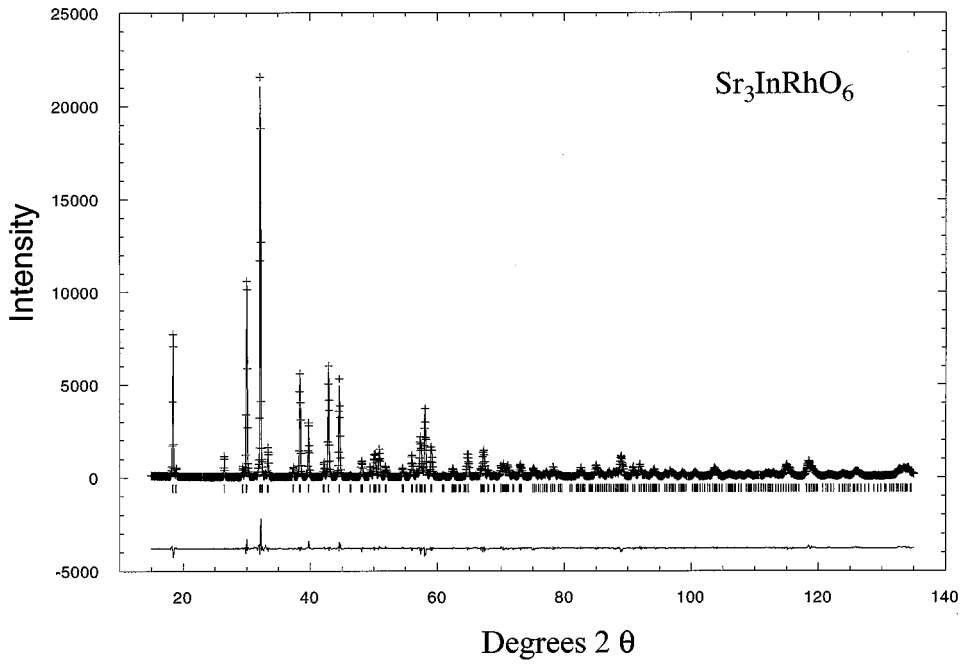

FIG. 3. Observed (cross) and calculated (solid line) X-ray diffraction pattern of Sr_3InRhO_6. Tick marks indicate the positions of allowed Bragg reflections. The difference line, observed minus calculated, is located at the bottom of the figure.

which can be seen in Fig. 4. The rhodium ions are located at the corners and center of the unit cell. Six equivalent oxygen ions are coordinated to the rhodium ion in an octahedral array at a distance of 2.109(3), 2.072(3), and 2.079(3) Å for Sr_3MRhO_6 ($M = Y, Sc, In$), respectively. The octahedral sites of oxides having this structure are typically occupied by the tetravalent metal, where the size of the octahedrally coordinated cation has a noticeable influence the magnitude of the c parameter. In our case, the trivalent cation, Rh(III) (0.67 Å), is larger than most of the tetravalent cations that have been found in the octahedral site, for instance Rh(IV) (0.60 Å), Ir(IV) (0.625 Å), and Pt(IV) (0.625 Å). This increase in the size is not, however, reflected in the c parameter, which is also affected by the size of the metal in the trigonal prismatic site. The gadolinium ion which we recently were able to place in the trigonal prismatic site has an ionic radius of 0.938 Å. Since we were able to place the gadolinium ion into the trigonal prismatic site, substitution for the gadolinium ion was carried out using ions with similar or slightly smaller ionic radii. We were successful in substituting Y (0.9 Å), Sc (0.745 Å), and In (0.8 Å) (18) into the trigonal prismatic site. Figure 5 shows the variation of V and c/a with M^{3+} ionic radius for Sr_3MRhO_6 ($M = Y, Sc, In$) and additional isostructural M^{3+} rare-earth oxides that have been previously reported (19). The scandium ion was the smallest $+3$ cation we were able to

TABLE 3
Interatomic Distances (Å) and Bond Angles (deg) with E.s.d.'s (in Parentheses) for Sr_3YRhO_6

Atom	Atom	Distance		Atom	Atom	Atom	Angle	
Rh	Sr	3.2332(3)	(×6)	Rh	O	Y	80.3(1)	
Rh	Y	2.82881(4)	(×2)	O	Rh	O	86.6(1)	(×6)
Rh	O	2.109(3)	(×6)	O	Rh	O	93.4(1)	(×6)
Sr	O	2.487(3)	(×2)	O	Rh	O	180	(×3)
Sr	O	2.686(4)	(×2)	O	Y	O	79.1(1)	(×6)
Sr	O	2.721(4)	(×2)	O	Y	O	86.1(1)	(×3)
Sr	O	2.646(3)	(×2)	O	Y	O	128.5(2)	(×3)
Y	O	2.273(3)	(×6)	O	Y	O	145.6(2)	(×3)

TABLE 4
Interatomic Distances (Å) and Bond Angles (deg) with E.s.d.'s (in Parentheses) for Sr_3ScRhO_6

Atom	Atom	Distance		Atom	Atom	Atom	Angle	
Rh	Sr	3.2036(3)	(×6)	Rh	O	Sc	81.5(1)	
Rh	Sc	2.76196(5)	(×2)	O	Rh	O	84.1(1)	(×6)
Rh	O	2.072(3)	(×6)	O	Rh	O	95.9(1)	(×6)
Sr	O	2.465(3)	(×2)	O	Rh	O	180	(×3)
Sr	O	2.654(4)	(×2)	O	Sc	O	79.9(1)	(×6)
Sr	O	2.720(4)	(×2)	O	Sc	O	85.1(2)	(×3)
Sr	O	2.672(3)	(×2)	O	Sc	O	127.2(2)	(×3)
Sc	O	2.160(3)	(×6)	O	Sc	O	146.1(2)	(×3)

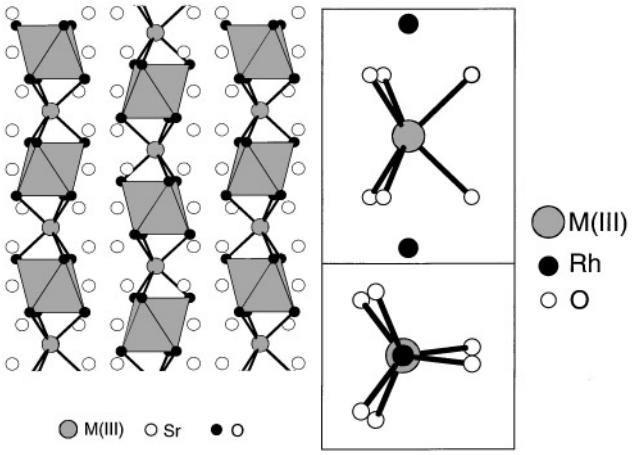

FIG. 4. The one-dimensional chain structure of Sr_3MRhO_6 (M = Y, Sc, In) viewed along the a axis is shown on the left. The [RhO_6] octahedra are shown as polyhedra, while all other atoms are shown in ball-and-stick format. The coordination environment around the trigonal prismatically coordinated metal (Y, Sc, and In) is shown on the right.

TABLE 5
Interatomic Distances (Å) and Bond Angles (deg) with E.s.d.'s (in Parentheses) for Sr_3InRhO_6

Atom	Atom	Distance		Atom	Atom	Atom	Angle	
Rh	Sr	3.2015(3)	(×6)	Rh	O	In	82.9(1)	
Rh	In	2.83991(3)	(×2)	O	Rh	O	83.8(1)	(×6)
Rh	O	2.079(3)	(×6)	O	Rh	O	96.2(1)	(×6)
Sr	O	2.487(3)	(×2)	O	Rh	O	180	(×3)
Sr	O	2.666(4)	(×2)	O	In	O	78.0(1)	(×6)
Sr	O	2.686(4)	(×2)	O	In	O	87.5(2)	(×3)
Sr	O	2.696(3)	(×2)	O	In	O	129.5(2)	(×3)
In	O	2.207(3)	(×6)	O	In	O	145.6(2)	(×3)

substitute into the trigonal prismatic site which could still stabilize the structure. Attempts to substitute ions smaller than scandium, such as Ga (0.62 Å), failed to stabilize this structure type. The Y, Sc, and In are coordinated in a trigonal prismatic array by six equivalent oxygens at a distance of 2.273(3), 2.160(3), and 2.207(3) Å, respectively. The trigonal prisms are distorted by a twist about the threefold axis of 12.5(1), 13.6(1), and 11.9(1)° for Sr_3MRhO_6 (M = Y, Sc, In), respectively. The Sr–O bond distances are in agreement with those found in analogous compounds (6) and the Rh–O bond distances are in agreement with those found for Rh(III) in other oxides (20). The oxygen content of the samples was determined by TGA. The weight loss corresponds to an oxygen content of 6.00(2), 6.05(2), and 5.99(2) for Sr_3MRhO_6 (M = Y, Sc, In), respectively. The weight loss onset temperature was determined to be approximately 870, 1100, and 650°C for Sr_3MRhO_6 (M = Y, Sc, In), respectively.

In summary, we have prepared and characterized the compounds Sr_3MRhO_6 (M = Y, Sc, In) which crystallizes with the $R\bar{3}c$ space group symmetry of the K_4CdCl_6 structure type. We succeeded in introducing and stabilizing rhodium(III) in this structure. The +3 oxidation state for the rhodium was confirmed by the structural data. The

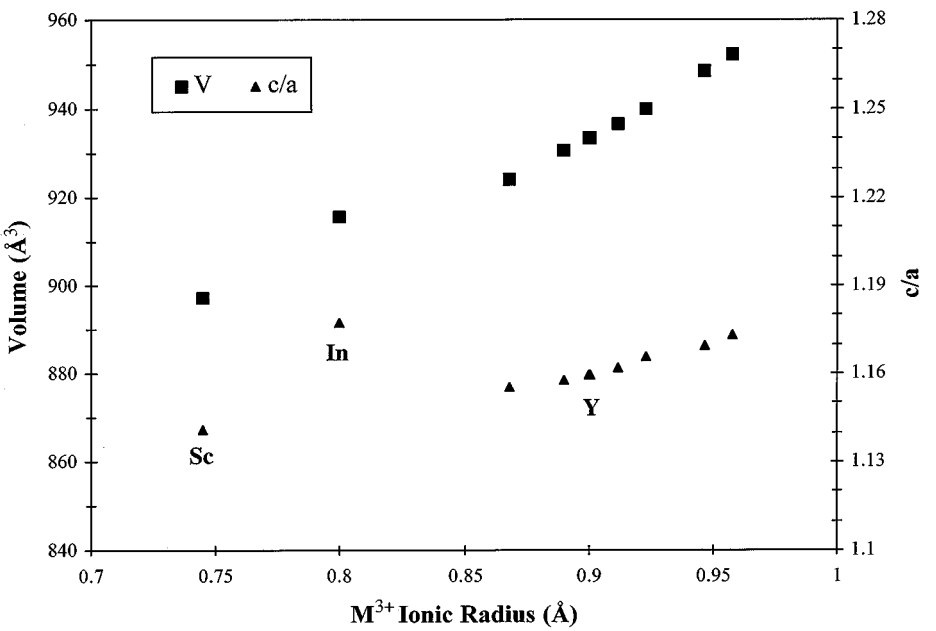

FIG. 5. The variation of the cell volume V (squares) and c/a (triangles) with M^{3+} ionic radius for Sr_3MRhO_6 (M = Sc, In, Yb, Er, Y, Ho, Dy, Tb, Eu, Sm) in order of increasing ionic radius.

preparation and structural and magnetic characterization of isostructural rhodium(III)–rare-earth(III) compounds are in progress.

ACKNOWLEDGMENTS

Financial support was provided by the National Science Foundation through Grant DMR 9696235. The funds used to purchase the powder X-ray diffractometer were provided by NSF/EPSCoR Cooperative Agreement EPS-9630167.

REFERENCES

1. T. N. Nguyen, D. M. Giaquinta, and H.-C. zur Loye, *Chem. Mater.* **6,** 1624 (1994).
2. T. N. Nguyen and H.-C. zur Loye, *J. Solid State Chem.* **117,** 300 (1995).
3. S. Frenzen and H. Müller-Buschbaum, *Z. Naturforsch. B* 50, 581 (1995).
4. J. F. Vente, J. K. Lear, and P. D. Battle, *J. Mater. Chem.* **5,** 1785 (1995).
5. G. Bergerhoff and O. Schmitz-Dumont, *Z. Anorg. Allg. Chem.* **284,** 10 (1956).
6. P. Núñez, S. Trail, and H.-C. zur Loye, *J. Solid State Chem.* **130,** 35 (1997).
7. V. A. Carlson and A. M. Stacy, *J. Solid State Chem.* **96,** 332 (1992).
8. G. Wehrum and R. Hoppe, *Z. Anorg. Allg. Chem.* **617,** 45 (1992).
9. J. B. Claridge, R. C. Layland, R. D. Adams, and H.-C. zur Loye, *Z. Anorg. Allg. Chem.* **623,** 1131 (1997).
10. M. James and J. P. Attfield, *J. Mater. Chem.* **4,** 575 (1994).
11. M. James and J. P. Attfield, *Chem. Eur. J.* **216,** 737 (1996).
12. H. Fjellvåg, E. Gulbrandsen, S. Aasland, A. Olsen, and B. C. Hauback, *J. Solid State Chem.* **124,** 190 (1996).
13. P. Núñez, M. A. Rzeznik, and H.-C. zur Loye, *Z. Anorg. Allg. Chem.* **623,** 1269 (1997).
14. J. J. Randall and L. Katz, *Acta Crystallogr.* **2,** 519 (1959).
15. I. Ben-Dor, J. T. Suss, and S. Cohen, *J. Cryst. Growth* **64,** 395 (1983).
16. H. M. Rietveld, *J. Applied Crystallogr.* **2,** 65 (1969).
17. A. C. Larson and R. B. Von Dreele, "General Structure Analysis System (GSAS)," Los Alamos National Laboratory Report No. LA-UR-86-748, 1994.
18. R. D. Shannon, *Acta Crystallogr.* **A32,** 751 (1976).
19. R. C. Layland, S. L. Kirkland, and H.-C. zur Loye, *J. Solid State Chem.* [In press]
20. K. Hobbie and R. Hoppe, *Z. Anorg. Allg. Chem.* **535,** 20 (1986).