PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Subsolidus Phase Relations in the Gd₂O₃-Rh₂O₃ System

V. N. Skrobot, V. L. Ugolkov, S. K. Kuchaeva, D. P. Romanov, R. G. Grebenshchikov, and V. V. Gusarov

Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, ul. Odoevskogo 24/2, St. Petersburg, 199155 Russia Received June 20, 2005

Abstract—The Gd_2O_3 –Rh₂O₃ system is studied using the anneal-and-quench technique, X-ray powder diffraction, thermal analysis, and chemical analysis. A schematic subsolidus phase diagram is designed. One double oxide of composition GdRhO₃ is found to exist. It was characterized using some physicochemical methods.

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The discovery of high-temperature superconductivity in $La_{2-x}Ba_{x}CuO_{4}$ [1] impelled extensive research in the field of the synthesis and characterization of the electric and magnetic properties of complex oxides containing f elements (rare-earth metals, and/or s elements (alkaline-earth and/or alkali metals), as well as copper and/or other d elements. Mixed oxides of platinum metals are the focus of research due to the variety of their compositions and crystal structures and, often, their unique physicochemical properties. Such mixed oxides are exemplified by mixed-metal perovskite oxides of ruthenium (Sr_2RuO_4 [2] and $RuSr_2GdCu_2O_8$ [3]). These and many other ruthenates and ruthenocuprates have been investigated for more than one decade [4]. Platinum-metal oxides that crystallize in the K₄CdCl₆type quasi-one-dimensional structure have also been studied; they have various magnetic properties, including a specific type of spin-chain paramagnetism first observed for $Sr_3CuPt_{0.5}Ir_{0.5}O_6$ [5]. Oxide $La_4Ru_6O_{19}$, which contains ruthenium in two oxidation states and is a non-Fermi-liquid metal, has unique electric and magnetic properties [6]. Superconductivity was discovered in osmium oxides with the general formula MOs_2O_6 (M = K, Rb, Cs) and pyrochlore-derivative crystal structures [7–9]. The synthesis and systematic investigation of such oxides can help to design novel materials with important magnetic and electric properties, superconductivity among others. Many complex oxides of platinum-group metals have been inspected for superconductivity, including perovskite mixed-metal oxides of rhodium with rare-earth and alkaline-earth elements: Sr_2RhO_4 [2], $Sr_2Ru_{1-x}Rh_xO_4$ and $BaRu_{1-x}Rh_xO_3$ [10], $La_{1-r}M'_{r}RhO_{3}$ (M' = Ca, Sr, Ba) [11, 12], and $Sr_{2-x}La_{x}RhO_{4}$ [13]. Although desired results have not been obtained in these studies, it is pertinent to synthesize and study complex oxide phases that exist in Ln-M'-Rh-O, Ln-M-Rh-O, and Ln-M'-M-Rh-O systems, where Ln is a rare-earth metal, M is an alkaline-earth metal, and M' is an alkali metal. The search for new oxides in the these types of systems should be based on the physicochemical analysis of simpler oxide systems, such as Ln–M'–O, Ln–M–O, M'–Rh–O, M–Rh–O, and Ln–Rh–O systems. Phase diagrams are well studied for the Ln–M'–O [14], Ln–M–O [14], and M'–Rh–O [15–20] systems. For M–Rh–O and Ln–Rh–O systems, phase relations have not been studied, although phase diagrams provide a reliable basis for the design of new materials.

Continuing the investigations into Ln–Rh–O systems [21–26], our goal in this work was to study subsolidus phase relations in the Gd_2O_3 –Rh₂O₃ system in air at temperatures up to 1600°C.

It was reported in 1964 [27] that a mixed oxide of composition $GdRhO_3$, an orthorhombically distorted perovskite, is formed in the Gd–Rh–O system. The synthesis, crystal-chemical properties, and some physicochemical properties of this mixed oxide were studied repeatedly [28–34], but phase relations in the Gd–Rh–O system have not been studied.

EXPERIMENTAL

The starting reagents used were gadolinium(III) oxide Gd_2O_3 (at least 99.9% pure) and pure grade rhodium trichloride crystal hydrate $RhCl_3 \cdot 4H_2O$. The latter forms the metastable polymorph α -Rh₂O₃ (a corundum-type hexagonal structure) when oxidized by atmospheric oxygen at 650–700°C [35]. The stable hightemperature orthorhombic polymorph β -Rh₂O₃ [36] was prepared in two ways: (i) metastable α -Rh₂O₃ was heat-treated in air at 800–950°C, or (ii) fine-powdered metallic rhodium was oxidized at 950–1000°C in flowing oxygen or in air for at least 20 h. The fine-powdered metallic rhodium (rhodium black) was prepared by reducing rhodium trichloride with metallic zinc in hydrochloric solution.

The samples used in the phase-relation investigations were mixtures of the low-temperatures phases of rhodium oxide (α -Rh₂O₃) and gadolinium oxide $(C-Gd_2O_3)$, a fluorite-like Tl_2O_3 -type cubic structure [37]). Before weighing, Gd_2O_3 was calcined at 900°C for 3 h in order to remove water and carbon dioxide adsorbed from air. The Gd₂O₃-to-Rh₂O₃ molar ratios were 9:1,4:1,3:1,2:1,3:2,1:1,3:5,1:2,1: 3, 1:4, or 1:9. The equimolar sample was also prepared from Gd₂O₃ and fine-powdered rhodium. The mixture was ground, triturated with ethanol in a jasper mortar, and dried in air; then, it was annealed in corundum crucibles at temperatures from 600 to 1600°C, being quenched every 100°C. For some compositions (e.g., for the equimolar composition), anneals and quenches were carried out every 10-20°C. The anneals at temperatures below 1000°C lasted up to 150 h; at temperatures above 1000°C, the anneals lasted up to 75 h. After every intermediate anneal that lasted longer than 20 h, samples were stirred in a jasper mortar to improve their homogeneity. An SNOL-I4 electrical furnace was used in the anneals below 1000°C. At higher temperatures, an electrical quenching furnace equipped with a Pt/Rh(30%) wire heater was used. The isothermic anneals and quenches were performed in air. The temperature during the anneal was measured with standard TPP-0555 or TPR-0679-01 thermocouples made of Pt-Pt/Rh(10%) or Pt/Rh(6%)-Pt/Rh(30%) wires; the temperature during the isothermal anneals was maintained with an accuracy of ± 10 K.

The phase composition of the starting reagents and mixtures, as well as annealed-and-quenched samples, was monitored using a DRON-3 diffractometer (Cu K_{α} radiation, $2\theta = 10^{\circ}-100^{\circ}$) or a Siemens D 500 HS diffractometer (Cu K_{α} radiation, $2\theta = 10^{\circ}-90^{\circ}$). X-ray phase analysis was performed and the unit cell parameters of individual compounds were calculated using the PDOS and PDWin program packages. X-ray diffraction patterns needed to calculate the unit cell parameters were measured in the Bragg angle (2 θ) range from 15° to 115°; high-purity germanium was the internal standard, and the sample was rotated during the experiment.

Thermoanalytical experiments at temperatures up to 1400°C were carried out on an MOM OD-103 derivatograph. Heating and cooling were carried out in the batch mode under an air atmosphere at 7.5 or 10 K/min. Sample weights were from 400 to 800 mg. Powdered alumina was the reference. The experiments at temperatures to 1600°C were carried out on a Setaram B70 thermal analyzer. Sample sizes were from 50 to 150 mg. In all thermoanalytical experiments, the temperature, DTA, TG, and DTG curves were simultaneously recorded. In addition, precision thermal analysis up to 1500°C was performed on a Netzsch STA 449 thermoanalyzer. Differential scanning calorimetry curves, their first derivatives, TG curves, and DTG curves were recorded simultaneously. A powdered sample, weighing (30.00 ± 0.05) mg, was placed in a corundum crucible and heated to 1500°C in air in the batch mode at 10 K/min; then, the sample was cooled at the same rate to 100°C. The reference used was an empty corundum crucible of the same weight. It was adequate to use air instead of the reference, because the sample size was less than one-sixth of the crucible weight. In addition, this allowed us to avoid interference from the properties of the reference (the dispersivity and bulk density) and from the dissimilar variations of these properties during the experiment. The shapes of the zero curves also demonstrate a positive effect of using air as a reference provided that the sample size is small. The efficiency of this procedure is described in [38]. Precision thermal analysis at temperatures up to 1600°C was performed on a Netzsch STA 429 thermoanalyzer using a similar procedure; powdered samples had an identical size, but here it was appreciably greater (90.00 \pm 0.05) mg. A test sample and a reference (powdered alumina) were placed in identical corundum crucibles, each crucible weighing about 1200 mg.

The chemical analysis of $GdRhO_3$ was carried out gravimetrically. First, the starting $GdRhO_3$ sample was weighed. Then, the weight of the solid thermolysis products ($Gd_2O_3 + Rh$) of this sample was determined as follows. The $Gd_2O_3 + Rh$ mixture was treated with concentrated nitric acid. The gadolinium oxide fully dissolved. The metallic rhodium remained insoluble; its weight was determined and then the Gd_2O_3 weight was calculated.

RESULTS AND DISCUSSION

A scheme of a subsolidus phase diagram for the Gd_2O_3 -Rh₂O₃ system is represented in the figure as a combination of two pseudobinary systems (Gd_2O_3 -Rh and Gd_2O_3 -Rh₂O₃). When we represent phase equilibria in this way, a reversible dissociation of a solid oxide phase is conventionally considered as a phase transition and the gas phase (oxygen) is ignored. If so, phase equilibria in a ternary system may be represented by a combination of binary systems, which gives us a planar scheme of phase relations. Muan [39] first used this technique when studying systems of iron oxides. Later, Schneider and colleagues [40] employed the technique to illustrate phase equilibria in systems containing platinum-metal oxides.

Our subsolidus phase diagram of the Gd_2O_3 -Rh₂O₃ system (figure) shows four stable solid phases (monoclinic *B*-Gd₂O₃, β -Rh₂O₃, Rh, and GdRhO₃) and two metastable phases (cubic *C*-Gd₂O₃ and α -Rh₂O₃). The crystal-chemical parameters and thermal features of these phases displayed in the table correlate with the related literature [28–37, 41–46]. When three solid phases and one gas phase (oxygen) are in equilibrium in the Gd–Rh–O system, the system is monovariant. In this case, at a fixed oxygen partial pressure, three condensed phases coexist at a unique temperature. Therefore, three-phase equilibria are represented by solid horizontal lines in the diagram. The metastable poly-



Scheme of a subsolidus phase diagram for the Gd_2O_3 - Rh_2O_3 system in air. The dashed lines show irreversible polymorphic transitions (1) and (2) observed in simple oxides Gd_2O_3 and Rh_2O_3 , respectively.

morph (cubic C-Gd₂O₃), crystallizing in a Tl₂O₃-type structure, above 1225°C irreversibly transforms to the stable monoclinic *B*-Gd₂O₃ phase [37]:

$$\operatorname{Gd}_2\operatorname{O}_3(C \text{ phase}) \longrightarrow \operatorname{Gd}_2\operatorname{O}_3(B \text{ phase}).$$
 (1)

Our thermoanalytical data, in combination with the X-ray powder diffraction data obtained from Gd_2O_3 samples that were calcined above or below $1225^{\circ}C$, confirm the aforementioned parameters of reaction (1). In the course of the reaction

$$\alpha - Rh_2O_3 \longrightarrow \beta - Rh_2O_3, \qquad (2)$$

metastable α -Rh₂O₃, with its classical corundum-type hexagonal structure [35], irreversibly transforms to stable β -Rh₂O₃, whose orthorhombic structure is also a derivative of the corundum-type structure [36]. The main features of this monotropic polymorphic transition were studied in [15–17, 21–26, 33, 34, 41–44]. It was found in those studies that the temperature range and rate of reaction (2) are affected by the impurities, structure perfection, and grain size of the starting α -Rh₂O₃. These parameters of α -Rh₂O₃ are strongly dependent on the starting rhodium-containing reagent used, the synthesis technique employed to prepare metastable α -Rh₂O₃, and the synthesis parameters. For the α -Rh₂O₃ sample synthesized in this work, polymorphic transition (2) and β -Rh₂O₃ formation can be

C detected by X-ray diffraction after the starting α -Rh₂O₃ is annealed at temperatures in the range from 750 to 1030°C. Above 1030°C, we observe reversible thermal dissociation by the equation

$$\beta - Rh_2O_3 = 2Rh + 3/2O_2.$$
(3)

Reaction (3) and some of its thermodynamic features are well understood [43, 45, 46]. When we use data from [43, 45] to calculate the β -Rh₂O₃ dissociation temperature in air at the standard atmospheric pressure (i.e., at the oxygen partial pressure of 21 kPa), we obtain 1034 and 1033°C, respectively. These temperatures correlate with the value calculated from [46] (1042°C). According to our data [15, 17, 21, 23–26, 44], equilibrium (3) is acquired in air at (1030 ± 5)°C. GdRhO₃ is also found to undergo only one phase transition while heated up to 1600°C:

$$GdRhO_3 = 1/2Gd_2O_3 + Rh + 3/4O_2.$$
 (4)

The thermal dissociation of GdRhO₃ appears in the DTA traces starting at 1370°C as an endotherm with an attendant weight loss of 7.62%. This weight loss correlates with the value calculated from Eq. (4) (7.79%). After single-phase GdRhO₃ samples are annealed at temperatures above 1370°C, their X-ray diffraction patterns display well-defined and narrow peaks associated with well-crystallized, coarse-grained metallic rhodium and the high-temperature gadolinium(III) oxide phase B-Gd₂O₃ (B-Gd₂O₃ is monoclinic [37]). These products do not react with each other or with atmospheric oxygen at 1370-1600°C. However, precisely this reaction, which yields GdRhO₃, is detected by X-ray diffraction in mixtures of Gd₂O₃ and fine-powdered rhodium after more than 100 h of annealing in air at 1300-1350°C. Thus, the isothermic anneal-andquench experiments, in combination with X-ray powder diffraction and thermal analysis data, validate the adequacy of Eq. (4); they also gave us the acquisition temperature for this equilibrium in air $(1370 \pm 10)^{\circ}$ C.

Note that the thermal decomposition of GdRhO₃ by Eq. (4) and that of β -Rh₂O₃ by Eq. (3) are alike. Reversible dissociation into metallic rhodium and oxygen is intrinsic to both oxides. The decomposition temperature for GdRhO₃ is far higher than for Rh₂O₃ (1370°C against 1030°C).

The following features are also of importance. After rhodium(III) oxide is heated above 1030°C, X-ray powder diffraction shows well-crystallized, coarse-grained rhodium with narrow diffraction peaks, in contrast to broader and diffuse diffraction peaks intrinsic to finegrained rhodium. Fine-grained rhodium can always be fully oxidized to single-phase β -Rh₂O₃ at temperatures in the range of 900–1000°C; coarse-grained, well-crystallized rhodium cannot be fully oxidized to Rh₂O₃ at the same temperatures even after 500 h of annealing in air or flowing oxygen. Similar effects are observed for

Phase	Crystal system; space group; structure type	Unit cell parameters; density	Phase transition and its temperatureIrreversible polymorphism $C-Gd_2O_3 \longrightarrow B-Gd_2O_3,$ $1225°C [37]$ $1200°C (our data)Reversible polymorphismB-Gd_2O_3 \longleftrightarrow H-Gd_2O_3,2170°C [37]$			
C-Gd ₂ O ₃	Cubic Ia3 $C-Ln_2O_3$ Type Tl_2O_3	a = 10.849(2) Å $V = 1277.0(6) \text{ Å}^3$ $\rho_x = 7.53 \text{ g/cm}^3$ Z = 16				
B-Gd ₂ O ₃	Monoclinic B2/m B-Ln ₂ O ₃	a = 14.058(9) Å b = 3.563(3) Å c = 8.765(5) Å $\beta = 79.9(2)^{\circ}$ $V = 432.2(6) \text{ Å}^{3}$ $\rho_{x} = 8.35 \text{ g/cm}^{3}$ Z = 6				
Rh	Cubic Fm3m Cu	a = 3.8033(2) Å $V = 55.02(3) \text{ Å}^3$ $\rho_x = 12.42 \text{ g/cm}^3$ Z = 4	Melting, 1960°C [41, 42]			
α-Rh ₂ O ₃	Hexagonal $R\bar{3}c$ Corundum (Al ₂ O ₃)	a = 5.127(4) Å c = 13.843(18) Å $V = 315.1(2) \text{ Å}^{3}$ $\rho_{x} = 8.022 \text{ g/cm}^{3}$ Z = 6	Irreversible polymorphism α -Rh ₂ O ₃ $\longrightarrow \beta$ -Rh ₂ O ₃ , 750°C (our data)			
β-Rh ₂ O ₃	Orthorhombic <i>Pbca</i> Derivative of corundum (Al_2O_3)	a = 5.1475(4) Å b = 5.4426(5) Å c = 14.698(11) Å $V = 411.8(8) \text{ Å}^{3}$ $\rho_{x} = 8.185 \text{ g/cm}^{3}$ Z = 8	Reversible thermal dissociation β -Rh ₂ O ₃ = 2Rh + 3/2O ₂ , 1030°C (our data)			
GdRhO ₃ Orthorhombic <i>Pbnm</i> Perovskite GdFeO ₃		a = 5.2296(4) Å b = 5.7248(5) Å c = 7.5828(6) Å $V = 227.2(3) \text{ Å}^{3}$ $\rho_{x} = 9.01 \text{ g/cm}^{3}$ Z = 4	Reversible thermal dissociation $GdRhO_3 = 1/2Gd_2O_3 + Rh + 3/2O_2,$ $1370^{\circ}C$ (our data)			

Selected	physicoche	mical pro	perties of th	e phases that	t exist in the	subsolidus	region of	the Gd ₂ O ₂ .	-Rh ₂ O ₂	² system
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equilibrium (4). These experiments indicate that the equilibrium acquisition times for the reverse reactions of equilibria (3) and (4) are appreciably affected by the rhodium grain size. Likely, the rate of these reactions is controlled by the oxygen mass transfer through a layer of a simple or mixed-metal rhodium oxide formed on the metal surface.

Thus, only one double oxide $(GdRhO_3)$ exists in the Gd_2O_3 -Rh₂O₃ system. The results of the chemical analysis for GdRhO₃ correlate with the calculated data (the discrepancy does not exceed 0.4%). Single-phase GdRhO₃ samples are homogeneous brown polycrystal-line powders; they are insoluble in water, mineral (hydrochloric, nitric, sulfuric, and phosphoric) acids,

and alkalis (NaOH, KOH). Note that rhodium(III) oxide is also highly resistant to acids and alkalis.

X-ray diffraction experiments confirm that GdRhO₃ crystallizes in the orthorhombically distorted perovskite structure of GdFeO₃ [27–34]. The main crystal data for GdRhO₃ listed in the table, including unit cell parameters, correlate with previous data [28, 30, 34] and satisfy the relationship $a < c/\sqrt{2} < b$. In terms of the Goodenough classification [47], we may classify the GdRhO₃ structure with O-type perovskites, in which structure distortion is due only to steric effects. Therefore, the ion size is the only factor that governs the formation of orthorhombically distorted perovskite GdRhO₃ and other O-type perovskites. This is the fundamental difference between the O-type perovskites and O'-type perovskites (such as LaMnO₃); in the latter,

the unit cell parameters are related as $c/\sqrt{2} < a < b$ because of the combination of steric effects (ion sizes) and the Yahn–Teller effect (electron ordering).

The subsolidus phase diagram we suggest for the Gd₂O₃-Rh₂O₃ system is topologically similar to the phase diagrams for the Ln₂O₃-Rh₂O₃ systems with Ln = La, Dv, Ho, Er, Yb, or Lu [21–26], if we ignore polymorphic transition (1) in Gd_2O_3 , the analogous irreversible polymorphic transition in La_2O_3 , and the absence of this type of polymorphism in Ln_2O_3 , where Ln = Dy, Ho, Er, Yb, or Lu. The dimensions of the subsolidus phase diagrams for Ln₂O₃-Rh₂O₃ systems are different only where they are due to different dissociation temperatures of LnRhO₃. The dissociation temperature decreases from 1450°C in LaRhO₃ to 1275°C in LuRhO₃ [21–26]. The position of the upper horizontal line, which corresponds to the temperature of the $LnRhO_3 = 1/2Ln_2O_3 + Rh + 3/4O_2$ equilibrium, changes accordingly.

The designed diagram shows the phase relations in air under the standard atmospheric pressure (21 kPa oxygen partial pressure). However, the changing oxygen partial pressure will change the dissociation temperature of β -Rh₂O₃ and GdRhO₃. The increase in the oxygen partial pressure from 1 to 96 kPa elevates the equilibrium dissociation temperature of Rh₂O₃ from 900 to 1126°C [43]. Such experiments for GdRhO₃ have not been carried out, but it was found in [22] that the dissociation temperature of LaRhO₃, a similar perovskite oxide, increased from 1455 to 1570°C when the oxygen partial pressure increased from 21 to 100 kPa. Evidently, something like that is expected for GdRhO₃. Thus, in accordance with previous data [15–18, 21–26, 42-46, 48-50], the dissociation temperatures of rhodium oxides in similar systems are significantly affected by the oxygen partial pressure; when the oxygen partial pressure changes, the temperature and concentration boundaries of the phase fields change accordingly.

The results of this work and previous research [21– 26, 29–34, 41–46, 48–50] show physicochemical analogy between the Rh–O system and Ln–Rh–O systems. Double oxides with the general formula LnRhO₃, existing in Ln_2O_3 –Rh₂O₃ systems, inherit their physicochemical properties from Rh₂O₃. In particular, Rh₂O₃ and LnRhO₃, as a rule, have high chemical stability, and their thermal behavior is similar; namely, they undergo reversible thermal dissociation to metal rhodium and oxygen.

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