

Calcium Ruthenates: Determination of Gibbs Energies of Formation Using Electrochemical Cells

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Metallic Ru has been found to coexist separately with CaO, RuO₂, and the interoxide phases, Ca₂RuO₄, Ca₃Ru₂O₇, and CaRuO₃, present along the pseudobinary system CaO-RuO₂. The standard Gibbs energies of formation ($\Delta_{f(ox)}G^{\circ}$) of the three calcium ruthenates from their component oxides have been measured in the temperature range 925-1350 K using solid-state cells with yttria-stabilized zirconia as the electrolyte and Ru + RuO₂ as the reference electrode. The standard Gibbs energies of formation ($\Delta_{f(ox)}G^{\circ}$) of the compounds can be represented by Ca₂RuO₄: $\Delta_{f(ox)}G^{\circ}/J mol^{-1} = -38,340 - 6.611 T (\pm 120)$, Ca₃Ru₂O₇: $\Delta_{f(ox)}G^{\circ}/J mol^{-1} = -75,910 - 11.26 T (\pm 180)$, and CaRuO₃: $\Delta_{f(ox)}G^{\circ}/J mol^{-1} = -35,480 - 3.844 T (\pm 70)$. The data for Ca₂RuO₄ corresponds to the stoichiometric composition, which has an orthorhombic structure, space group *Pbca*, with short *c* axis ("S" form). The structural features of the ternary oxides responsible for their multi entropy stabilization are discussed. A three-dimensional oxygen potential diagram for the system Ca-Ru-O is developed as a function of composition and temperature from the results obtained. Using the Neumann-Kopp rule to estimate the heat capacity of the ternary oxides relative to their constituent binary oxides, the standard enthalpies of formation of the three calcium ruthenates from the elements and their standard entropies at 298.15 K are evaluated.

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Crystal, magnetic, and electronic structures of the three calcium ruthenates, CaRuO₃, Ca₂RuO₄, and Ca₃Ru₂O₇, have been studied extensively.¹⁻¹⁷ The compounds $ARuO_3$ (A = Ca, Sr, and Ba) are good electrical conductors with Ru^{4+} ion in low-spin $t_{2g}^4 e_g^o$ configuration.¹ The compound CaRuO₃ exhibits metallic behavior with low resistivities of the order of 10^{-3} Ω cm at room temperature.² Recent studies show that CaRuO₃ has the orthorhombic perovskite structure, space group Pnma, with a = 0.5519 nm, b = 0.5364 nm, and c = 0.7665 nm.¹ To maintain consistency with extensive literature on transition metal oxides, the long axis has been reassigned as the c direction. Earlier crystallographic data²⁻⁵ are consistent with this description. Although the compound CaRuO₃ had been characterized earlier by Longo *et al.*⁶ as being antiferromagnetic with a Néel temperature of $T_{\rm N} = 110 \ (\pm 10) \ {\rm K}$, ⁹⁹Ru Mössbauer spectroscopy^{7,8} has shown conclusively that there is no magnetic ordering even at 4.2 K. The compound CaRuO₃ is a paramagnetic metal following the Curie-Wiess law at high temperatures. It is used as a metallic barrier layer in making superconductornormal metal-superconductor (SNS) type Josephson junctions.⁹ The conducting oxide CaRuO₃ grows epitaxially on YBa₂Cu₃O_{7- δ}. SNS-type high- $T_{\rm C}$ step-edge junction dc superconducting quantum interference devices (SQUIDs) with CaRuO3 as the normal metal have been fabricated by Lee et al.¹⁰

 Ca_2RuO_4 compound shows nonmetallic behavior for T < 357K.^{11,12} An antiferromagnetic transition has been identified at $T_{\rm N}$ = 110 K.¹¹ Nakatsuji *et al.*¹³ have reported that the two distinct phases of Ca₂RuO₄, denoted as "S" and "L" phases characterized by shorter and longer c axis parameters, behave as Mott insulators. A recent neutron powder diffraction pattern of S is indexed for orthorhombic structure, consistent with space group Pbca with a = 0.54097 nm, b = 0.54924 nm, and c = 1.19613 nm.¹⁴ The pattern of L is also indexed for orthorhombic structure, but with space group $P2_1/c$ with a = 0.53292 nm, b = 0.53194 nm, and c = 1.23719 nm at 295 K.¹⁴ Both structures are derived from the ideal K₂NiF₄ structure type by rotation of the RuO₆ octahedra around the long axis, combined with a tilt around an axis lying in the RuO₂ plane. The orientation of the tilt axis seems to distinguish the two room-temperature symmetries; the L phase is characterized by significantly smaller tilt angle, slightly higher rotation angle, and shorter Ru-O in-plane distances.¹³ The structure changes from orthorhombic to tetragonal at the insulator to near-metal transition at 357 K.¹² The S phase is stoichiometric and thermodynamically stable in air at temperatures above ~1623 K, while the L phase probably contains excess oxygen and is stable in air at much lower temperatures.¹³⁻¹⁵ Although the single S phase can be obtained easily by heating the component oxides in the temperature range from 1633 to 1653 K, the single L phase was not always easy to synthesize because of the frequent presence of the S phase. Annealing the powder or pellets of the S phase in air at 673 K for 50 h reliably made single-phase L.¹³⁻¹⁵

The structure of Ca₃Ru₂O₇ has been reported to be isostructural with both Sr₃Ru₂O₇ and Ca₃Ti₂O₇, having a body-centered tetragonal unit cell with the symmetry of *I4/mmm* with a = 0.3841 nm and c = 1.9609 nm.¹⁶ Single-crystal Ca₃Ru₂O₇ shows a metallic antiferromagnetic phase intermediate between first-order metal to nonmetal transition at $T_{\rm M} = 48$ K and the antiferromagnetic ordering (Néel) temperature $T_{\rm N} = 56$ K.¹⁶ Guertin *et al.*¹⁷ observed very unusual nonohmic dc current-voltage characteristics, including negative differential resistivity (NDR) for $T < T_{\rm M}$.¹⁷

Mallika and Sreedharan¹⁸ have reported high-temperature thermodynamic studies on CaRuO₃. Their measurements were based on an incorrect assumption that CaRuO₃ is the only ternary oxide in the pseudobinary system CaO-RuO₂. No information is available in the literature on enthalpy and Gibbs energy of formation of the compounds Ca₂RuO₄ and Ca₃Ru₂O₇. In this study, the thermodynamic data on all three calcium ruthenates were determined using solidstate electrochemical cells. These data are useful for assessing the compatibility of CaRuO₃ with other materials in device applications.

Experimental

Materials.—Calcium oxide was prepared by the decomposition of 99.99% pure CaCO₃ at 1100 K under vacuum. Ruthenium powder was produced from 99.99% RuO₂ by reducing the fine oxide powder in dry hydrogen at 1073 K for 3 h. Samples of the three calcium ruthenates were prepared by the solid-state reaction between CaO and RuO₂. The three ternary oxides, CaRuO₃, Ca₂RuO₄, and Ca₃Ru₂O₇, were prepared by heating pellets containing CaO and RuO₂ powders in the appropriate stoichiometric ratio at 1300, 1640, and 1700 K, respectively, for 6 days in dry oxygen with six intermediate grindings. The pellets were prepared from an intimate mixture of the component oxides by compaction at 100 MPa using a steel die. The pellets were contained in a closed platinum crucible and supported on a sacrificial pellet of the same composition. $CaRuO_3$ forms first at lower temperatures and prolonged heating at higher temperatures are necessary to obtain Ca_2RuO_4 and $Ca_3Ru_2O_7$. The Ca_2RuO_4 phase from synthesis at 1640 K was a mixture of S and L phases. The sample was annealed at 773 K for 3 days in pure dry oxygen to convert phase S into phase L. The pure L phase contains excess oxygen and can be represented as $Ca_2RuO_{4,08}$. The S phase is almost stoichiometric. The oxygen content was determined from mass loss on hydrogen reduction.

The formation of the three ternary compounds was confirmed by X-ray powder diffraction (XRPD). The XRPD pattern for Ca₃Ru₂O₇ obtained in this study indicates that the structure is orthorhombic rather than tetragonal as reported earlier.¹⁶ The lattice parameters of Ca₃Ru₂O₇ are a = 0.5523 nm, b = 0.5379 nm, and c = 1.9568 nm. The lattice parameters for black-colored CaRuO₃ obtained in this study are a = 0.5526 nm, b = 0.5359 nm, and c = 0.76619 nm, in fair agreement with data available in the literature.¹⁻⁵ The lattice parameters of S and L phases of Ca₂RuO_{4+ δ} obtained in this study are fully compatible with the crystal parameters given by Braden *et al.*¹⁴ Yttria-stabilized zirconia solid-electrolyte tubes used in this study were obtained from a commercial source.

Phase relations.-Each of the three ternary oxides was equilibrated with Ru metal separately at 1300 K in evacuated quartz ampoules. Intimate mixtures of the oxides and Ru powders in the molar ratio 1:1 were pelletized. The pellets were contained in zirconia crucibles, each placed and sealed individually in evacuated quartz ampoules. The samples were equilibrated for 6 days. The phasecomposition of the samples was investigated after quenching to room temperature by XRPD and scanning electron microscopy (SEM) equipped with an energy-dispersive system (EDS). The phase composition of the samples after equilibration was found to be the same as in the starting material. Each of the ternary oxides was found to coexist with Ru metal. However, the starting L form of Ca₂RuO₄ had changed to the S form after equilibration with Ru. This suggests that both S and L forms are stable, the L form in oxygen-rich atmospheres and the S form at low oxygen chemical potentials. The S form is almost stoichiometric. Since the space group $P2_1/c$ characterizing the L form is a subgroup of *Pbca* corresponding to the S form, there is probably a continuous solid solution between the two forms, at least at the higher temperatures. Pure CaO and RuO₂ were also found to coexist separately with metallic Ru. A tentative phase diagram for the system Ca-Ru-O based on these results is shown in Fig. 1.

Measurement of Gibbs energies of formation of ternary oxides.—The reversible electromotive force (emf) of the following solid-state cells was measured as a function of temperature in the range 925–1350 K:

1. Pt, CaO + Ca₂RuO₄ + Ru//(Y₂O₃)ZrO₂//Ru + RuO₂, Pt 2. Pt, Ca₂RuO₄ + Ca₃Ru₂O₇ + Ru//(Y₂O₃)ZrO₂//Ru + RuO₂, Pt 3. Pt, Ca₃Ru₂O₇ + CaRuO₃ + Ru//(Y₂O₃)ZrO₂//Ru + RuO₂, Pt

The cells were designed based on phase relations depicted in Fig. 1. All the cells are written such that electrodes on the right are positive. $(Y_2O_3)ZrO_2$ is an oxygen ion conductor with ionic transport number greater than 0.99 at the temperatures and oxygen partial pressures encountered in this study. Two experiments were conducted on each cell.

In earlier studies,¹⁹⁻²² an advanced version of the solid-state cell incorporating a buffer electrode was used along with pure oxygen gas as a reference electrode to prevent polarization of the three-phase electrode. The polarization is caused by the electrochemical flux of oxygen through the solid electrolyte from the electrode with the higher oxygen potential to the electrode with the lower oxygen potential. The oxygen transport occurs by coupled migration of oxygen ions and trace concentration of electrons or holes. In this study, the polarization effect was minimized by using $Ru + RuO_2$ as the



Figure 1. Isothermal section of the phase diagram for the Ca-Ru-O system at 1300 K.

reference electrode. In this arrangement, the cell emf and hence the driving force for oxygen transport are significantly reduced. Moreover, the standard Gibbs energy of formation of calcium ruthenates from their component binary oxides CaO and RuO₂ can be directly obtained from the emf by using Ru + RuO₂ as the reference electrode. In all the cells, the partial pressures of oxygen at both electrodes were quite appreciable, especially at the higher temperatures. Therefore, the static-sealed design used by Charette and Flengas²³ was found more appropriate than other designs that employ either dynamic vacuum or inert gas flow over the electrodes.^{24,25} The cell design used for high-temperature emf measurements is shown in Fig. 2. It consisted of two distinct compartments, separated by an impervious yttria-stabilized zirconia (YSZ) tube. The working electrode was contained inside the zirconia tube. The electrodes were sealed under vacuum in separate compartments. The equilibrium oxygen partial pressure is established at each electrode by decomposition of an oxide phase.

The working electrode consisted of an intimate mixture of CaO + Ca_2RuO_4 + Ru in the molar ratio 1:1.5:1 in cell 1, a mixture of Ca_2RuO_4 + $Ca_3Ru_2O_7$ + Ru in the same ratio in cell 2, and a mixture of $Ca_3Ru_2O_7$ + $CaRuO_3$ + Ru in the same ratio in cell 3. The



Figure 2. A schematic diagram of the apparatus for high-temperature emf measurements.

reference electrode consisted of an intimate mixture of Ru + RuO_2 in the molar ratio 1:1.5. In each case, an excess of the component that decomposed to establish the oxygen pressure in the closed system was taken. The phase mixture was rammed against the closed end of a stabilized zirconia tube with a short Ru wire embedded in the mixture. The Ru wire was spot-welded to a Pt lead, ~ 10 mm above the electrode. An alumina sheath was used to insulate the metallic lead and to press the working electrode against the flat end of the zirconia tube. The top of the zirconia tube was closed with a tight-fitting bell-shaped Pyrex tube, which supported a tungsten electrode connection sealed into the glass. The joint between the bell and the zirconia tube was sealed with De Khotinsky cement. A spring placed between the bell and the alumina sheath applied pressure on the working electrode. The assembled working electrode half-cell was first evacuated using a sidearm tube shown in the diagram, then heated to \sim 600 K, and finally the tube was flame sealed under vacuum.

The cell was assembled inside a fused quartz enclosure. The zirconia crucible containing the reference electrode was placed on the zirconia beads. The working electrode assembly was then loaded into the crucible. The annular space between the zirconia tube and crucible was filled with the reference electrode mixture. The working electrode assembly was pressed down by means of a second metal spring placed between the bell and the top Pyrex cover. The top cover supported two tungsten-glass seals through which electrical connections were made. All electrode connections were silversoldered. Finally, the top cover was cemented in place by melting the De Khotinsky cement in the ring container shown in the diagram. The cement was allowed to solidify while pressing the top cover against the spring. Then the outer quartz enclosure was also evacuated from a sidearm tube and flame sealed under vacuum. The cell assembly, shown in Fig. 2, was essentially identical to that developed by Charette and Flengas.23

The entire assembly shown in Fig. 2 was placed inside a vertical resistance furnace with the electrodes located in the eventemperature zone $(\pm 1 \text{ K})$. The oxygen partial pressure in the evacuated and sealed enclosures around the working and reference electrodes was established by the dissociation of the oxides. Because the joints between Ru and Pt leads were located in the even-temperature zone, there was no significant thermoelectric contribution to the emf from this source. The cell assembly, where cement seals were located, remained at room temperature during measurements. A Faraday cage made from thick stainless steel foil was placed between the furnace and the cell assembly. The foil was grounded to minimize induced emf on cell leads. The temperature of the furnace was controlled to $(\pm 1 \text{ K})$. The temperature was measured by a Pt/Pt-13% Rh thermocouple, checked against the melting point of gold. The cell potentials were measured with a high-impedance digital voltmeter with a sensitivity of $(\pm 0.1 \text{ mV})$. The potential readings were corrected for small thermal emfs, measured separately using a symmetric cell with identical electrodes. At the end of each experiment, the electrodes were cooled to room temperature and examined by optical microscopy, SEM, and XRPD. Although small changes in the relative concentration of the constituents were observed in each case, the number and nature of the phases remained unaltered. The change in relative concentration was consistent with the expected decomposition of one of the oxides at high temperature to generate the equilibrium oxygen pressures in sections of the apparatus.

Results and Discussion

High-temperature thermodynamic properties of ternary oxides.—The reversible emfs of cells 1, 2, and 3 in the temperature range 925–1350 K are plotted as a function of temperature in Fig. 3. Reversibility of the emf was established by microcoulometric titration in both directions. A small current (\sim 50 µA) was passed through the cell using an external potential source for \sim 3 min, and the open-circuit emf was subsequently monitored as a function of time. The emf was found to return to the steady value before each perturbation. During the titration, the chemical potential of oxygen



Figure 3. The reversible emf of cells 1, 2, and 3 as a function of temperature.

at each electrode was displaced from equilibrium by an essentially infinitesimal amount. Since the electrodes returned to the same potential after such displacements in opposite directions, equilibrium was experimentally verified. The emfs of all the cells were also found reproducible on repeated temperature cycling. Within experimental uncertainty, the emfs show a slight linear increase with temperature. The linear least-squares regression analysis of the emf of cell 1 gives

$$E_{\rm I} = 99.33 + 0.01713 \,\,{\rm T} \,\,(\pm 0.31) \,\,{\rm mV}$$
 [1]

The uncertainty limit corresponds to twice the standard error estimate. The emf of cell 1 is related to the standard Gibbs energy change for the overall cell reaction

$$2\text{CaO} + \text{RuO}_2 \rightarrow \text{Ca}_2\text{RuO}_4$$
 (S form) [2]

$$\Delta_{r(2)}G^{\circ} = \Delta_{f(ox)}G^{\circ}(Ca_{2}RuO_{4}) = -4FE_{I} = -38,340$$

- 6.611 T (±120) J mol⁻¹ [3]

where *F* is the Faraday constant and $\Delta_{r(2)}G^{\circ}$ represents the standard Gibbs energy change for Reaction 2. The temperature-independent term on the right side of Eq. 3 is the enthalpy of formation of Ca₂RuO₄ (S form) from component oxides at an average temperature of ~1140 K. The temperature-dependent term is related to the corresponding entropy of formation. The oxygen chemical potential over the three-phase electrode of cell 1 is established by the reaction

$$2\text{CaO} + \text{Ru} + \text{O}_2 \rightarrow \text{Ca}_2\text{RuO}_4$$
 [4]

The oxygen potential can be computed using the emf of cell 1 and refined values for the Gibbs energy of formation of RuO_2 reported recently²⁶

$$\Delta \mu_{O_2} (\text{CaO} + \text{Ca}_2 \text{RuO}_4 + \text{Ru})$$

= -363,060 + 347.60 T
- 23.49 T ln T (±150) J mol⁻¹ [5]

The least-square regression analysis of the emf of cell 2 gives

$$E_2 = 95.38 + 0.00695 \text{ T} (\pm 0.12) \text{ mV}$$
 [6]

The emf of cell 2 is related to the standard Gibbs energy change for the net cell reaction

$$3Ca_2RuO_4 + RuO_2 \rightarrow 2Ca_3Ru_2O_7$$
^[7]

$$\Delta_{r(7)}G^{\circ} = -4FE_2 = -36,810 - 2.682 \text{ T} (\pm 50) \text{ J} \text{ mol}^{-1}$$
[8]

By combining Reactions 2 and 7, one obtains the reaction representing the formation of $Ca_3Ru_3O_7$ from its component oxides

$$3\text{CaO} + 2\text{RuO}_2 \rightarrow \text{Ca}_3\text{Ru}_2\text{O}_7 \qquad [9]$$

$$\Delta_{\rm f(ox)}G^{\circ}({\rm Ca_3Ru_2O_7}) = -75,910 - 11.26 \ {\rm T} \ (\pm 180) \ {\rm J} \ {\rm mol^{-1}} \ [10]$$

The oxygen chemical potential over the three-phase electrode of cell 2 is established by the reaction

$$3\operatorname{Ca}_{2}\operatorname{RuO}_{4} + \operatorname{Ru} + \operatorname{O}_{2} \rightarrow 2\operatorname{Ca}_{3}\operatorname{Ru}_{2}\operatorname{O}_{7}$$
[11]

The oxygen potential can be computed using the emf of cell 2 and the Gibbs energy of formation of RuO_2^{26}

$$\begin{split} \Delta \mu_{O_2} (Ca_2 RuO_4 + Ca_3 Ru_2 O_7 + Ru) &= -361,530 + 351.53 \ T \\ &- 23.49 \ T \ln T \ (\pm 100) \ J \ mol^{-1} \end{split} \label{eq:Delta}$$

The measured emf of cell 3 can be expressed by the equation

$$E_3 = 79.09 + 0.000706 \text{ T} (\pm 0.07) \text{ mV}$$
 [13]

The emf of cell 3 is related to the standard Gibbs energy change for the cell reaction

$$Ca_3Ru_2O_7 + RuO_2 \rightarrow 3CaRuO_3$$
 [14]

$$\Delta_{r(14)}G^{\circ} = -4FE_3 = -30,530 - 0.273 \text{ T} (\pm 30) \text{ J} \text{ mol}^{-1}$$
[15]

The standard Gibbs energy of formation of $CaRuO_3$ from its component oxides can be computed by combining the standard Gibbs energy changes associated with Eq. 9 and 14

$$CaO + RuO_2 \rightarrow CaRuO_3$$
 [16]

$$\Delta_{f(ox)}G^{\circ}(CaRuO_3) = -35,480 - 3.844 \text{ T} (\pm 70) \text{ J} \text{ mol}^{-1}$$
[17]

Assuming that CaRuO₃ is the only ternary oxide present in the system Ca-Ru-O, Mallika and Sreedharan¹⁸ have evaluated $\Delta_{f(ox)}G^{\circ}(CaRuO_3)$ from its component oxides as

$$\Delta_{f(ox)}G^{\circ}(CaRuO_3) = 14,396 - 44.221 \text{ T} (\pm 1905) \text{ J} \text{ mol}^{-1}$$
[18]

They used a solid oxide cell with CaO + CaRuO₃ + Ru as the working electrode and air at the reference. Three ternary oxides are found to be stable in this study. The phases CaO and CaRuO₃ cannot coexist with Ru metal under equilibrium conditions. Figure 4 compares $\Delta_{f(ox)}G^{\circ}$ (CaRuO₃) obtained in this study with the data of Mallika and Sreedharan.¹⁸ The reported uncertainty limits are also shown in the figure. The results of this study indicate that the formation of CaRuO₃ from component oxides is exothermic ($\Delta_{f(ox)}H$



Figure 4. Comparison of the Gibbs energy of formation of $CaRuO_3$ from their component binary oxides obtained in this study with data reported in the literature.¹⁸

= -35.48 kJ mol⁻¹), whereas the results of Mallika and Sreedharan¹⁸ suggest that the reaction is endothermic $(\Delta_{f(ox)}H$ = 14.4 kJ mol⁻¹). According to the data of Mallika and Sreedharan,¹⁸ the compound CaRuO₃ is mainly entropy stabilized. From a theoretical point of view, it is difficult to understand the large positive entropy of formation suggested by Mallika and Sreedharan.¹⁸ This discrepancy is caused by the unstable nature of their working electrode. They mixed CaO, CaRuO₃, and Ru in the mass ratio 3:4:2. This corresponds to $X_{RuO_2} \approx 0.36$ in the pseudobinary system CaO-RuO₂, and at equilibrium a mixture of Ca₂RuO₄ and Ca₃Ru₂O₇ should be stable. Hence, during their hightemperature electrochemical measurements, the starting compounds CaO and CaRuO₃ would have gradually reacted to form a mixture of Ca₂RuO₄ and Ca₃Ru₂O₇, causing spurious effects.

The oxygen chemical potential over the three-phase electrode of cell 3 is established by the reaction

$$Ca_3Ru_2O_7 + Ru + O_2 \rightarrow 3CaRuO_3$$
[19]

The oxygen potential can be computed using the emf of cell 3 and refined values for the Gibbs energy of formation of RuO_2^{26}

$$\begin{split} \Delta \mu_{O_2}(Ca_3Ru_2O_7 + CaRuO_3 + Ru) &= -355,250 + 353.94 \text{ T} \\ &- 23.49 \text{ T}\ln\text{T} \ (\pm90) \text{ J} \ \text{mol}^{-1} \end{split} \label{eq:eq:eq:optimal_states}$$

The enthalpy and Gibbs energy of mixing at 1100 K for the system $CaO-RuO_2$ is shown in Fig. 5 as a function of composition. The value of the Gibbs energy of mixing for each compound is obtained by dividing its standard Gibbs energy of formation from binary oxides by the number of molecules of the binary oxides present in the compound. The minimum in the Gibbs energy of mixing occurs at the 1:1 composition corresponding to the compound $CaRuO_3$. The enthalpy of mixing also has a similar shape.



Figure 5. The Gibbs energy and enthalpy of mixing as a function of composition for the pseudobinary system $CaO-RuO_2$.

There is little entropy stabilization of all the three interoxide compounds. However, the shape of the curves indicates that all the compounds are stable at low temperatures.

To understand the origin of the small positive entropy of formation of calcium ruthenates from component oxides, it is useful to review the structural features associated with these compounds. CaRuO₃ has GdFeO₃-type orthorhombic perovskite structure consisting of a framework of corner-sharing RuO₆ octahedra linked to zig-zag chains. In the ideal perovskite structure ABO_3 , the BO_6 octahedra are set at corners of a cubic unit cell with their axis oriented along the cell edges. In the center, there is space for A ion which will fit perfectly with 12-fold coordination if d_{AO} $= \sqrt{2}d_{BO}$. When A is too small to satisfy this criterion, BO₆ octahedra are rotated and tilted to fill the extra space around the A ion. These rotations cause the unit cell to be smaller and distorted from the ideal cubic cell. The A-O bond lengths split into two groups of eight short and four long. The distortion is discussed in terms of the Goldschmidt tolerance factor, $t = d_{AO}/(\sqrt{2}d_{BO})$. The factor for CaRuO₃ is 0.88. There are no significant distortions in the RuO₆ octahedra. The rigid character of RuO₆ octahedra is related to the strong overlap between Ru-4d and O-2p orbitals and the pronounced covalent character of the Ru-O bond. The density of states (DOS) at the Fermi level (E_F) of CaRuO₃ consists primarily of Ru-4d states with a small contribution from O-2p states. The contribution of Ca to the DOS at $E_{\rm F}$ is negligibly small.¹

Because of the larger radial extent of the 4*d* shell compared to the 3*d* shell, it should be more strongly affected by the crystal-field interaction of surrounding ions. This in turn should cause the t_{2g} - e_g splitting to be quite large, so that the filling of the lower-lying triplet t_{2g} should precede the filling of the much more highly excited doublet e_g level. Thus, low spin state (S = 1) is expected for the Ru⁴⁺(4*d*⁴) ion. The asymmetric filling of the t_{2g} orbitals can result

Table I. Thermodynamic properties of Ca_2RuO_4 , $Ca_3Ru_2O_7$, and $CaRuO_3$ at 298.15 K.

Compound	$\begin{array}{c} \Delta_{\rm f(ox)}H^{\circ}_{298.15} \\ (\rm kJ\ mol^{-1}) \end{array}$	$\frac{\Delta_{\rm f} H_{298.15}^\circ}{\rm (kJ\ mol^{-1})}$	$\Delta_{f(ox)} S^{\circ}_{298.15} (J \text{ mol}^{-1} \text{ K}^{-1})$	$S_{298.15}^{\circ}$ (J mol ⁻¹ K ⁻¹)
Ca_2RuO_4	-38.34	-1622.034	6.611	128.91
	(± 0.25)	(± 1.78)	(± 0.22)	(± 0.34)
Ca ₃ Ru ₂ O ₇	-75.91	-2608.215	11.260	217.78
5 2 1	(± 0.37)	(± 2.67)	(± 0.50)	(± 0.64)
CaRuO ₃	-35.48	-984.090	3.844	88.07
	(± 0.13)	(± 0.89)	(± 0.17)	(± 0.22)

in small Jahn-Teller distortion. The flattening of the RuO_6 octahedra along the *c* axis of S-Ca₂RuO₄ is indicative of the Jahn-Teller effect.

The three calcium ruthenates can be considered as members of the Ruddelsdon-Popper series, $Ca_{n+1}Ru_nO_{3n+1}$ ($n = 1, 2, and \infty$). The structure is composed of planes of corner-sharing RuO₆ octahedra separated by CaO rock-salt layers. The number of RuO₆ planes between two adjacent rock-salt layers is determined by the number *n*. Half a unit cell offsets the RuO₆ planes on opposite sides of a rock-salt layer relative to one another. Tilting and rotation of the RuO₆ octahedra away from the idealized structure results in orthorhombic distortions. The amount of distortion within the planes appreciably decreases with *n*. It is interesting to note that the Néel temperature of the compounds varies inversely with the number of planes *n*. Reduction in RuO₆ planar distortion probably increases the degree of overlap Ru-4*d* and O-2*p* orbitals, resulting in stronger magnetic interactions between neighboring ions.

The small positive entropy of formation of calcium ruthenates may be related to (a) excess entropy associated with rotation and tilting of RuO₆ octahedra, and/or (b) randomization of the direction of the small Jahn-Teller distortion associated with Ru⁴⁺ ion at high temperatures. The volume change in forming the ternary oxide from their component binary oxides at 298 K calculated from unit cell parameters is mildly negative for CaRuO₃ ($\Delta V = -1.53$ cm³ mol⁻¹) and Ca₃Ru₂O₇ ($\Delta V = -0.61$ cm³ mol⁻¹) and slightly positive for Ca₂RuO₄ ($\Delta V = 1.064$ cm³ mol⁻¹ for the S form and $\Delta V = 0.36$ cm³ mol⁻¹ for the L form).

The strong misfit between Ca^{2+} and Ru^{4+} ionic sizes, which drives the structural deformation in Ca_2RuO_4 , favors the insertion of interstitial oxygen. The additional oxygen relaxes the pressure caused by the misfit, because it oversaturates the Ca coordination, and the charge transfer toward the RuO_2 planes results in smaller Ru-O distances. This is reflected by the volume change associated with the formation of the two forms of Ca_2RuO_4 .

Room-temperature thermodynamic properties of ternary oxides.—By invoking the Neumann-Kopp rule to estimate the heat capacity of the ternary oxides relative to their constituent binary oxides, standard enthalpies and entropies of formation of the three calcium ruthenates from their component binary oxides at 298.15 K can be estimated from the measured high-temperature data. Using auxiliary thermodynamic data for CaO²⁷ and RuO₂^{26,28} from the literature, the standard enthalpy of formation of the ternary compounds from elements and their standard entropies at 298.15 K can be assessed. The thermodynamic data for CaO ($S_{298,15}^{\circ}/J$ mol⁻¹ K⁻¹ = 38.0744; $\Delta_{\rm f} H_{298,15}^{\circ}/kJ$ mol⁻¹ = -635.089)²⁷ and RuO₂ ($S_{298,15}^{\circ}/J$ mol⁻¹ K⁻¹ = 46.15;²⁸ $\Delta_{\rm f} H_{298,15}^{\circ}/kJ$ mol⁻¹ = -313.52)²⁶ are used in the evaluation. The derived data for the ternary oxides are summarized in Table I. Calorimetric measurements on low and high-temperature heat capacities and enthalpies of formation can provide independent confirmation of the values given in the table.

Three-dimensional oxygen potential diagram.—The oxygen potential diagram for the Ca-Ru-O system as a function of composition



Figure 6. Three-dimensional representation of oxygen potential diagram for the Ca-Ru-O system as a function of composition and temperature, where P° is the standard pressure (0.1 MPa).

and temperature, computed from the results of this study, is shown in Fig. 6. The composition variable is cationic fraction, $\eta_{Ru}/(\eta_{Ca} + \eta_{Ru})$, where η_i represents moles of component i. Since oxygen is not included in the composition parameter, information on oxygen stoichiometry cannot be displayed on the diagram. Nevertheless, the diagram provides useful information on the oxygen potential range for the stability of various phases. The diagram is complementary to the conventional Gibbs triangle representation of phase relations in ternary systems, where the composition of each phase can be unambiguously displayed. All the topological rules of construction for conventional temperature-composition phase diagrams are applicable to an isothermal section of the oxygen potential diagram shown in Fig. 6.

When three condensed phases coexist with a gas phase at equilibrium in a ternary system such as Ca-Ru-O, the system is monovariant; the logarithm of the oxygen partial pressure varies linearly with the reciprocal of absolute temperature. At constant temperature, the three condensed phases coexist only at a unique partial pressure of oxygen. Therefore, horizontal lines on isothermal sections of the diagram represent three-phase equilibria. Each shaded plane represents the variation of oxygen partial pressure for a three-phase equilibrium in the temperature range 925-1350 K. Each vertical line represents the composition of a compound expressed as cationic fraction of Ru. On reducing the oxygen partial pressure, RuO2 dissociates first followed by the ternary oxides in order of decreasing cationic fraction of Ru. The phase equilibria at very low oxygen potentials between Ca-Ru alloys and CaO are not shown in the figure, since accurate data on Gibbs energies for the binary system Ca-Ru required for the calculation are not available. The oxygen potentials corresponding to Ca-Ru alloy/CaO equilibria are too low to be measured directly by any technique currently available.²⁴ Isobaric sections of the diagram in Fig. 6 give information on phase relations as a function of temperature.

Conclusions

A partial phase diagram of the system Ca-Ru-O has been delineated by equilibration of metallic Ru with the three ternary oxides, Ca_2RuO_4 , $Ca_3Ru_2O_7$, and $CaRuO_3$, separately at 1300 K. Based on the phase relations, three solid-state cells were designed to measure the chemical potential of oxygen corresponding to three-phase fields in the ternary, each involving three condensed phases. The measurements were conducted from 925 to 1350 K with Ru/RuO_2 as the reference electrode. The Gibbs energy changes corresponding to the following reactions were directly measured

$$\begin{split} & 2\text{CaO} + \text{RuO}_2 \rightarrow \text{Ca}_2\text{RuO}_4 \\ & \Delta_r G^\circ = -38,340 - 6.611 \ \text{T} \ (\pm 120) \ \text{J} \ \text{mol}^{-1} \\ & 3\text{Ca}_2\text{RuO}_4 + \text{RuO}_2 \rightarrow 2\text{Ca}_3\text{Ru}_2\text{O}_7 \\ & \Delta_r G^\circ = -36,810 - 2.682 \ \text{T} \ (\pm 50) \ \text{J} \ \text{mol}^{-1} \\ & \text{Ca}_3\text{Ru}_2\text{O}_7 + \text{RuO}_2 \rightarrow 3\text{Ca}\text{RuO}_3 \\ & \Delta_r G^\circ = -30,530 - 0.273 \ \text{T} \ (\pm 30) \ \text{J} \ \text{mol}^{-1} \end{split}$$

Gibbs energies, enthalpies, and entropies of formation of three calcium ruthenates from their component binary oxides were deduced. The standard enthalpies of formation of these oxides from elements and their standard entropies at 298.15 K were also evaluated for the first time. Correlations between electronic and crystallographic structure and thermodynamic properties of the ternary oxides are outlined. The chemical potential diagram for the Ca-Ru-O system is developed as a function of composition and temperature based on the thermodynamic data obtained in this study and auxiliary information on RuO₂ from the literature.

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