

Thermodynamic properties of the pyrochlore $Gd_2Ru_2O_7(s)$ by solid oxide electrochemical cell

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Gibbs energy of formation of $Gd_2Ru_2O_7(s)$ has been determined using solid state electrochemical technique employing oxide ion conducting electrolyte. The reversible electromotive force of the following solid-state electrochemical cell, $(-)Pt/\{Gd_2O_3(s)+Gd_2Ru_2O_7(s)+Ru(s)\}/CSZ//O_2(p(O_2)=21.21\text{ kPa})/Pt(+)$ has been measured. The Gibbs energy of formation of $Gd_2Ru_2O_7(s)$ from elements in their standard state, calculated by the least squares regression analysis of the data obtained in the present study, is represented by: $\{\Delta_r G^O(Gd_2Ru_2O_7, s)/(kJ\ mol^{-1}) \pm 1.7\} = -2549.1 + 0.6438 \cdot (T/K)$; $1030.9 \leq T/K \leq 1193.6$. The second law method gives the value of standard molar enthalpy of formation of the compound from the elements at 298.15 K.

Keywords: Pyrochlores, Electrochemical cells, Oxides, Rare earth rutenates, Ruthenates, Thermodynamic parameters, Gibbs energy of formation

The solid state chemistry of metal oxides containing both lanthanides and 4d transition metals has attracted a great deal of interest¹. Ruthenium based oxides, with the pyrochlore structure, with the general formula $Ln_2Ru_2O_7$ ($Ln = \text{rare-earth}$) show a variety of interesting transport and magnetic properties². This is because the Ru 4d electrons show behavior that is borderline between localized and itinerant that leads to many surprising properties³. The pyrochlores are good refractory materials and have good chemical resistivity making them prospective candidates for nuclear waste matrices^{4,5}. Pyrochlores are also geometrically frustrated magnetic systems exhibiting spin-ice behavior^{6,7}.

Though structural studies, magnetic measurements and theoretical simulations⁸ of a few rare earth rutenate pyrochlores have been carried out, thermodynamic data is scarce. Knowledge about the thermodynamic stability of these compounds is

essential to determine their behavior in various process conditions. This information is also important for the design of processes for the recovery of rare-earth and precious metals from scrap. In the Gd-Ru-O system, the ternary compounds $Gd_3RuO_7(s)$ ⁹, $Gd_2RuO_5(s)$ ¹⁰ and $Gd_2Ru_2O_7(s)$ ¹¹ have been reported. The orthorhombic phase $Gd_3RuO_7(s)$ was prepared by van Berkel and the precise structure was determined by Groen *et al.*¹² by neutron powder diffraction data. $Gd_2Ru_2O_7(s)$ was synthesized by Kobayashi¹¹ and magnetic susceptibility and specific heat measurements were determined in the low temperature region, for the pyrochlore $Gd_2Ru_2O_7(s)$ by Taira *et al.*¹³ The thermal stability of the pyrochlore $Gd_2Ru_2O_7(s)$ has been determined in this study. Based on the phase relations, a solid-state electrochemical cell was designed to measure the Gibbs energy of formation of the ternary oxide $Gd_2Ru_2O_7(s)$ using 0.15 mole fraction calcia stabilized zirconia (CSZ) solid electrolyte, in the temperature range from 1030.9 K to 1193.6 K.

Experimental

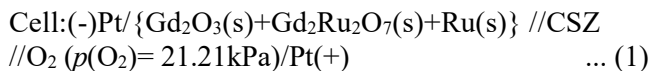
$Gd_2Ru_2O_7(s)$ was synthesized from stoichiometric proportions of preheated $Gd_2O_3(s)$ (mass fraction 0.9985, Leico Ind. Inc.) and $RuO_2(s)$ (mass fraction 0.997, Prabhat Chemicals, India). The oxides were intimately ground and the mixture was then pelletized. Pellets were made using tungsten carbide die at a pressure of 10 MPa. The pellets were then sealed in an evacuated quartz ampoule and heated to $T = 1400\text{ K}$ for 24 h. Interaction of the sample material with quartz ampoule was prevented by stacking pellets in the ampoule and using the pellet in contact with the quartz as the sacrificial pellet. The formation of the compound was confirmed by X-ray diffractometry. The values of the interplanar spacing d obtained for $Gd_2Ru_2O_7(s)$ using STOE diffractometer with Cu- K_α radiation ($\lambda = 1.5406\text{ \AA}$) is in good agreement with those reported in JCPDS¹¹ file no. 830245.

In the Gd-Ru-O system, the oxides, $Gd_2Ru_2O_7(s)$, $Gd_2RuO_5(s)$ and $Gd_3RuO_7(s)$, are reported, and the former two lie on the tie line between $Gd_2O_3(s)$ and $RuO_2(s)$. Phase relations were explored involving different phase mixtures of oxide phases and metal, by equilibration at 1200 K and phase analysis of quenched samples. The phase composition of

{Gd₂O₃(s)+Gd₂Ru₂O₇(s)+Ru(s)} remained unaltered by equilibration. Hence, a phase mixture of {Gd₂O₃(s)+Gd₂Ru₂O₇(s)+Ru(s)} in the molar ratio of 1:1:2 was pelletized into a pellet of dimension 10 mm diameter and 3 mm in thickness, and used for emf measurements.

For the oxide cell assembly, a double compartment cell assembly with 0.15 mole fraction calcia-stabilized-zirconia (CSZ) solid electrolyte tube with one end closed and flat was used to separate the gaseous environments of the two electrodes. A schematic diagram of the in-house fabricated experimental set-up used and experimental details is shown in an earlier publication¹⁴. All the measurements were carried out at 101.325 kPa, the atmospheric pressure. Purified argon gas that served as the cover gas over the working electrode, was bubbled out at a steady rate through an oil bubbler without disturbing the equilibrium at the working electrode, maintaining the internal pressure at ambient.

A Faraday cage was placed between the furnace and cell assembly and grounded to minimize induced electromotive force (emf) on the cell leads. Alumina sheathed Pt leads were used to measure the emf. Synthetic dry air from an air generator was used as the reference electrode. The sample pellet was made by compaction of a mixture of Gd₂O₃(s)+Gd₂Ru₂O₇(s)+Ru(s) at a pressure of 100 MPa. The temperature of the cell was measured by a calibrated chromel-alumel thermocouple located in the vicinity of the pellet. The emf was measured using a high impedance Keithley 614 electrometer after initially equilibrating the galvanic cells at 1000 K for at least 24 h. The following cell configuration was employed in the present study:



The reversibility of the solid-state electrochemical cell was checked by microcoulometric titration in both directions. The range of permissible oxygen partial pressures¹⁵ for purely ionic conduction for CSZ electrolytes is 10⁻²⁰ Pa at 1000 K and 10⁻¹³ Pa at 1273 K. The oxygen partial pressure of the above designed cell falls within this range.

Results and discussion

The emf of the solid state oxide electrochemical cell is related to the partial pressure of oxygen at the two electrodes and is given by the relation,

$$E = (RT/nF) \cdot \int_{p'(\text{O}_2)}^{p''(\text{O}_2)} t(\text{O}^{2-}) \cdot d \ln p(\text{O}_2) \quad \dots (2)$$

where E is the measured emf of the cell in volts, $R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant, n is the number of electrons participating in the electrode reaction, $F = 96486.4 \text{ C mol}^{-1}$ is the Faraday constant, T is the absolute temperature, $t(\text{O}^{2-})$ is the effective transference number of O^{2-} ion for the solid electrolyte and $p''(\text{O}_2)$ and $p'(\text{O}_2)$ are the equilibrium oxygen partial pressures at the positive and negative electrodes respectively. The transport number of oxygen ion in the present electrolyte cell arrangement is nearly unity ($t(\text{O}^{2-}) > 0.99$) at the oxygen pressures and temperatures covered in this study. Hence, the emf of the cell is directly proportional to logarithm of the ratio of partial pressures of oxygen at the electrodes:

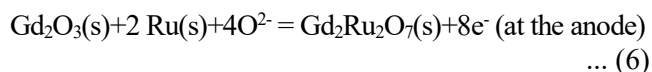
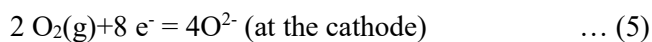
$$E = (RT/nF) \ln \{ p''(\text{O}_2)/p'(\text{O}_2) \} \quad \dots (3)$$

Thus,

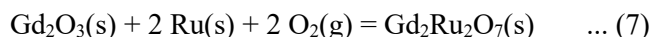
$$nFE = RT \ln p''(\text{O}_2) - RT \ln p'(\text{O}_2) \quad \dots (4)$$

where $RT \ln p''(\text{O}_2)$ is the oxygen chemical potential over the positive electrode and $RT \ln p'(\text{O}_2)$ is the oxygen chemical potential over the negative electrode.

The reversible emfs of the cell measured as a function of temperature is shown in Fig. 1, and are taken at 101.325 kPa. The half-cell reaction at the cathode and the anode for the cell can be given by Eqs (7) and (8).



The overall cell reaction can be represented by Eq. (7).



The least square regression analysis of the emf gives

$$E/V (\pm 0.0022) = 0.9238 - 5.02 \times 10^{-4} (T/\text{K}) \times (1030.9 \leq T/\text{K} \leq 1193.6) \quad \dots (8)$$

The uncertainties quoted are the standard deviation in emf. The $\Delta_r G^\circ(T)$ for the reaction given in Eq. (7) involves the transfer of eight electrons, and hence, from Nernst equation we get Eq. (9),

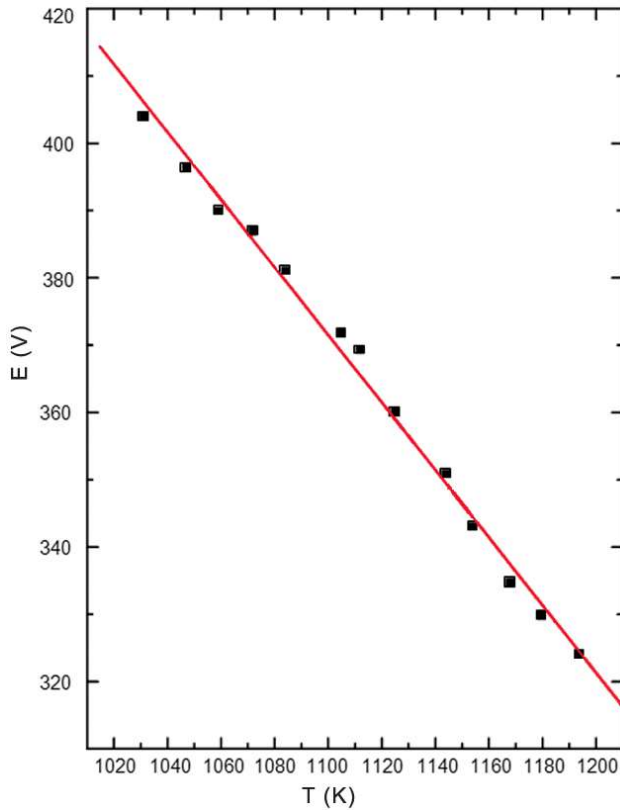


Fig. 1 — Plot of emf as a function of temperature for the cell: (-)Pt/{Gd₂Ru₂O₇(s)+Gd₂O₃(s)+Ru(s)}//CSZ//O₂(p(O₂) = 21.21 kPa)/Pt(+).

$$\begin{aligned} \Delta_r G^\circ(T) &= -8FE \\ &= \Delta_r G^\circ\{\text{Gd}_2\text{Ru}_2\text{O}_7(\text{s})\} - \Delta_r G^\circ\{\text{Gd}_2\text{O}_3(\text{s})\} \\ &\quad - 2RT \ln p(\text{O}_2) \end{aligned} \quad \dots (9)$$

From Eqs (7), (8) and (9) and literature value¹⁶ of $\Delta_r G^\circ\{\text{Gd}_2\text{O}_3(\text{s})\}$, $\Delta_r G^\circ$ of Gd₂Ru₂O₇ (s) has been obtained as:

$$\{\Delta_r G^\circ(\text{Gd}_2\text{Ru}_2\text{O}_7, \text{s})/(\text{kJ}\cdot\text{mol}^{-1}) \pm 1.7\} = -2549.1 + 0.6438 (T/\text{K}) \quad \dots (10)$$

The error includes the standard deviation in emf and the uncertainty in the data taken from the literature. The Gibbs energy of formation is a linear function of temperature within the investigated temperature range. The slope and the intercept of this linear equation correspond, respectively, to the average values of the standard molar entropy and enthalpy of formation in the temperature range covered by emf measurement. The values of heat capacities were estimated in the present study by the Neumann Kopp's rule, i.e., from the heat capacity data of the constituent binary oxides¹⁷, RuO₂(s) and Gd₂O₃(s) and the following mathematical expression was obtained:

$$\begin{aligned} C_p^\circ(\text{Gd}_2\text{Ru}_2\text{O}_7, \text{s}, T) (\text{J K}^{-1} \text{mol}^{-1}) &= 258.94 + 33.87 \times 10^{-3} T(\text{K}) \\ &\quad - 45.52 \cdot 10^5 / T^2(\text{K}) \end{aligned} \quad \dots (11)$$

The heat capacity at 298.15 K was estimated from Eq. (11) and was found to be 221.6 J K⁻¹ mol⁻¹. The enthalpy of formation of Gd₂Ru₂O₇(s) at 298.15 K has been calculated by the second law method. Heat capacity data from Eq. (11) along with transition enthalpies of Ru(s), Gd(s), and O₂(g)¹⁶, were used to determine the second law value of $\Delta_r H^\circ(\text{Gd}_2\text{Ru}_2\text{O}_7, \text{s}, 298.15 \text{ K})$ and was found to be -2584 kJ·mol⁻¹. The decomposition temperature of Gd₂Ru₂O₇(s) in air from the Gibbs energy of formation data obtained in this study was found to be 2297 K and that of RuO₂(s) calculated from the data of Cordfunke & Konings¹⁸ was found to be 1647 K. The decomposition temperature of Gd₂Ru₂O₇(s) was found to be higher than that of RuO₂(s) at all partial pressures of oxygen, and hence, Gd₂Ru₂O₇(s) will be more stable than RuO₂(s) at all partial pressure of oxygen.

In the present study, the pyrochlore Gd₂Ru₂O₇(s) in the Gd-Ru-O system was prepared by the solid-state reaction route and characterized by X-ray diffraction method. The Gibbs energy of formation of the ternary compound was obtained by using solid state electrochemical oxide cell. The Gibbs energy of formation of Gd₂Ru₂O₇(s) from elements in their standard state is: $\{\Delta_r G^\circ(\text{Gd}_2\text{Ru}_2\text{O}_7, \text{s})/(\text{kJ}\cdot\text{mol}^{-1}) \pm 1.7\} = -2549.1 + 0.6438 (T/\text{K}) \times \Delta_r H^\circ(\text{Gd}_2\text{Ru}_2\text{O}_7, \text{s}, 298.15 \text{ K})$ and was found to be -2584 kJ mol⁻¹.

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