

# The Lu–Ru–O System: Thermodynamic properties and impedance measurements of the pyrochlore Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>(s)

Aparna Banerjee<sup>a,\*</sup>, R. Mishra<sup>b</sup>, Ziley Singh<sup>a</sup>

<sup>a</sup> Product Development Division, R C and I Group, Bhabha Atomic Research Centre, Mumbai-400 085, India

<sup>b</sup> Chemistry Division, Chemistry Group, Bhabha Atomic Research Centre, Mumbai-400 085, India

## ARTICLE INFO

### Article history:

Received 16 September 2010

Received in revised form 2 August 2011

Accepted 3 August 2011

Available online 7 September 2011

### Keywords:

System Lu–Ru–O

Lutetium ruthenate

Solid-state electrochemical technique

Impedance measurements

Gibbs energy of formation

Heat capacity

## ABSTRACT

The Gibbs free energy of formation of Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>(s) has been determined using solid-state electrochemical technique employing oxide ion conducting electrolyte. The reversible electromotive force (e.m.f.) of the following solid-state electrochemical cell has been measured:



The Gibbs free energy of formation of Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>(s) from elements in their standard state, calculated by the least squares regression analysis of the data obtained in the present study, can be represented by:

$$\{\Delta_f G^\circ(\text{Lu}_2\text{Ru}_2\text{O}_7, \text{s}) / (\text{kJ} \cdot \text{mol}^{-1}) \pm 2.7\} = -2513.7 + 0.6265 \cdot (T / \text{K}); 943.9 \leq T / \text{K} \leq 1230.$$

Standard molar heat capacity  $C_{p,m}^\circ(T)$  of Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>(s), was measured using a heat flux type differential scanning calorimeter (DSC) in two different temperature ranges, from 127 K to 299 K and 307 K to 845 K. The heat capacity in the higher temperature range was fitted into a polynomial expression and can be represented by:

$$C_{p,m}^\circ(\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})) (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 294.535 + 2.0 \cdot 10^{-4} T(\text{K}) - 49.00688 \cdot 10^5 / T^2(\text{K}).$$

The second law method gave the value of standard enthalpy of formation and entropy, of the compound from elements at 298.15 K. An oxygen potential diagram for the Lu–Ru–O system was computed based on the thermodynamic data obtained. Impedance measurements on Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>(s), suggests a semiconductor like behavior with low activation energy.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Pyrochlores are cubic and the structural formula is ideally A<sub>2</sub>B<sub>2</sub>O<sub>6</sub>O' where A and B sites contain metal cations. This cubic structure can accommodate a wide variety of combinations of A and B site cations as well as oxygen vacancies [1]. The pyrochlore ruthenates are technologically important as electrode materials as they are electronic and ionic mixed conductors [2], as catalysts [3], as components in thick film resistors [4] and have unusual electronic properties [5]. The ruthenium 4d electrons are the borderline between localized and itinerant behavior and depending on the A-type cation the materials are either metallic Pauli paramagnet or semiconductors. The relationship between the electrical properties and the crystal structure of pyrochlore ruthenates

was investigated by Kano et al. [6]. Metallic ruthenate pyrochlores are characterized by relatively short Ru–O bonds ~1.95 Å compared to 1.98 Å in the semiconducting analogs and more open Ru–O–Ru angles 135°–140° for metallic species versus 129°–134° for semiconducting oxides. The effect of smaller Ru–O distances and larger Ru–O–Ru angles is to increase the overlap between Ru 4d and O<sub>2</sub> 2p orbital. Thus Ln<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> (Ln=Pr–Lu) and Y<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> are semiconducting with low activation energy [7].

The structures of four semiconducting ruthenium pyrochlores, Ln<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> (Ln=Pr, Nd, Tb and Yb) were determined by neutron diffraction by Kennedy and Vogt [8]. Cox et al. [5] studied the structure of the pyrochlore ruthenium (IV) oxides by ultra-violet and x-ray photoelectron spectroscopy. Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> shows magnetic transition at 85 K, below this temperature it transforms to a spin glass like state. This is attributable to Ru<sup>+4</sup> ion in the pyrochlore structure as Lu<sup>+3</sup> ion is diamagnetic [9]. λ-Type heat anomaly has been observed at 78 K for Lu<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>(s) in the low temperature specific heat measurements [10].

\* Corresponding author. Tel.: +91 22 25590648; fax: +91 22 25505151.  
E-mail address: [aparnab@barc.gov.in](mailto:aparnab@barc.gov.in) (A. Banerjee).

The crystal structure and magnetic properties of the oxide has been thoroughly investigated by many researchers. However, thermodynamic properties of these oxides need investigation. The Lu–Ru–O system, investigated in this study, comprises of only one binary oxide:  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$ . In this study, based on the phase relations, a solid-state cell was designed to measure the Gibbs free energies of formation of the ternary oxide. The Gibbs free energy of formation of  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  was determined by an oxide electrochemical cell using 0.15 mole fraction calcia stabilized zirconia (CSZ) solid electrolyte, in the temperature range from 943.9 K to 1230 K. The heat capacity of  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  was measured in the temperature range from 127 K to 845 K using a differential scanning calorimeter (DSC-131). Other thermodynamic parameters were evaluated from these experimental results. A Solatron Impedance Frequency Analyzer was used to investigate the electronic properties of the sample.

## 2. Experimental

### 2.1. Materials

$\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  was synthesized from stoichiometric proportions of preheated  $\text{Lu}_2\text{O}_3(\text{s})$  (0.9985 mass fraction, Leico Industries Inc.) and  $\text{RuO}_2(\text{s})$  (0.997 mass fraction, Prabhat Chemicals, India). The oxides were intimately ground and the mixture was then pelletized. The pellets were then sealed in an evacuated quartz ampoule and heated to  $T = 1423$  K for several hours. The formation of the compound was confirmed by X-ray diffractometer. For the XRD pattern well ground sample of  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  was smeared on a glass slide and diffraction data was collected on a Philips Powder X-ray diffractometer (model PW 1710) using monochromatic Cu- $K_\alpha$  radiation ( $\lambda = 0.15406$  nm) in reflection mode. The diffraction data was collected in the  $2\theta$  range from  $10^\circ$  to  $70^\circ$ . The values of the interplanar  $d$  spacing obtained for  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  recorded on Powder Diffractometer using Cu- $K_\alpha$  radiation is in good agreement with those reported in JCPDS file number #28-614 [11]. The XRD pattern as shown in Fig. 1 includes low intensity peaks attributable to  $\text{Lu}_2\text{O}_3(\text{s})$ . The cationic ratio of Lu/Ru of the compound  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  was confirmed to be 1 by energy dispersive X-ray fluorescence (EDXRF). An isothermal section of the phase diagram for the system Lu–Ru–O at 1200 K is shown in Fig. 2. The Lu–Ru–O system comprises of only one oxide  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  that lies on the tie line between  $\text{Lu}_2\text{O}_3(\text{s})$  and  $\text{RuO}_2(\text{s})$ . Phase relations were explored involving the oxide phases and metal mixtures by

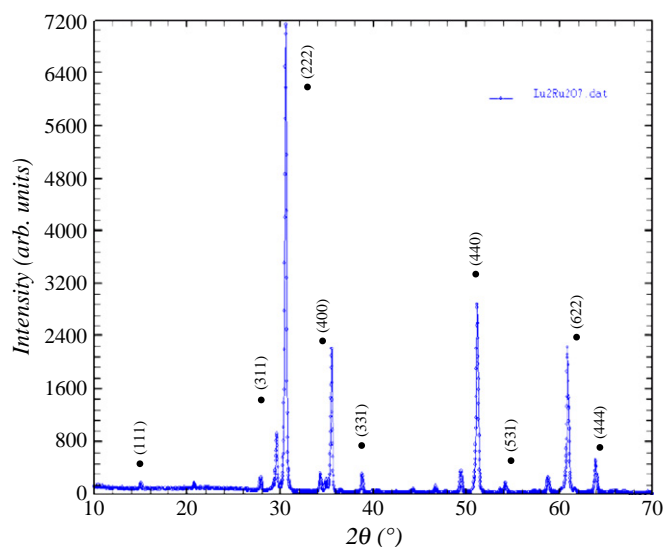


Fig. 1. XRD pattern of  $\text{Lu}_2\text{Ru}_2\text{O}_7(\text{s})$  with the (hkl) values.

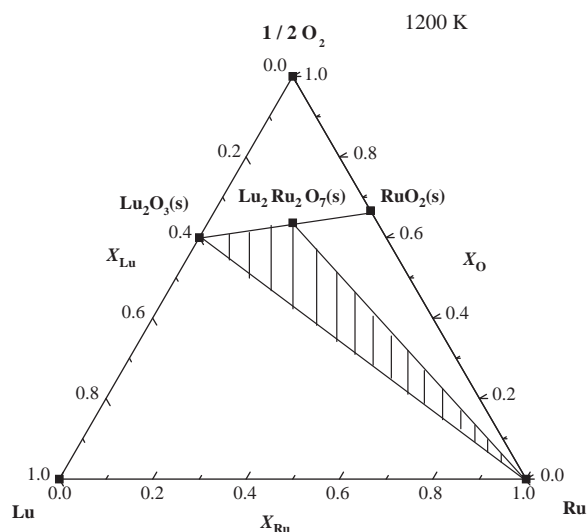


Fig. 2. Isothermal section of the phase fields for the system Lu–Ru–O at 1200 K. The hashed portion indicates the phase field under consideration.

equilibration at 1200 K and phase analysis of quenched samples. The hashed portion is the phase field under consideration. A phase mixture of  $\{\text{Lu}_2\text{O}_3(\text{s}) + \text{Lu}_2\text{Ru}_2\text{O}_7(\text{s}) + \text{Ru}(\text{s})\}$  in the appropriate molar ratio was made into pellet of dimension 10 mm diameter and 3 mm in thickness using a tungsten carbide die at a pressure of 100 MPa. The pellets were sintered in purified argon gas atmosphere at  $T = 1000$  K for several hours. The sintered pellets were reexamined by X-ray diffraction and the phase compositions were found to be unchanged after sintering. These pellets were then used for e.m.f. measurements.

### 2.2. 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 for electrochemical measurements is shown in an earlier publication [12]. The dimensions of the CSZ tube used were 13 mm outer diameter, 9 mm inner diameter and 380 mm in length. Argon gas, flowing at a rate of  $1 \text{ dm}^3\text{h}^{-1}$ , purified by passing it through towers containing the reduced form of BASF (Akteingesellschaft, D-6700 Ludiwigshafen, Germany) catalyst, molecular sieves and magnesium perchlorate served as the gaseous atmosphere for the cell. The sample electrode compartment was initially evacuated and flushed with argon gas. This procedure was repeated several times while simultaneously the cell was heated to around 573 K so as to drive all moisture and other atmospheric gases present in the electrode compartment. The argon gas served as the cover gas over the working electrode and is bubbled out at a steady rate through an oil bubbler without disturbing the equilibrium at the working electrode. An alumina guide tube directs the argon cover gas to the working electrode. A Faraday cage was placed between the furnace and cell assembly. The cage was grounded to minimize induced electro-motive force (e.m.f.) on the cell leads. Alumina sheathed Pt leads were used to measure the e.m.f. The sample pellet was made by compaction and pelletization of a mixture of  $\text{Lu}_2\text{O}_3(\text{s}) + \text{Lu}_2\text{Ru}_2\text{O}_7(\text{s}) + \text{Ru}(\text{s})$  in the ratio of 1:1:2 into pellets of dimension 10 mm diameter and 3 mm thickness at a pressure of 100 MPa. Synthetic dry air from an air generator was used as the reference electrode. The oxygen partial pressure of synthetic air does not depend on humidity or pressure variation. The temperature of the cell was measured by a calibrated chromel–alumel thermocouple located in the vicinity of the pellet. The e.m.f. of the cell was measured when

Download English Version:

<https://daneshyari.com/en/article/1297298>

Download Persian Version:

<https://daneshyari.com/article/1297298>

[Daneshyari.com](https://daneshyari.com)