



Thermodynamic studies on $\text{LnCoO}_3(\text{s})$ ($\text{Ln} = \text{Dy}, \text{Ho}$) by solid-state electrochemical cells

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ABSTRACT

Ternary oxides, $\text{DyCoO}_3(\text{s})$ and $\text{HoCoO}_3(\text{s})$ have been synthesized by citrate–nitrate gel combustion method and characterized by X-ray powder diffraction method. The standard molar Gibbs energies of formation of $\text{DyCoO}_3(\text{s})$ and $\text{HoCoO}_3(\text{s})$ have been measured using solid oxide galvanic cell technique employing yttria-stabilized zirconia (YSZ) and calcia-stabilized zirconia (CSZ) as solid electrolyte tubes, respectively. The standard molar Gibbs energies of formation of $\text{DyCoO}_3(\text{s})$ and $\text{HoCoO}_3(\text{s})$ were calculated from the measured e.m.f. data and are given as:

$$\Delta_f G_m^\circ(\text{DyCoO}_3, \text{s}, T) \text{ kJ mol}^{-1} (\pm 4) = -1211.3 + 0.2449^*(T \text{ K}), \quad (1013 \text{ K} \leq T \leq 1167 \text{ K}),$$

$$\Delta_f G_m^\circ(\text{HoCoO}_3, \text{s}, T) \text{ kJ mol}^{-1} (\pm 4) = -1237.8 + 0.2590^*(T \text{ K}), \quad (964 \text{ K} \leq T \leq 1102 \text{ K}),$$

A set of self consistent thermodynamic functions for $\text{LnCoO}_3(\text{s})$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}$) has been computed from available experimental data in the literature.

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1. Introduction

Rare earth cobalt oxides $\text{LnCoO}_3(\text{s})$ have potential applications in diverse fields such as in magnetohydrodynamic (MHD) generators [1], oxygen ion conductors [2], catalysts for oxidation of CO [3] and thermoelectric materials [4]. There have been a number of studies on rare earth oxides focusing on its electronic, magnetic, catalytic and thermoelectric properties [5–12], however its thermodynamic properties such as entropy, enthalpy of formation and Gibbs energy of formation have not been systematically studied [13–21]. The successful use of rare earth oxide materials in technical processes requires the knowledge of their thermodynamic stability at high-temperatures, particularly under reducing and oxidizing environments. A set of reliable and consistent thermodynamic data may enable the material scientists to select rare earth ternary oxides for specific technological applications. It is therefore, decided to carry out systematic thermodynamic investigation on these compounds. Recently, present authors [21,23,24] have published results on Gibbs energy of formation of $\text{LnCoO}_3(\text{s})$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Tb}$) and heat capacities of $\text{LnCoO}_3(\text{s})$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$). The present work primarily deals with synthesis, characterization of $\text{LnCoO}_3(\text{s})$ ($\text{Ln} = \text{Dy}, \text{Ho}$) and determi-

nation of standard molar Gibbs energy of formation of $\text{DyCoO}_3(\text{s})$ and $\text{HoCoO}_3(\text{s})$ using solid-state electrochemical technique. This study also reports thermodynamic functions for $\text{LnCoO}_3(\text{s})$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$), which have been computed from the experimental data.

2. Experimental

2.1. Materials preparation

Ternary oxides, $\text{DyCoO}_3(\text{s})$, and $\text{HoCoO}_3(\text{s})$ have been synthesized by citrate–nitrate gel combustion route. Preheated $\text{Ln}_2\text{O}_3(\text{s})$ ($\text{Ln} = \text{Dy}, \text{Ho}$) (E. Merck, India, mass fraction purity 0.995) and $\text{Co}_3\text{O}_4(\text{s})$ (STREM Chemicals, USA, mass fraction purity 0.999) with stoichiometric ratios were dissolved in dilute $\text{HNO}_3(\text{aq})$. Excess amount of citric acid (E. Merck, India, mass fraction purity 0.999) was added to the solution to assist in complete dissolution. Then pH of the solution was adjusted to 6–7 by adding liquor ammonia. This solution was heated at 450 K, a viscous gel was formed which was dried, crushed in an agate mortar and heated at 1425 K in a platinum crucible for 120 h with two intermediate grindings. The products were identified as $\text{DyCoO}_3(\text{s})$ [25] and $\text{HoCoO}_3(\text{s})$ [26] by X-ray diffraction (XRD) analysis using a STOE X-ray diffractometer with $\text{Cu K}\alpha$ radiation using graphite monochromator.

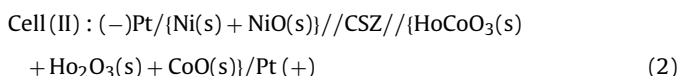
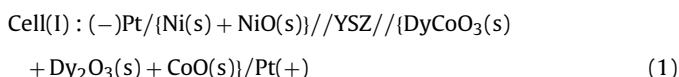
Phase mixtures $\{\text{DyCoO}_3(\text{s}) + \text{Dy}_2\text{O}_3(\text{s}) + \text{CoO}(\text{s})\}$, $\{\text{HoCoO}_3(\text{s}) + \text{Ho}_2\text{O}_3(\text{s}) + \text{CoO}(\text{s})\}$ and $\{\text{Ni}(\text{s}) + \text{NiO}(\text{s})\}$ in the molar ratios of 4:2:4,

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4:2:4 and 1:1 respectively, were made using a steel die at a pressure of 100 MPa for the e.m.f. measurements. The {Ni(s) + NiO(s)} pellet was sintered in purified argon gas atmosphere ($p(\text{O}_2) \cong 10^{-16}$ kPa) at 1000 K for 7 h. The argon gas was purified by passing it through towers containing the reduced form of BASF catalyst (BASF Aktiengesellschaft, D-6700 Ludwigshafen, Germany), molecular sieves, magnesium perchlorate, and hot uranium metal at 550 K. The {LnCoO₃(s) + Ln₂O₃(s) + CoO(s)} pellet was sintered under air at 800 K for 10 h.

2.2. Solid-state electrochemical technique

The experimental details and the cell assembly used for e.m.f. measurements have been reported earlier [27]. A double compartment cell assembly was used. The gas phase over the two electrodes was separated by the use of electrolyte tube so that transport of oxygen from the higher oxygen potential electrode via the gas phase was prevented. The yttria-stabilized zirconia (YSZ) electrolyte tube with 6 mol% Y₂O₃, supplied by Karatec Advanced Materials SA, Spain was used for {DyCoO₃(s) + Dy₂O₃(s) + CoO(s)} phase field. The calcia-stabilized zirconia (CSZ) electrolyte tube with 15 mol% calcia, supplied by Nikatto Corporation, Japan was used for {HoCoO₃(s) + Ho₂O₃(s) + CoO(s)} phase field. The dimensions of both YSZ and CSZ electrolyte tubes were; 13 mm o.d., 9 mm i.d. and 380 mm long with a flat closed end. Argon gas with different partial pressures of oxygen was flown over the electrodes. An inert environment was maintained over {Ni(s) + NiO(s)} electrode throughout the experiment by streams of purified argon gas ($p(\text{O}_2) = 10^{-16}$ kPa). Impure argon gas (bypassing only uranium getter) ($p(\text{O}_2)\mu \cong 10^{-4}$ kPa) was flown over {LnCoO₃(s) + CoO(s) + Ln₂O₃(s)} (Ln = Dy, Ho) electrode to prevent decomposition of LnCoO₃(c) phase at lower oxygen potential. The cell temperature (± 1 K) was measured by a calibrated chromel/alumel thermocouple (ITS-90), and the cell e.m.f. (± 0.02 mV) by a Keithley 614 electrometer (impedance $> 10^{14}$ Ω). The reversible e.m.f.s of the following solid-state galvanic cells were measured as a function of temperature.



E.m.f. measurements were carried out in the temperature range of 1000–1200 K. The reversibility of the solid-state electrochemical cells was checked by micro-coulometric titration in both directions. A small quantity of current was passed (~ 100 μA for ~ 10 min) through the cell in either direction. The e.m.f. of the cell returned to its original value after the removal of applied voltage. The e.m.f. of cells was also found to be independent of flow rate of the inert gas passing over the electrodes in the range from 120 to 360 dm³ h⁻¹. E.m.f. values were taken after temperature became constant. At each temperature at least three readings were taken at an interval of 30 min. Then temperature was changed to a desired value and similar procedure was followed. The cell temperature was raised and lowered, alternatively. E.m.f. started drifting after 75 h. Then both electrodes were replaced by previously annealed fresh electrodes. These electrodes were annealed to shorten the equilibrium time. The X-ray diffraction patterns of the {DyCoO₃(s) + Dy₂O₃(s) + CoO(s)} and {HoCoO₃(s) + Dy₂O₃(s) + CoO(s)} pellets, before and after the experiments are shown in Fig. 1. It shows the presence of LnCoO₃(s) [25,26], Ln₂O₃(s) [28,29] and

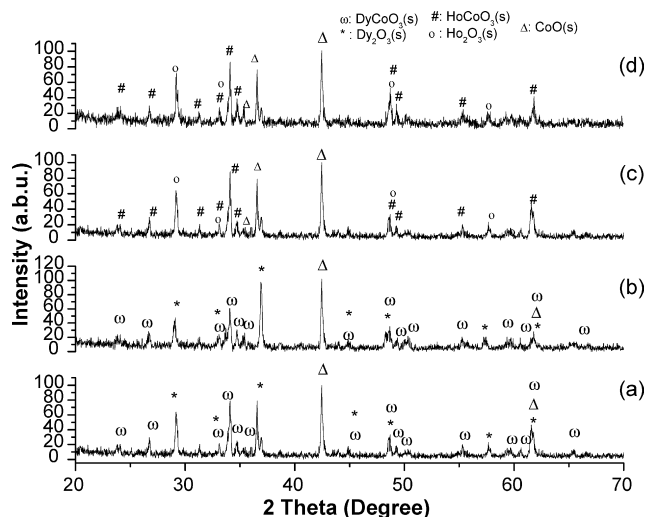


Fig. 1. X-ray diffraction pattern of three phase mixture: {LnCoO₃(s) + Ln₂O₃(s) + CoO(s)}. Intensity (I in arbitrary units) of peaks is plotted against the diffraction angle 2θ (in degrees). The XRD pattern of (DyCoO₃(s) + Dy₂O₃(s) + CoO(s)) pellet, before and after the e.m.f. measurements are shown in (a) and (b), respectively. Similarly, (c) and (d) give XRD pattern of (HoCoO₃(s) + Ho₂O₃(s) + CoO(s)) pellet, before and after the e.m.f. measurements.

CoO(s) [30] phases and no new phase after the e.m.f. measurements.

3. Results

3.1. Solid-state electrochemical measurements

The e.m.f. of the solid oxide galvanic cell is related to the partial pressure of oxygen at the two electrodes by the relation:

$$E = \left(\frac{RT}{nF} \right) \int_{p''(\text{O}_2)}^{p'(\text{O}_2)} t(\text{O}^{2-}) d \ln p(\text{O}_2) \quad (3)$$

where E is the measured e.m.f. of the cell in volts, R ($=8.3144$ J K⁻¹ mol⁻¹) is the universal gas constant, n ($=4$) is the number of electrons participating in the electrode reaction, F ($=96486.4$ C mol⁻¹) is the Faraday constant, T is the absolute temperature, $t(\text{O}^{2-})$ is the effective transference number of O²⁻ ion for the solid electrolyte and $p'(\text{O}_2)$ and $p''(\text{O}_2)$ are the equilibrium oxygen partial pressures at the {LnCoO₃(s) (Ln = Dy, Ho) + Ln₂O₃(s) + CoO(s)} and {Ni(s) + NiO(s)} electrodes, respectively. The transference number of oxygen ion in the solid electrolyte used in the present study is nearly unity ($t(\text{O}^{2-}) > 0.99$) at the oxygen pressures and temperatures covered. Hence, the e.m.f. of the cell is directly proportional to the logarithm of the ratio of partial pressures of oxygen at the electrodes

$$E = \left(\frac{RT}{4F} \right) \ln \left\{ \frac{p'(\text{O}_2)}{p''(\text{O}_2)} \right\}. \quad (4)$$

Thus,

$$4FE = \Delta\mu'(\text{O}_2) - \Delta\mu''(\text{O}_2), \quad (5)$$

where $\mu''(\text{O}_2)$ is the oxygen potential over {Ni(s) + NiO(s)} electrode and can be given as:

$$\Delta\mu''(\text{O}_2) = 2\Delta_f G_m^\circ(\text{NiO}, s, T). \quad (6)$$

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