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Letter

Measurement of the thermodynamic stability of lanthanum ferrite using a calcium fluoride solid electrolyte galvanic cell

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1. Introduction

According to the phase diagram [1], the compounds $LaFeO_3$ and Fe_2O_3 coexist below 1648 K in the system La_2O_3–Fe_2O_3. Sreedharan and Chandrasekharaiah [2] determined the Gibbs energy of formation of $LaFeO_3$ in the temperature range 1094–1299 K from e.m.f. measurements on solid oxide galvanic cells using a ZrO_2–CaO solid electrolyte. They employed an Fe/"FeO" reference electrode in these cells and obtained the free energies of formation of $LaFeO_3$ from knowledge of the experimental cell e.m.f.s and the free energy of formation of "FeO". The oxygen potential in the system $LaFeO_3/La_2O_3/Fe$ was measured using the gas equilibrium technique by Leontev *et al.* [3] and Katsura *et al.* [4], while Nakamura *et al.* [5] employed thermogravimetry for the same purpose. The Gibbs energies of formation of $LaFeO_3$ obtained from the four sets of data are in reasonable agreement with each other. It is possible to measure the Gibbs energy of formation of this compound directly by setting up the following cell incorporating CaF_2 as the solid electrolyte:

$$O_2(g),\ Pt/La_2O_3,\ LaF_3//CaF_2//LaFeO_3,\ Fe_2O_3,\ LaF_3/Pt,\ O_2(g)$$

The two half-cell reactions in this cell are

$$La_2O_3 + 6F^- = 2LaF_3 + \tfrac{3}{2}O_2(g) + 6e^-$$

$$2LaF_3 + Fe_2O_3 + \tfrac{3}{2}O_2(g) + 6e^- = 2LaFeO_3 + 6F^-$$

Therefore the net cell reaction is

$$La_2O_3 + Fe_2O_3 = 2LaFeO_3 \qquad (1)$$

The standard Gibbs energy change for reaction (1) is given by

$$\Delta G^\circ = -6Fe$$

where E is the e.m.f. of the cell and F the Faraday.

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2. Materials

$LaFeO_3$ was prepared from dried reagent grade La_2O_3 and Fe_2O_3 by mixing in stoichiometric proportions and sintering the oxide mixture pellets at 1523 K for 48 h with intermittent grinding. The formation of the ferrite was confirmed by X-ray diffraction. The electrode pellets were prepared by mixing the appropriate compounds in roughly equimolar proportions. An equal weight of LaF_3 was then added to the mixture, the mixed powder was pressed into cylindrical pellets and sintered at 1273 K in dry CO_2-free oxygen gas before use. Polycrystalline calcium fluoride solid electrolyte pellets were prepared according to the method of Taylor and Schmalzried [6].

3. Experimental details

In the cell the calcium fluoride solid electrolyte pellet was sandwiched between the reference electrode and working electrode pellets. The cell was electrically connected to a Keithley 617 electrometer by platinum leads connected to platinum foils pressing against the outer pellets. The whole cell assembly was enclosed inside a sillimanite reaction tube and kept in the even temperature zone of the furnace. The assembly used was similar to that employed by Vecher and Vecher [7]. A Pt–PtRh (13% Rh) thermocouple welded to the platinum foil in contact with the reference electrode was used

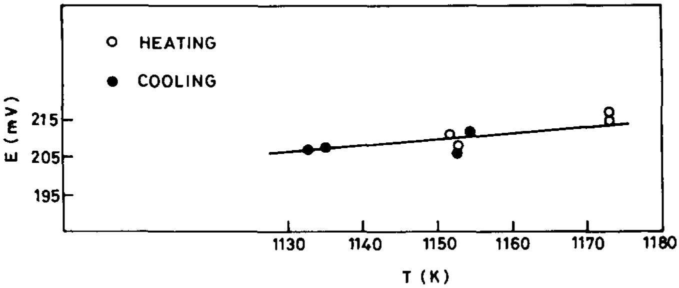

Fig. 1. E.m.f. *E* *vs.* temperature *T* for the cell
$O_2(g)$, Pt/La_2O_3, $LaF_3//CaF_2//LaFeO_3$, Fe_2O_3, LaF_3/Pt, $O_2(g)$

TABLE 1

Molar Gibbs energy of formation of lanthanum ferrite by the reaction $\frac{1}{2}La_2O_3+\frac{1}{2}Fe_2O_3=LaFeO_3$

Temperature (K)	$\Delta G°$ (kJ mol^{-1})				
	Present work (CaF_2 cell)	Ref. 2 (ZrO_2–CaO cell)	Ref. 3 (gas equilibrium measurements)	Ref. 4 (gas equilibrium measurements)	Ref. 5 (thermo-gravimetry)
1153	-60.9 ± 0.6	-59.4 ± 1.4	-62.9	-66.0 ± 2.5	-63.1 ± 2.5

to monitor the cell temperature. The temperature of the furnace was controlled by a proportional power controller to better than ±3 K. The cell e.m.f. and the thermal e.m.f. were measured using a Keithley 617 digital electrometer with an input impedance of 10^{14} Ω. An atmosphere of dry, CO_2-free oxygen gas was provided throughout the working period of the cell. The reversible e.m.f.s of the cell were measured in the temperature range 1133–1173 K. The reproducibility of the e.m.f. data was checked by thermal cycling and coulometric titration. The cell with an La_2O_3/LaF_3 electrode on either side gave a near null e.m.f.

4. Results and discussion

The experimental values of the e.m.f.s of the cell on heating and cooling are plotted as a function of temperature in Fig. 1. The least-mean-square analysis of the e.m.f.s in Fig. 1 suggests the value of 210.2 ± 2.0 mV for the cell at a mean temperature of 1153 K. This e.m.f. is directly related to the standard molar Gibbs energy change of -60.9 ± 0.6 kJ mol^{-1} for the formation of $LaFeO_3$ from the component oxides. This value is compared with the corresponding values reported by other authors in Table 1. Considering the different experimental techniques and uncertainties involved, the agreement between the different sets of results is reasonably good.

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