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Standard Gibbs' energy of formation of $LaFeO_3$ and comparison of stability of $LaMO_3$ (M = Mn, Fe, Co or Ni) compounds

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The thermodynamic stability of $LaFeO_3$ at high temperatures is of interest in materials technology. For evaluating the thermodynamic data of $LaFeO_3$, the e.m.f. of the following galvanic cell was studied over the range 1094 to 1299 K: Pt, $LaFeO_3$, Fe, La_2O_3/15 mol % CaO stabilized ZrO_2/FeO, Fe, Pt. For the galvanic cell reaction $\frac{1}{2}La_2O_3 + 3/2\ FeO \rightleftharpoons \frac{1}{2}Fe + LaFeO_3$, the standard Gibbs' energy change, ΔG_r^0, was measured to be $(\Delta G_r^0 \pm 0.34)\ (kJ) = -22.67 - 0.011\,55\ T(K)$ for the passage of 3 F of electricity. From this, the stability of $LaFeO_3$ with respect to La_2O_3 and FeO as well as with La_2O_3 and Fe_2O_3 was computed and compared with other equilibrium measurements on $LaFeO_3$ reported in the literature. In addition, a comparison was made on the stabilities of $LaMO_3$ compounds (where M = Mn, Fe, Co or Ni) with respect to dissociation into La_2O_3 and MO making use of the published data on other compounds. Likewise a comparison of disproportionation of $LaFeO_3$ and $LaMO_3$ into their respective sesquioxides was also made.

1. Introduction

The thermal and thermodynamic stability of the perovskite type of compounds of the formula $LaMO_3$ where M is Mn, Fe, Co or Ni, are of importance as these materials are used as electrodes in magnetohydrodynamic (MHD) generators and as catalysts in pollution control [1, 2]. The thermodynamic stability of $LaMnO_3$ with respect to reduction was studied by Nakamura *et al.* [3] using thermogravimetry, Kamegashira *et al.* [4] using electrical conductivity, and Sreedharan *et al.* [5] using a solid electrolyte e.m.f. method. The phase transition and thermodynamic stability of $LaCoO_3$ was studied using a solid electrolyte e.m.f. method by Sreedharan and Chandrasekharaiah [6] whereas Nakamura *et al.* studied the reduction of $LaCoO_3$ as well as $LaNiO_3$ by isothermal thermogravimetry. The oxygen potential in the system $LaFeO_3/La_2O_3$/Fe was measured by Katsura *et al.* [7] and Leontev *et al.* [8] using a gas equilibration technique and by Nakamura *et al.* [3] using thermogravimetry. Owing to better precision of the e.m.f. technique [9] it was adopted for the study of this system, the results of which are presented here. A comparison of the stability of $LaFeO_3$ with other $LaMO_3$ compounds has also been made.

2. Experimental procedures

The compound $LaFeO_3$ was synthesized from coprecipitated hydroxides as per the procedure adopted by Foex [10]. The starting materials for this were La_2O_3 and Fe_2O_3 (purity of better than 99.99%, Johnson-Matthey, UK). An equal mass mixture of $LaFeO_3$, La_2O_3 and Fe was compacted into pellets of 10 mm diameter and 3 mm thickness at a pressure of 100 MPa. The coexistence of these three phases was verified by X-ray diffraction (XRD) analyses of the pellets after heating them to 1273 K for 24 h in purified argon. A 4 : 1 mixture of Fe and Fe_2O_3 was likewise compacted into pellets of similar dimensions which were then sintered in evacuated and sealed silica ampoules at 1273 K for 24 h. The iron and wüstite phases were confirmed by XRD analysis. Pellets of 15 mol % CaO stabilized ZrO_2 (15 CSZ) prepared from reagent grade $CaCO_3$ and ZrO_2 (greater than 99.99% purity) and having the dimensions 12 mm diameter and 3 mm thickness were used as solid electrolytes. The density of the pellets was better than 98%. An open-cell-stacked-pellet assembly was employed for the galvanic cell e.m.f. measurements. A calibrated Pt–10% Rh/Pt thermocouple was used to measure the temperature. Only the e.m.f. readings which were reproducible on subsequent heating cycles were taken. The other experimental details are described elsewhere [11–13].

3. Results and discussion

The e.m.f. of the galvanic cell

$$\text{Pt, } LaFeO_3\text{, Fe, } La_2O_3/15\ \text{CSZ/FeO, Fe, Pt} \quad (I)$$

over the range 1094 to 1299 K shown in Fig. 1 can be fitted into the following least squares expression:

$$(E \pm 1.17)\ (mV) = 78.31 + 0.039\,91\ T(K) \quad (1)$$

For the passage of 3F of electricity, the standard

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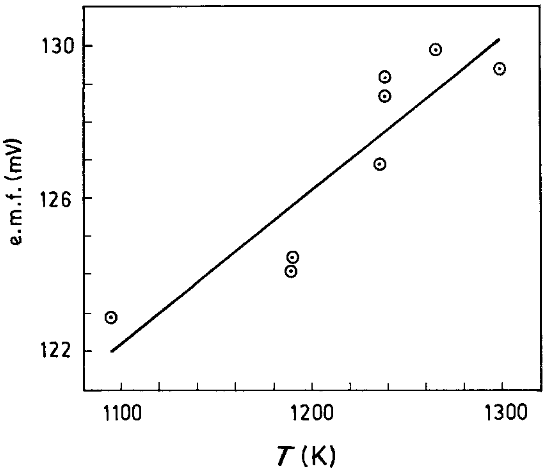

Figure 1 The e.m.f. of the cell Pt, La_2O_3, Fe, $LaFeO_3$/15CSZ/Fe_xO, Fe, Pt.

Gibbs' energy change, ΔG_r^0 for the galvanic cell reaction

$$\tfrac{1}{2}La_2O_3 + 3/2\ FeO \rightleftharpoons \tfrac{1}{2}Fe + LaFeO_3 \qquad (2)$$

is given in Table I. Using the values for the standard Gibbs' energy of formation, ΔG_f^0 of FeO assessed by Giddings and Gordon [14], ΔG_r^0 for the reaction

$$\tfrac{1}{2}La_2O_3 + Fe + \tfrac{3}{4}O_2 \rightleftharpoons LaFeO_3 \qquad (3)$$

was computed and is shown in Table I along with those derived from the gas equilibrium measurements by Katsura *et al.* [7] and Leontev *et al.* [8] and from thermogravimetry by Nakamura *et al.* [3]. The agreement amongst the four sets of data is quite reasonable. However, the individual slope and intercept values from Leontev *et al.* are in considerable disagreement with those from others. The log P_{O_2} values at 1273 K for a coexisting phase mixture $LaFeO_3/Fe/La_2O_3$ in Table II shows that the value from Leontev *et al.* differ from that of others by more than their quoted precision.

To make an assessment of the individual values of the slopes and intercepts for the oxygen potential in the three-phase mixture $LaFeO_3/Fe/La_2O_3$, the standard Gibbs' energy change for the reaction

$$\tfrac{1}{2}La_2O_3 + \tfrac{1}{2}\ Fe_2O_3 \rightleftharpoons LaFeO_3 \qquad (4)$$

was calculated and is given in Table I. It can be seen from the Table that the value of 80 J K^{-1} mol^{-1} from Leontev *et al.* [8] for the ΔS^0 of the solid–solid Reaction 4 is higher than those from other investigators. Generally, ΔS^0 for the solid–solid reaction should be a smaller positive value. The ΔG_r^0 values for the relevant equilibria of the couples FeO/Fe_3O_4 and Fe_3O_4/Fe_2O_3 used for the computation of $\Delta G_r^0(4)$ are also listed in Table I.

To make a comparison of the thermodynamic data of $LaFeO_3$ with those of $LaCoO_3$, the results of e.m.f. studies employing $LaCoO_3$ by Sreedharan and Chandrasekharaiah [6] were used. From thermogravimetric studies, it was pointed out by Nakamura *et al.* [3] that La_2CoO_4 and CoO coexist with $LaCoO_3$. Further, the stability of La_2CoO_4 with respect to reduction to La_2O_3 and Co was determined from e.m.f. studies by Sreedharan and Pankajavalli [15]. The above sets of data were compiled in Table III to evaluate ΔG_r^0 for the reaction

$$\tfrac{1}{2}La_2O_3 + CoO + \tfrac{1}{4}O_2 \rightleftharpoons LaCoO_3 \qquad (5)$$

In this computation the values of ΔG_f^0 of NiO assessed by Kellogg [16] (Table III) were used. There are two equations for ΔG_r^0 of Reaction 5 corresponding to the two forms of $LaCoO_3$ in the respective temperature ranges of stability. The log P_{O_2} value at 1273 K for the mixture $LaCoO_3/La_2CoO_4/CoO$ from e.m.f. [6] and from thermogravimetry [3] are compared in Table II. It should be noted that Sreedharan and Chandrasekharaiah [6] wrongly attributed the e.m.f. to an equal mass mixture of $LaCoO_3/La_2O_3/CoO$. However, steady e.m.f. could be observed only after 24 h

TABLE I Standard Gibbs' energy of formation per mole of $LaFeO_3$ from La_2O_3 and Fe_2O_3 or Fe

Reactions	ΔG^0 (kJ)	Precision ($\pm$kJ)	Remarks
1. $\frac{1}{2}La_2O_3 + 3/2\ FeO \rightleftharpoons \frac{1}{2}Fe + LaFeO_3$	$-22.67 - 0.011\ 55T$	0.34	This work (from cell reaction)
2. $Fe + \frac{1}{2}O_2 \rightleftharpoons FeO$	$-261.30 + 0.063\ 30T$	1.00	[14]
3. $3FeO + \frac{1}{2}O_2 \rightleftharpoons Fe_3O_4$	$-311.87 + 0.123\ 00T$	0.40	[14, 19]
4. $2Fe_3O_4 + \frac{1}{2}O_2 \rightleftharpoons 3Fe_2O_3$	$-247.05 + 0.140\ 90T$	1.50	[19–21]
5. $\frac{1}{2}La_2O_3 + \frac{1}{2}Fe_2O_3 \rightleftharpoons LaFeO_3$	(a) $-8.19 - 0.044\ 40T$	1.40	This work (computed from Equations 1 to 5a)
	(b) $-51.40 - 0.012\ 68T$	2.50	From Katsura *et al.* [7] (computed from Equations 2 to 4, 5b)
	(c) $29.33 - 0.079\ 98T$	–	From Leontev *et al.* [8] (computed from Equations 2 to 4, 5c)
	(d) $-40.07 - 0.019\ 98T$	2.50	From Nakamura *et al.* [3]
6. $\frac{1}{2}La_2O_3 + Fe + \frac{3}{4}O_2 \rightleftharpoons LaFeO_3$	(a) $-414.62 + 0.083\ 40T$	1.90	This work
	(b) $-457.80 + 0.115\ 10T$	1.00	[7]
	(c) $-377.10 + 0.047\ 80T$	–	[8]
	(d) $-446.50 + 0.107\ 80T$	1.00	[3]

TABLE II Equilibrium oxygen pressure at 1273 K in the coexisting phases bearing $LaMO_3$ (M = Fe, Co, Ni or Mn)

Coexisting phases	$\log P_{O_2}$ (atm) at 1273 K	Precision ($\pm$kJ mol^{-1})	Technique	Reference
$LaFeO_3$, Fe, La_2O_3	-16.90	0.10	Solid electrolyte e.m.f.	This work
	-17.03	0.05	Gas equilibrium measurements	[7]
	-17.30	–	Gas equilibrium measurements	[8]
	-16.92	0.05	Thermogravimetry	[3]
$LaCoO_3$, La_2CoO_4, CoO	-6.64	0.09	Solid electrolyte e.m.f.	[6]
	-7.00	0.20	Thermogravimetry	[3]
$LaNiO_3$, La_2NiO_4, NiO	-6.00	0.20	Thermogravimetry	[3]
$LaMnO_3$, Mn, La_2O_3	-14.02	0.07	Solid electrolyte e.m.f.	[5]
	-14.61	–	Electrical conductivity	[4, 22]
	-15.05	0.05	Thermogravimetry	[3]

heating of about 1273 K. The reason for this was later found to be due to the *in situ* formation of La_2CoO_4 from La_2O_3 and excess CoO in the equal mass mixture resulting in the co-existence of $LaCoO_3$, La_2CoO_4 and CoO. These observations were taken into account in the computations given in Table III.

For comparing the stability of $LaFeO_3$ with $LaNiO_3$, a single value of $\log P_{O_2}$ obtained for the coexisting mixture $LaNiO_3/La_2NiO_4/NiO$ at 1273 K reported by Nakamura *et al.* [3] (Table II) was used. This equilibrium could be represented as follows:

$$\tfrac{1}{2}La_2NiO_4 + \tfrac{1}{2}NiO + \tfrac{1}{4}O_2 \rightleftharpoons LaNiO_3 \qquad (6)$$

Making use of the Gibbs' energy data for the formation of La_2NiO_4 from La_2O_3 and NiO reported by Sreedharan *et al.* [17] in conjunction with the value of -0.6 (atm) for $\log P_{O_2}$ [3] for the Reaction 6 at 1273 K, a value of -10.1 kJ mol^{-1} was calculated for the following reaction.

$$\tfrac{1}{2}La_2O_3 + NiO + \tfrac{1}{4}O_2 \rightleftharpoons LaNiO_3 \qquad (7)$$

Likewise the stability of $LaFeO_3$ could be compared with that of $LaMnO_3$ from thermogravimetry by Nakamura *et al.* [3], from electrical conductivity by Kamegashira *et al.* [4] and from e.m.f. measurements by Sreedharan *et al.* [5] for the equilibrium reaction

$$\tfrac{1}{2}La_2O_3 + MnO + \tfrac{1}{4}O_2 \rightleftharpoons LaMnO_3 \qquad (8)$$

In order to assess the existence of a systematic trend in the ΔG_r^0 for the reaction

$$\tfrac{1}{2}La_2O_3 + MO + \tfrac{1}{4}O_2 \rightleftharpoons LaMO_3 \qquad (9)$$

where M = Fe, Co, Ni or Mn, the ΔG_r^0 values for Reaction 9 are compared in Table IV. It can be seen from the table that the stability of $LaMO_3$ with respect to MO and La_2O_3 decreases from iron to nickel whereas the manganese compound has a stability which is intermediate between that of iron and cobalt. The fact that the stability of the +3 state of the transition metal ion decreases from manganese to nickel makes it difficult to compare the $\Delta G^0_{r,ox}$ for the formation of $LaMO_3$ from La_2O_3 and M_2O_3 except in the case where M is Mn or Fe as shown below (cf. Reaction 4).

$$(\Delta G^0_{r,ox,LaFeO_3} \pm 1.40)\ (\text{kJ mol}^{-1}) = -8.19 - 0.044\,39T\ (\text{K}) \qquad (10)$$

$$(\Delta G^0_{r,ox,LaMnO_3} \pm 0.67)\ (\text{kJ mol}^{-1}) = -75.12 + 0.012\,60\,T\ (\text{K}) \qquad (11)$$

At 1273 K, both $LaMnO_3$ and $LaFeO_3$ have about the same stability (-59 and -64 kJ mol^{-1}) with respect to disproportionation into their sesquioxides. This would enable one to estimate a value of about -60 kJ mol^{-1} for the $\Delta G^0_{r,ox}$ of $LaCrO_3$ which in turn corresponds to a $\log P_{O_2}$ value of -25.0 (atm) for the coexisting mixture $LaCrO_3/La_2O_3/Cr$ making use of

TABLE III Standard Gibbs' energy of formation per mole of $LaCoO_3$ from La_2O_3 and CoO

Reaction	ΔG_r^0 (kJ)	Precision ($\pm$kJ)	Remarks
1. $2LaCoO_3 + Ni \rightleftharpoons La_2CoO_4 + CoO + NiO$	$4.59 - 0.040\,12T$*	0.77	Sreedharan *et al.* [6]
	$-26.09 - 0.014\,67T$†	0.77	(from cell reaction)
2. $Ni + \frac{1}{2}O_2 \rightleftharpoons NiO$	$-234.30 + 0.085\,30T$	0.30	Kellogg [16]
3. $La_2O_3 + CoO \rightleftharpoons La_2CoO_4$	$12.24 - 0.014\,90T$	1.02	Sreedharan *et al.* [15]
4. $\frac{1}{2}La_2O_3 + CoO + \frac{1}{4}O_2 \rightleftharpoons LaCoO_3$	$-113.33 + 0.055\,26T$*	1.05	Computed from
	$-97.99 + 0.042\,54T$†	1.05	Equations 1 to 3

*For the range 1100 to 1200 K.
†For the range 1250 to 1325 K.

TABLE IV Standard Gibbs' energy of formation per mole of $LaMO_3$ from La_2O_3 and MO (M = Mn, Fe, Co or Ni)

M	ΔG_r^0 (kJ)	Temperature range (K)	Precision ($\pm$kJ)	$\Delta G^0_{r,1273\,K}$ (kJ mol^{-1})	Remarks
Mn	$-168.17 + 0.065\,00T$	1064–1308	0.42	−85.5	Sreedharan *et al.* [5]
Fe	$-153.32 + 0.020\,10T$	1094–1299	0.84	−127.7	This work
Co	$-113.33 + 0.055\,26T$	1100–1200	1.05	*	Computed from Table III
Co	$-97.99 + 0.042\,53T$	1250–1325	1.05	−43.9	Computed from Table III
Ni	-10.1†	1273	1.50	−10.1	Nakamura *et al.* [3]

*The low temperature form of $LaCoO_3$ is unstable at 1273 K.

†Only one value of ΔG_f^0 was available at 1273 K for $LaNiO_3$ from Nakamura *et al.* [3].

the ΔG_f^0 of Cr_2O_3 assessed in the literature [18]. Values of log P_{O_2} in this range are rather difficult to measure directly.

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