Measurement of Gibbs energy of formation of LaGaO₃ using a composition-graded solid electrolyte

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A composition-graded solid electrolyte $(LaF_3)_{\nu} \cdot (CaF_2)_{1-\nu}$ was used for the measurement of the standard Gibbs energy of formation of LaGaO₃ from its component oxides. An equimolar mixture of CaO and CaF2 was employed as the reference electrode. The composition of the working electrode depended on temperature. A three-phase mixture of $LaGaO_3 + Ga_2O_3 + LaF_3$ was used in the temperature range from 910 to 1010 K, while a mixture of $LaGaO_3 + Ga_2O_3 + LaO_{1-x}F_{1+2x}$ was employed from 1010 to 1170 K. Both the reference and working electrodes were placed under pure oxygen gas. Because of the high activity of LaF_3 at the working electrode, there was significant diffusion of LaF₃ into CaF₂. The composition-graded electrolyte was designed to minimize the electrode-electrolyte interaction. The concentration of LaF_3 varied across the solid electrolyte; from y = 0 near the reference electrode to a maximum value y = 0.32 at the working electrode. For the correct interpretation of the electromotive force at T > 1010 K, it was necessary to use thermodynamic properties of the lanthanum oxyfluoride solid solution. The standard Gibbs energy of formation of LaGaO₃ from its component oxides according to the reaction, $\frac{1}{2}La_2O_3$ (A-rare earth) + $\frac{1}{2}Ga_2O_3$ (β) \rightarrow LaGaO₃ (rhombohedral) can be represented by the equation: $\Delta G_{f,(ox)}^{o}/J \text{ mol}^{-1} = -46\ 230 + 7.75\ T/K\ (\pm 1500).$

I. INTRODUCTION

Doped LaGaO₃ is an excellent oxide ion conductor with potential application in solid-oxide fuel cells.^{1,2} Doping of Sr on the La site and Mg on the Ga site is an effective method for increasing oxygen vacancies and enhancing ionic conductivity of LaGaO₃. Thermodynamic data for pure and doped LaGaO₃ are useful for evaluating the stability of the electrolyte under reducing conditions and its compatibility with electrode materials. Phase diagram for the system La₂O₃–Ga₂O₃ shows the presence of two congruent melting interoxide compounds; LaGaO₃ melting at 1988 (±20) K, and La₄Ga₂O₉ melting at 1977 (±20) K.³

Azad *et al.*⁴ attempted to measure the standard Gibbs energy of formation of $LaGaO_3$ from its constituent sesquioxides using a cell based on CaF_2 as the solid electrolyte, $La_2O_3 + LaF_3$ as the reference electrode, and $LaF_3 + LaGaO_3 + Ga_2O_3$ as the working electrode. Both electrodes were placed under flowing oxygen gas. The formation of lanthanum oxyfluoride from a mixture of La_2O_3 and LaF_3 is well established in the literature.^{5–7} Therefore, the reference electrode used by Azad *et al.*⁴ is unstable in the temperature range of their measurements. Because Azad *et al.*⁴ ignored the formation of the oxyfluoride phase, their results are unreliable. Kanke and Navrotsky⁸ have measured the enthalpy of formation of LaGaO₃ from oxides as $-50.86 (\pm 2.92)$ kJ mol⁻¹ using high-temperature solution calorimetry.

Recently, the thermodynamic properties of the system $La_2O_3-LaF_3$ were measured by the authors in the temperature range from 910 to 1170 K.⁹ A solid solution with fluorite structure $LaO_{1-x}F_{1+2x}$, $0 \le x \le 0.33$, is present at high temperature. On cooling the stoichiometric LaOF transforms to a rhombohedral structure ($R\overline{3}m$) at temperatures below 778 (±3) K. The solid solution containing excess fluorine has a tetragonal structure at room temperature.^{5,7}



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Both oxide and fluoride solid electrolytes can be used to measure the standard Gibbs energy of formation of LaGaO₃ at high temperatures. The oxygen chemical potentials established by phase mixtures Ga + La₂O₃ + La₄Ga₂O₉ and Ga + La₄Ga₂O₉ + LaGaO₃ can be determined using a cell incorporating yttria-doped thoria as the solid electrolyte. At the low oxygen potentials established by these mixtures, stabilized-zirconia solid electrolytes exhibit significant electronic conductivity ($t_e > 0.01$). For the design of a suitable solid-state cell based on a fluoride solid electrolyte, it is important to know the composition of the fluoride phase in equilibrium with LaGaO₃ and Ga₂O₃. The aim is to measure the activity of La₂O₃ in the two-phase mixture containing LaGaO₃ and Ga₂O₃.

Presented in this article is the measurement of the Gibbs energy of formation of LaGaO₃ from its component oxides using a solid electrolyte based on CaF_2 . Preliminary experiments indicated that the fluoride phase that coexists with LaGaO₃ and Ga₂O₃ was LaF₃ for T < 1010 K and an oxyfluoride solid solution $LaO_{1-x}F_{1+2x}$ at T > 1010 K. Therefore, working electrodes consisting of $LaGaO_3 + Ga_2O_3 + LaF_3$ and $LaGaO_3 + Ga_2O_3 + LaO_{1-x}F_{1+2x}$ were used in a solidstate cell incorporating single-crystal CaF2 as the solid electrolyte and $CaO + CaF_2$ as the reference electrode. Both electrodes were placed under flowing oxygen gas. However, there was significant interaction between the working electrode and the solid electrolyte, with migration of La³⁺ from the electrode into the electrolyte. A composition-graded solid electrolyte $(LaF_3)_{v} \cdot (CaF_2)_{(1-v)}$, with axial variation of y, was designed to minimize the effect of La³⁺ diffusion on cell performance. The composition of the graded electrolyte in equilibrium with LaF_3 was defined by y = 0.32. The composition of the graded electrolyte in equilibrium with $LaO_{1-x}F_{1+2x}$ was found by trial and error. The cells can be represented as:

(Cell I) Pt, O₂, CaO
+ CaF₂ || CaF₂ || (LaF₃)_y · (CaF₂)_(1-y) || LaGaO₃
$$y = 0$$
 $y = 0.32$
+ Ga₂O₃ + LaF₃, O₂, Pt

(Cell II) Pt, O₂, CaO
+ CaF₂ || CaF₂ || (LaF₃)_y · (CaF₂)_(1-y) || LaGaO₃
$$y = 0$$
 $y = 0.28$
+ Ga₂O₃ + LaO_{1-x}F_{1+2x}, O₂, Ptτ

with the right-hand electrodes positive. Single-crystal CaF_2 was coupled with a polycrystalline compositiongraded solid electrolyte to form a bielectrolyte combination. The single-crystal CaF_2 , placed adjacent to the $CaO + CaF_2$ reference electrolyte, prevented grainboundary diffusion of CaO into the solid electrolyte.

II. EXPERIMENTAL METHODS

A. Materials

Optical-grade single crystals of CaF_2 , in the form of disks 1.5 cm in diameter and 0.2 cm thick, were obtained from Harshaw Chemical Company. Ultrapure anhydrous powders of CaF₂, LaF₃, CaO, La₂O₃, and Ga₂O₃ were supplied by Johnson Matthey Ltd., London, UK. The oxides were heated at 1273 K in dry inert gas for 10 ks before use. For the preparation of LaGaO₃, stoichiometric amounts of La2O3 and Ga2O3 were ball milled, pelletized, and reacted at 1673 K for 36 ks. The pellet was reground, repelletized, and reacted again at the same temperature for an identical period. The formation of LaGaO₃ was confirmed by powder x-ray diffraction (XRD). At room temperature, LaGaO₃ has an orthorhombic unit cell (space group *Pbnm*) with a = 0.5524, b =0.5492, and c = 0.7775 nm. At 1023 K, XRD revealed a unit cell with rhombohedral symmetry (space group R3c), with lattice parameters a = 0.5561 and c =1.3567 nm in the hexagonal setting.

Solid solutions, $LaO_{1-x}F_{1+2x}$, were prepared by solidstate reaction. Fine powder of La_2O_3 was mixed with LaF_3 in the required ratio. The fully homogenized mixtures were compacted into pellets, buried in a powder mixture of the same composition, and reacted in a prepurified inert-gas atmosphere first at 1275 K for 36 ks and subsequently at 1475 K for 18 ks:

$$a \operatorname{LnF}_3 + b \operatorname{Ln}_2 O_3 \rightarrow (a + 2b) \operatorname{Ln}O_{1-x} F_{1+2x}$$
, (1)

with x = (a - b)/(a + 2b). The high-purity Ar gas (99.999%) used was first dehydrated by passing through anhydrous Mg(ClO₄)₂ and P₂O₅, and then deoxidized by passing through Cu turnings at 750 K and Ti granules at 1150 K. Pellets were pulverized after heat treatment. The formation of LaO_{1-x}F_{1-2x} was confirmed by XRD. The oxyfluoride solid solution has cubic structure at high temperature and tetragonal structure at low temperature. The high-temperature phase can be retained by rapid quenching into chilled mercury. The lattice parameters of the tetragonal phase are plotted as a function of composition in Fig. 1. The lattice parameters of the cubic phase at room temperature vary linearly from a = 0.5765 nm for x = 0 to a = 0.5793 nm for x = 0.3.

Lanthanum oxyfluoride solid solutions of various compositions were equilibrated at different temperatures with an equimolar mixture of $LaGaO_3$ and Ga_2O_3 . The fluoride phase in equilibrium was identified by XRD. Below 1010 K, LaF_3 was the equilibrium phase. At higher temperatures, the oxyfluoride solid solution was stable. The equilibrium composition of the oxyfluoride phase was obtained from its lattice parameter as shown in Fig. 1. The equilibrium composition of the lanthanum oxyfluoride phase is defined

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FIG. 1. Lattice parameters of the solid solution $LaO_{1-x}F_{1+2x}$ with tetragonal structure as a function of composition (*x*) at room temperature. The composition of the oxyfluoride solid solution in equilibrium with $LaGaO_3 + Ga_2O_3$ at 1150 K is shown by the vertical dotted line.

by x = 0.281 (or $X_{\text{LaF}_3} = 0.685$) at 1150 K. The equilibrium value of x was found to very from 0.313 at 1010 K to 0.280 at 1170 K.

Similarly, the composition of the fluoride solid solution $(LaF_3)_y \cdot (CaF_2)_{(1-y)}$ in equilibrium with the oxyfluoride phase LaO_{0.72}F_{1.56} was determined by direct equilibration of the phases at 1150 K under prepurified inert gas, and subsequent analysis by XRD. A large excess of the oxyfluoride phase was used so that its composition was relatively unaltered. The lattice parameters of the phases present in the quenched sample were determined by XRD at room temperature. The lattice parameter of the solid solution $(LaF_3)_v \cdot (CaF_2)_{(1-v)}$ has been determined earlier as a function of composition (a/nm = 0.5465 + 0.0554y).¹⁰ Using this information, the equilibrium value y was found to be 0.25 at 1150 K. The equilibrium value of y also changed with temperature, from 0.32 at 1010 K to 0.24 at 1170 K. An average value of y = 0.28 was used at the terminal composition of the solid electrolyte in cell II. Small adjustments in composition at the electrode occurred during equilibration at each temperature of measurement.

Although it is preferable to have a composition-graded solid electrolyte $(LaF_3)_y \cdot (CaF_2)_{(1-y)}$ with linear variation in composition (y), in practice it is difficult to pre-

pare such a structure. In the present study, pellets were prepared in which the composition was varied in steps of 5 mol%; homogeneous solid solutions of CaF₂ containing 5, 10, 15, 20, 25, 28, and 32 mol% LaF₃. Homogeneous solid solutions were first prepared by solid-state diffusion. Intimate mixtures of fine powders ($d < 1 \mu$ m) of CaF₂ and LaF₃ in the required proportions were pelletized and heat treated at 1475 K for approximately 400 ks under prepurified Ar gas.

The functionally graded solid electrolyte was prepared by repeated consolidation of layers, each having a uniform composition. A weighed quantity of CaF_2 powder was pressed in a steel die at 150 MPa, solid solution having the next composition $(5 \text{ mol}\% \text{ LaF}_3)$ was then placed over it and consolidated again at the same pressure. The procedure was repeated with successive compositions of the solid solution until the graded structure visualized in Fig. 2 was obtained of the type. A similar graded structure with terminal composition y = 0.28 was used in cell II. After final compacting at 200 MPa, the composite pellet was sintered under prepurified Ar gas at 1375 K for approximately 300 ks. Processing of the solid solutions containing lanthanum was carried out in a glove box to prevent contamination, especially by moisture.



FIG. 2. Profile of the composition-graded solid electrolyte $(\text{LaF}_3)_y \cdot (\text{CaF}_2)_{1-y}$. The value of y varies from 0 to 0.25 in steps of 0.05.

Oxygen gas of purity greater than 99.999% was dried by passing it through towers containing silica gel and anhydrous magnesium perchlorate, and finally over boats containing anhydrous phosphorus pentoxide before use in the solid-state cell.

B. Procedure

The reference electrodes of cells I and II were prepared by heating a compacted equimolar mixture of CaO and CaF₂ under dry oxygen at 1280 K. The two working electrodes were prepared in a similar way using equimolar mixtures of Ga₂O₃ + LaGaO₃ + LaF₃ and Ga₂O₃ + LaGaO₃ + LaO_{0.72}F_{1.56}. Intimate mixing of the fluoride and oxide phases at the electrodes was required to generate the equilibrium fluorine potential at each electrode under an atmosphere of oxygen gas.

A schematic diagram of the apparatus used in this study is shown in Fig. 3. The electrode pellets were spring loaded on either side of the bielectrolyte assembly, with a thin platinum gauze placed between the electrolyte and each electrode. Platinum wires, spot welded to the platinum gauze, were used as electrical leads to a high-impedance ($10^{16} \Omega$) voltmeter. The working electrode was placed in contact with the composition-graded electrolyte. The pellets were held together under pressure by a system that consisted of a closed-end alumina tube, an alumina rod, and springs that were attached to the brass cap. Direct contact of the electrode pellets with the alumina rod or tube was prevented by inserting platinum



FIG. 3. Schematic diagram of the apparatus used for EMF measurement.

foils between them. The cell assembly was mounted inside a vertical outer alumina tube, the ends of which were closed with water-cooled brass caps. After assembling the cell and fitting the brass caps with O-ring seals to the outer alumina tube, the tube was evacuated and leak tested. The outer alumina tube was then suspended in a vertical resistance furnace such that the electrodes were in the constant temperature zone $(\pm 1 \text{ K})$. The cell was maintained under dry oxygen gas at a pressure of 0.1 MPa, flowing at 2.5 ml s^{-1} . The flow rate was set by a mass flow controller. Even trace amounts of water vapor in the gas were found to react with CaF₂, which produced tiny specks of CaO on the surface of CaF₂. Unless water vapor was eliminated, the transparent single CaF₂ crystals soon became opaque. The compositiongraded electrolyte was also very susceptible to degradation by moisture.

The electromotive force (EMF) of cell I was measured in the temperature range from 910 to 1010 K; cell II from 1010 to 1170 K. A Pt/Pt–13%Rh thermocouple that was calibrated against the melting point of gold was used for measuring the temperature of the cell. All temperatures in this study refer to the ITS-90 scale.

The time required to attain steady EMF value varied from approximately 60 ks at a temperature of 910 K to about 18 ks at a temperature of 1170 K. The reversibility of the cell EMF was checked by passing a small direct current of approximately 10 µA in either direction through the cell for approximately 0.6 ks using an external potential source, and verifying that the EMF returned to the steady value before each microcoulometric titration. The chemical potentials at each electrode were displaced from equilibrium by an essentially infinitesimal amount during each titration. Because the cell EMF returned to the same value after successive displacements in opposite directions, the attainment of equilibrium at each electrode was confirmed. The EMF was independent of the flow rate of oxygen through the cell in the range 1.5 to 5 ml s⁻¹. After each run, the electrode pellets were examined by XRD and energy-dispersive x-ray analysis. No significant change in composition of the electrodes was detected.

III. RESULTS AND DISCUSSION

A. Interpretation of the EMF of the solid-state cell

The excess anions in the cubic solid solution $La_yCa_{1-y}F_{2+y}$ occupy interstitial sites as they do in solutions of YF₃ in CaF₂.¹¹ The solid solution has higher ionic conductivity than pure CaF₂. Because fluoride ions are the mobile species in CaF₂ and La_yCa_{1-y}F_{2+y}, the EMF of a solid-state cell (*E*) based on these electrolytes is given by

$$\eta F E = \mu'_{F_2} - \mu''_{F_2} \quad , \tag{2}$$

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where μ'_{F_2} and $\mu''_{F_2}(\mu'_{F_2} > \mu''_{F_2})$ are the chemical potentials of fluorine at the two electrodes, $\eta = 2$ is the number of electrons associated with the electrode reactions, and $F = 96485.3 \text{ C mol}^{-1}$ is the Faraday constant. Under the experimental conditions used in this study, the transport number of fluoride ion is greater than 0.99 in both pure and doped CaF₂.^{12,13}

The Nernstian response of a cell incorporating the composition-graded solid electrolyte $La_yCa_{1-y}F_{2-y}$ has been demonstrated in an earlier study.¹⁰ It has been shown both by experiment and theoretical analysis that the EMF of a cell that incorporates a composition-graded electrolyte is determined by the chemical potentials of the neutral form of the mobile species at the electrodes, when there is only one mobile ion with transport number close to unity.^{14–18} The concentration gradient of relatively immobile ions does not result in a diffusion potential.^{14–18}

B. Gibbs energy of formation of LaGaO₃

The reversible EMFs of cells I and II are plotted as a function of temperature in Fig. 4. The EMF of cell I is almost constant at 452.5 (± 0.1) mV. The linear least-squares regression analysis gives the relation

$$E_{\rm I}/{\rm mV} = 453.3 - 7.6 \times 10^{-4} T/{\rm K} (\pm 0.1)$$
 . (3)

FIG. 4. Temperature dependence of the reversible EMF of cells I and II.

T/K

1000

For cell II, the temperature dependence of EMF can be expressed by the relation

$$E_{\rm II}/{\rm mV} = 552.1 - 0.0986 \ T/{\rm K} \ (\pm 0.43)$$
 . (4)

The uncertainty limit corresponds to twice the standard error estimate. When attempts were made to measure the EMF of cell I at T > 1010 K, the EMF drifted down gradually and approached the EMF of cell II after approximately 50 ks. This indicates gradual conversion of LaF₃ to LaO_{1-x}F_{1+2x} at T > 1010 K. In an earlier investigation of the system La₂O₃–LaF₃, the authors measured the EMF of the cell,

(Cell III) Pt, O₂, CaO
+ CaF₂ || CaF₂ || (LaF₃)_y · (CaF₂)_(1-y) || ,
$$y = 0$$
 y
LaO_{1-y}F_{1+2y}, O₂, Pt

as a function of temperature and composition (x) of the oxyfluoride phase.⁹ The reference electrode was the same in cells I, II, and III. The EMF of cell III is related to the ratio of activities, $(a_{\text{La}_2\text{O}_3}/a_{\text{La}F_3}^2)$, in the oxyfluoride solid solution. Figure 5 shows the EMF of cell II superimposed on the plot of E_{III} as a function of composition of the oxyfluoride $(X_{\text{La}F_3})$ at 1150 K. The point of inter-



FIG. 5. Superimposition of the EMF of cell II on the EMF of cell III as a function of composition $(X_{\text{La}F_3})$ of the lanthanum oxyfluoride solid solution at 1150 K.

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2840

900

455

450

445

440

435

E/mV

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1200

E"

1100

section of the EMFs defines the composition of the oxyfluoride phase in equilibrium with the phase mixture $Ga_2O_3 + LaGaO_3$ at the working electrode of cell II. As seen from Fig. 5, the composition is defined by $X_{LaF_3} = 0.685$ (x = 0.281) at 1150 K. This value is identical to that obtained from lattice parameter measurement of the sample quenched from 1150 K.

The electrochemical reaction at the working electrode on the right-hand side of cell I can be written as

The corresponding reaction at the reference electrode on the left-hand side of cell I can be represented as

$$CaO + 2 F^{-} \rightarrow CaF_2 + \frac{1}{2}O_2 + 2 e^{-}$$
 . (6)

When the oxygen partial pressure is the same over both electrodes, the EMF of cell I is related to the standard Gibbs energy change for the virtual cell reaction

$$\frac{2}{3} \operatorname{LaF}_3 + \frac{1}{3} \operatorname{Ga}_2 \operatorname{O}_3 + \operatorname{CaO} \rightarrow \frac{2}{3} \operatorname{LaGaO}_3 + \operatorname{CaF}_2 \quad , \quad (7)$$

$$\Delta G_{(7)}^{0} / J \text{ mol}^{-1} = -2FE_{I} / 1000$$

= -87 473 + 0.15 T/K (±20) . (8)

For the reaction

$$CaF_2 + \frac{1}{3} La_2O_3 \rightarrow CaO + \frac{2}{3} LaF_3$$
, (9)

standard Gibbs energy change in the temperature range from 900 to 1200 K, computed from data in the compilation of Knacke *et al.*,¹⁹ can be represented by the equation

$$\Delta G_{(9)}^0 / \text{J mol}^{-1} = 56\ 645 + 5.02\ T / \text{K}\ (\pm 1500) \quad . \tag{10}$$

By combining Reactions (7) and (9), one obtains the reaction that represents the formation of rhombohedral $LaGaO_3$ from β -Ga₂O₃ and La₂O₃ with A-rare-earth oxide structure:

¹/₂ La₂O₃ (A-rare earth) + ¹/₂ Ga₂O₃ (
$$\beta$$
)
 \rightarrow LaGaO₃ (rhombohedral) , (11)

$$\Delta G_{(11)}^0 / \text{J mol}^{-1} = -46\ 240 + 7.76\ T/\text{K}\ (\pm 1500) \quad , \qquad (12)$$

in the temperature range from 910 to 1010 K. The relatively large uncertainty limit arises from inaccuracies in the thermodynamic data for oxides and fluorides of calcium and lanthanum reported in the literature.¹⁹ When more precise data for these compounds become available, it will be possible to derive more accurate data for LaGaO₃.

The electrochemical reaction at the working electrode on the right-hand side of cell II can be written as

$$\frac{2}{(1+2x)} \operatorname{LaO}_{1-x} F_{1+2x} + \frac{1}{2}O_2 + 2 e^{-1}$$

$$\rightarrow \frac{1}{(1+2x)} \operatorname{La}_2 O_3 + 2 F^{-1} . \qquad (13)$$

The activity of La_2O_3 at the electrode is defined by the dissociation of $LaGaO_3$ (two-phase equilibria involving $LaGaO_3$ and Ga_2O_3):

$$\frac{2}{(1+2x)} \operatorname{LaGaO}_{3} \to \frac{1}{(1+2x)} \operatorname{Ga}_{2} \operatorname{O}_{3} + \frac{1}{(1+2x)} \operatorname{La}_{2} \operatorname{O}_{3} \quad .$$
(14)

The overall reaction at the working electrode, obtained by combining Eqs. (13) and (14), is

$$\frac{2}{(1+2x)} \operatorname{LaO}_{1-x} F_{1+2x} + \frac{1}{(1+2x)} \operatorname{Ga}_2 \operatorname{O}_3 + \frac{1}{2} \operatorname{O}_2 + 2 \operatorname{e}^- \to \frac{2}{(1+2x)} \operatorname{LaGaO}_3 + 2 \operatorname{F}^- \quad . \tag{15}$$

Basically, the lanthanum oxyfluoride phase converts the activity of La_2O_3 established by the phase mixture $LaGaO_3 + Ga_2O_3$ into an equivalent fluorine potential under an atmosphere of pure oxygen. Reaction at the reference electrode of cell II is identical to that of cell I, which has been discussed above. Because the oxygen partial pressure is the same over both electrodes, the EMF of cell II is related to the standard Gibbs energy change for the virtual cell reaction

$$\frac{2}{(1+2x)} \operatorname{LaO}_{1-x} F_{1+2x} + \frac{1}{(1+2x)} \operatorname{Ga}_2 \operatorname{O}_3 + \operatorname{CaO} \to \frac{2}{(1+2x)} \operatorname{LaGaO}_3 + \operatorname{CaF}_2 \quad , \qquad (16)$$

$$\Delta G_{(16)}^{0} / J \text{ mol}^{-1} = -2FE_{II} / 1000$$

= -106 540 + 19.03 T/K (±85) .
(17)

The Gibbs energy of mixing of $LaO_{1-x}F_{1+2x}$ solid solution relative to its component oxide (La_2O_3) and fluoride (LaF_3) has been determined recently as a function of temperature and composition (x).⁹ By combining Gibbs energy change for Reactions (9) and (16) with the Gibbs energy of mixing of the lanthanum oxyfluoride solid solution, one obtains the standard Gibbs energy of formation of LaGaO₃ from Ga₂O₃ and La₂O₃, represented by Reaction (11):

$$\Delta G_{(11)}^{\rm o}/{\rm J} \,\,{\rm mol}^{-1} = -46220 + 7.74 \,\, T/{\rm K} \,\,(\pm 1500) \quad, \tag{18}$$

in the temperature range from 1010 to 1170 K. Thus, the Gibbs energies of formation of $LaGaO_3$ obtained from the EMFs of cells I and II in different ranges of temperature are almost identical.

The Gibbs energy change for reaction (11) can also be evaluated by an alternate procedure involving EMFs of cells II and III. By combining EMF of cell III with a modified version of the Gibbs–Duhem equation,²⁰ the variation of chemical potentials of La₂O₃ and LaF₃ with composition in the binary system La₂O₃–LaF₃ has been delineated.⁹ From this information, a plot of the EMF of cell III as a function of chemical potential can be constructed as shown in Fig. 6. Superimposing the EMF of cell II on this graph directly yields the chemical potential of La₂O₃ corresponding to the phase mixture Ga₂O₃ + LaGaO₃. The value of the Gibbs energy of formation is equal to half the chemical potential of La₂O₃: $\Delta G_{(11)}^{\circ} = \frac{1}{2}\Delta\mu_{La_2O_3}$. Values obtained by this method are almost identical to that given by Eq. (18).

The standard Gibbs energy of formation of LaGaO₃ obtained in this study is compared with the value reported by Azad *et al.*⁴ in Fig. 7. The values obtained in this study are more negative by approximately 19 kJ mol⁻¹. In their attempt to measure the Gibbs energy of formation of LaGaO₃, Azad *et al.*⁴ used the cell

$$(Cell IV) Pt, O_2, La_2O_3 + LaF_3 \parallel CaF_2 \parallel LaF_3 \\ + LaGaO_3 + Ga_2O_3, O_2, Pt \quad .$$



FIG. 6. EMF of cell III as a function of the relative chemical potential of La₂O₃ in the lanthanum oxyfluoride solid solution LaO_{1-x}F_{1+2x}. The value of $\Delta\mu_{\text{La}_2\text{O}_3}$ in the phase mixture LaGaO₃ + Ga₂O₃ is defined when $E_{\text{II}} = E_{\text{III}}$.



FIG. 7. Comparison of the Gibbs energy of formation of $LaGaO_3$ obtained in this study with that reported by Azad *et al.*⁴

Their reference electrode consisted of a mixture of LaF₃ and La₂O₃ in approximately equal mass ratio. At high temperature, this would have resulted in a singlephase oxyfluoride solid solution characterized by $X_{\text{LaF}_2} = 0.625$ (or x = 0.182). According to the results of this study, LaF₃ is also not stable at their working electrode at T > 1010 K; it would have equilibrated with the other phases Ga₂O₃ and LaGaO₃ to form an oxyfluoride solid solution rich in LaF_3 . If the equilibrium phases had formed during measurement, the EMF produced by their cell can be estimated from the results of this study. For example, at 1150 K their EMF would be the difference between E_{II} , and E_{III} at $X_{\text{La}F_3} = 0.625$. Their cell, interpreted to function in the manner described above, should have produced an EMF of 65.1 mV at 1150 K. This is very close to the value of 65.4 mV at 1150 K reported by Azad et al.⁴. The coincidence is remarkable, especially because the composition of their reference electrode is not precisely defined. However, the Gibbs energy values reported by Azad et al.⁴ are clearly incorrect.

The temperature-independent term in Eq. (12) or (18) is related to the enthalpy of formation of LaGaO₃ from La₂O₃ and Ga₂O₃ at a mean temperature of 1040 K; $\Delta H_{f(ox)}^{o}/kJ \text{ mol}^{-1} = -46.23 (\pm 4.5)$. This is in reasonable agreement with the value of -50.86 (±2.92) kJ mol⁻¹ at 977 K reported by Kanke and Navrotsky.⁸ The corresponding value from the EMF study of Azad *et al.*⁴ is -24.5 (±4.5) kJ mol⁻¹. The enthalpy of formation of

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LaGaO₃ from the elements computed from the results of this study using the Neumann–Kopp rule is $\Delta H_{f(298.15)}^{o}/kJ \text{ mol}^{-1} = -1488.25 (\pm 5.5)$. The enthalpies of formation of Ga₂O₃ and La₂O₃ at 298.15 K from Knacke *et al.*¹⁹ are used in this evaluation. The temperature-dependent term in Eq. (12) or (18) is related to the entropy of formation of LaGaO₃ from oxides; $\Delta S_{f(ox)}^{o}/kJ \text{ mol}^{-1} \text{ K}^{-1} = -7.75 (\pm 4.4)$. Assuming that the heat capacity of LaGaO₃ is the sum of the heat capacities of La₂O₃ and Ga₂O₃, the standard entropy of LaGaO₃ at 298.15 K can be estimated as $S_{f(298.15)}^{o}/J \text{ mol}^{-1} \text{ K}^{-1} = 98.38 (\pm 5)$. It would be useful to measure the heat capacity of LaGaO₃ accurately at both low and high temperatures in order to obtain an independent assessment of its entropy.

IV. CONCLUSION

A composition-graded solid electrolyte was used for the determination of the standard Gibbs energy of formation of LaGaO₃ in the temperature range from 910 to 1170 K. The value of y in the composition-graded $(LaF_3)_{v} \cdot (CaF_2)_{1-v}$ polycrystalline solid electrolyte was varied from 0 near the reference electrode, consisting of a mixture of CaO + CaF₂, up to 0.32 at the working electrode. The terminal composition of the graded electrolyte was adjusted such that the activity of LaF_3 in electrolyte was approximately equal to that at the working electrode. The cell essentially measures the activity of La_2O_3 in the two-phase region $LaGaO_3 + Ga_2O_3$ in the binary system La_2O_3 -Ga₂O₃. Under pure oxygen gas, the equilibrium fluoride phase at the working electrode converts the activity of La₂O₃ into an equivalent fluorine chemical potential that can be measured using a cell essentially based on doped CaF_2 .

The values of Gibbs energy of formation obtained in this study are significantly different (approximately 19 kJ mol⁻¹) from those reported earlier by Azad *et al.*⁴ The use of phase-incompatible mixtures, especially at the reference electrode, by Azad *et al.*⁴ is the prime reason for the difference. Their measurements, when correctly interpreted, support the results obtained in this study.

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