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

K. Thomas Jacob[a)]
*Department of Metallurgy and Materials Research Center, Indian Institute of Science,
Bangalore 560 012, India*

Niladri Dasgupta
Ceramic Technology Institute, Bharat Heavy Electricals Limited, Bangalore 560 012, India

Helfried Näfe and Fritz Aldinger
Max-Planck-Institut für Metallforschung, Heisenbergstrasse 5, D-70569 Stuttgart, Germany

A composition-graded solid electrolyte $(LaF_3)_y \cdot (CaF_2)_{1-y}$ was used for the measurement of the standard Gibbs energy of formation of $LaGaO_3$ from its component oxides. An equimolar mixture of CaO and CaF_2 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 LaF_3 into CaF_2. 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 $LaGaO_3$ from its component oxides according to the reaction, $\frac{1}{2}La_2O_3$ (A-rare earth) + $\frac{1}{2}Ga_2O_3$ (β) → $LaGaO_3$ (rhombohedral) can be represented by the equation: $\Delta G^o_{f,(ox)}/J\ mol^{-1} = -46\ 230 + 7.75\ T/K\ (\pm1500)$.

I. INTRODUCTION

Doped $LaGaO_3$ 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 $LaGaO_3$. Thermodynamic data for pure and doped $LaGaO_3$ are useful for evaluating the stability of the electrolyte under reducing conditions and its compatibility with electrode materials. Phase diagram for the system La_2O_3–Ga_2O_3 shows the presence of two congruent melting interoxide compounds; $LaGaO_3$ melting at 1988 (±20) K, and $La_4Ga_2O_9$ melting at 1977 (±20) K.[3]

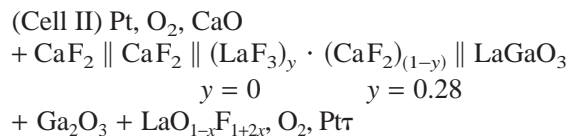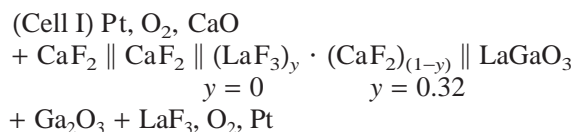Azad *et al.*[4] attempted to measure the standard Gibbs energy of formation of $LaGaO_3$ from its constituent sesquioxides using a cell based on CaF_2 as the solid electrolyte, $La_2O_3 + LaF_3$ as the reference electrode, and $LaF_3 + LaGaO_3 + Ga_2O_3$ as the working electrode. Both electrodes were 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 Navrotsky[8] have measured the enthalpy of formation of $LaGaO_3$ from oxides as −50.86 (±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 $LaO_{1-x}F_{1+2x}$, $0 \leq x \leq 0.33$, is present at high temperature. On cooling the stoichiometric LaOF transforms to a rhombohedral structure ($R\bar{3}m$) at temperatures below 778 (±3) K. The solid solution containing excess fluorine has a tetragonal structure at room temperature.[5,7]

[a)]Address all correspondence to this author.
e-mail: katob@metalrg.iisc.ernet.in

Both oxide and fluoride solid electrolytes can be used to measure the standard Gibbs energy of formation of LaGaO$_3$ at high temperatures. The oxygen chemical potentials established by phase mixtures Ga + La$_2$O$_3$ + La$_4$Ga$_2$O$_9$ and Ga + La$_4$Ga$_2$O$_9$ + LaGaO$_3$ 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 LaGaO$_3$ and Ga$_2$O$_3$. The aim is to measure the activity of La$_2$O$_3$ in the two-phase mixture containing LaGaO$_3$ and Ga$_2$O$_3$.

Presented in this article is the measurement of the Gibbs energy of formation of LaGaO$_3$ from its component oxides using a solid electrolyte based on CaF$_2$. Preliminary experiments indicated that the fluoride phase that coexists with LaGaO$_3$ and Ga$_2$O$_3$ was LaF$_3$ 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$_2$O$_3$ + LaF$_3$ and LaGaO$_3$ + Ga$_2$O$_3$ + LaO$_{1-x}$F$_{1+2x}$ were used in a solid-state cell incorporating single-crystal CaF$_2$ 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 La^{3+} from the electrode into the electrolyte. A composition-graded solid electrolyte (LaF$_3$)$_y$ · (CaF$_2$)$_{(1-y)}$, with axial variation of y, was designed to minimize the effect of La^{3+} 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, O$_2$, CaO
+ CaF$_2$ ‖ CaF$_2$ ‖ (LaF$_3$)$_y$ · (CaF$_2$)$_{(1-y)}$ ‖ LaGaO$_3$
$\qquad\quad y = 0 \qquad\qquad y = 0.32$
+ Ga$_2$O$_3$ + LaF$_3$, O$_2$, Pt

(Cell II) Pt, O$_2$, CaO
+ CaF$_2$ ‖ CaF$_2$ ‖ (LaF$_3$)$_y$ · (CaF$_2$)$_{(1-y)}$ ‖ LaGaO$_3$
$\qquad\quad y = 0 \qquad\qquad y = 0.28$
+ Ga$_2$O$_3$ + LaO$_{1-x}$F$_{1+2x}$, O$_2$, Ptτ

with the right-hand electrodes positive. Single-crystal CaF$_2$ was coupled with a polycrystalline composition-graded solid electrolyte to form a bielectrolyte combination. The single-crystal CaF$_2$, placed adjacent to the CaO + CaF$_2$ reference electrolyte, prevented grain-boundary 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 CaF$_2$, LaF$_3$, CaO, La$_2$O$_3$, and Ga$_2$O$_3$ 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 LaGaO$_3$, stoichiometric amounts of La$_2$O$_3$ and Ga$_2$O$_3$ 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 LaGaO$_3$ was confirmed by powder x-ray diffraction (XRD). At room temperature, LaGaO$_3$ 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 *R*3*c*), 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 solid-state reaction. Fine powder of La$_2$O$_3$ 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 pre-purified inert-gas atmosphere first at 1275 K for 36 ks and subsequently at 1475 K for 18 ks:

$$a \text{ LnF}_3 + b \text{ Ln}_2\text{O}_3 \rightarrow (a + 2b) \text{ LnO}_{1-x}\text{F}_{1+2x} \quad , \text{ (1)}$$
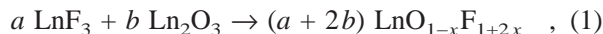
with x = $(a - b)/(a + 2b)$. The high-purity Ar gas (99.999%) used was first dehydrated by passing through anhydrous Mg(ClO$_4$)$_2$ and P$_2$O$_5$, and then deoxidized by passing through Cu turnings at 750 K and Ti granules at 1150 K. Pellets were pulverized after heat treatment. The formation of LaO$_{1-x}$F$_{1-2x}$ 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$_2$O$_3$. 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
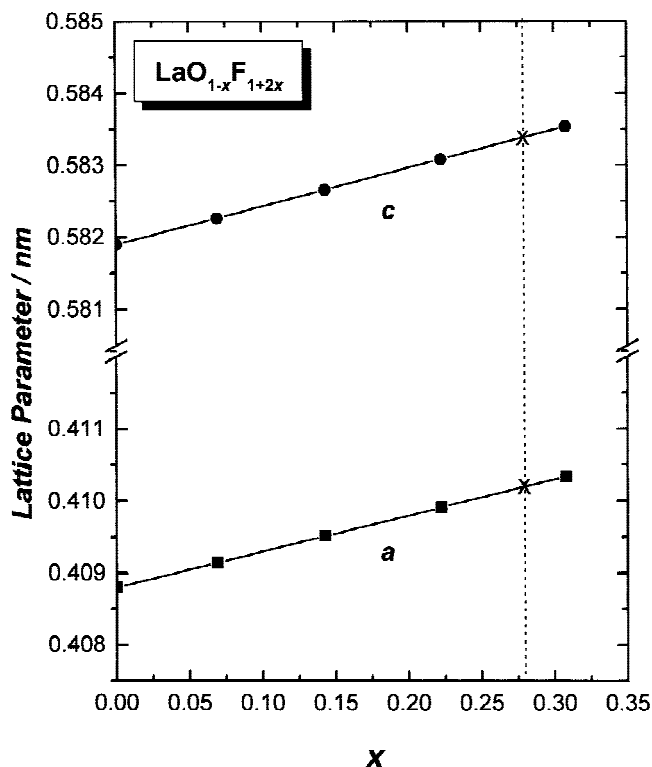
FIG. 1. Lattice parameters of the solid solution $LaO_{1-x}F_{1+2x}$ with tetragonal structure as a function of composition (x) at room temperature. The composition of the oxyfluoride solid solution in equilibrium with $LaGaO_3 + Ga_2O_3$ at 1150 K is shown by the vertical dotted line.

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 CaF_2 containing 5, 10, 15, 20, 25, 28, and 32 mol% LaF_3. Homogeneous solid solutions were first prepared by solid-state diffusion. Intimate mixtures of fine powders ($d < 1$ μm) of CaF_2 and LaF_3 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 mol% 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.
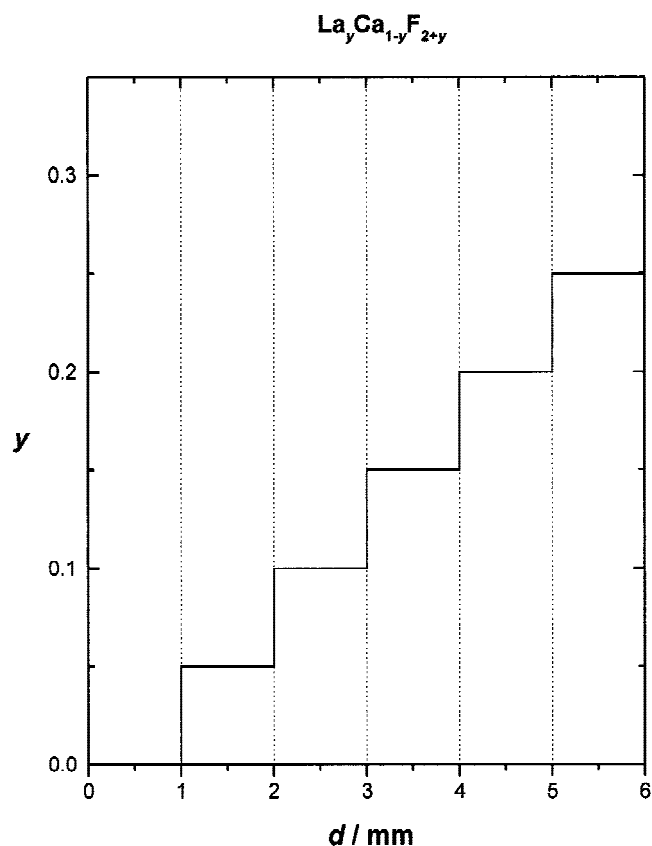
by $x = 0.281$ (or $X_{LaF_3} = 0.685$) at 1150 K. The equilibrium value of x was found to very from 0.313 at 1010 K to 0.280 at 1170 K.

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 $(LaF_3)_y \cdot (CaF_2)_{(1-y)}$ 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-

$La_yCa_{1-y}F_{2+y}$

FIG. 2. Profile of the composition-graded solid electrolyte $(LaF_3)_y \cdot (CaF_2)_{1-y}$. 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 CaF$_2$ under dry oxygen at 1280 K. The two working electrodes were prepared in a similar way using equimolar mixtures of Ga$_2$O$_3$ + LaGaO$_3$ + LaF$_3$ and Ga$_2$O$_3$ + LaGaO$_3$ + 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} Ω) 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
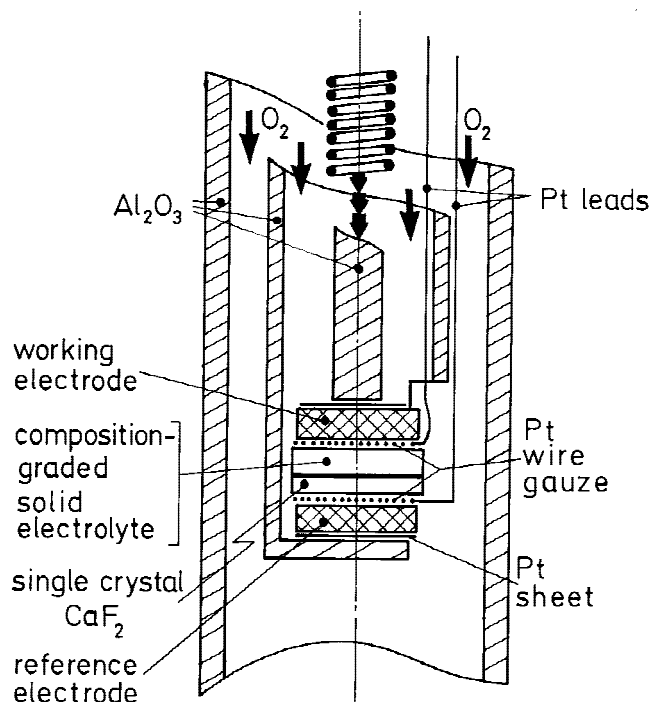
foils between them. The cell assembly was mounted inside a vertical outer alumina tube, the ends of which were closed with water-cooled brass caps. After assembling the cell and fitting the brass caps with O-ring seals to the outer alumina tube, the tube was evacuated and leak tested. The outer alumina tube was then suspended in a vertical resistance furnace such that the electrodes were in the constant temperature zone (± 1 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 CaF$_2$, which produced tiny specks of CaO on the surface of CaF$_2$. Unless water vapor was eliminated, the transparent single CaF$_2$ crystals soon became opaque. The composition-graded 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$_y$Ca$_{1-y}$F$_{2+y}$ occupy interstitial sites as they do in solutions of YF$_3$ in CaF$_2$.[11] The solid solution has higher ionic conductivity than pure CaF$_2$. Because fluoride ions are the mobile species in CaF$_2$ and La$_y$Ca$_{1-y}$F$_{2+y}$, the EMF of a solid-state cell (E) based on these electrolytes is given by

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

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

where μ'_{F_2} and μ''_{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 $F = 96\,485.3$ 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$_y$Ca$_{1-y}$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 ($\pm$0.1) mV. The linear least-squares regression analysis gives the relation

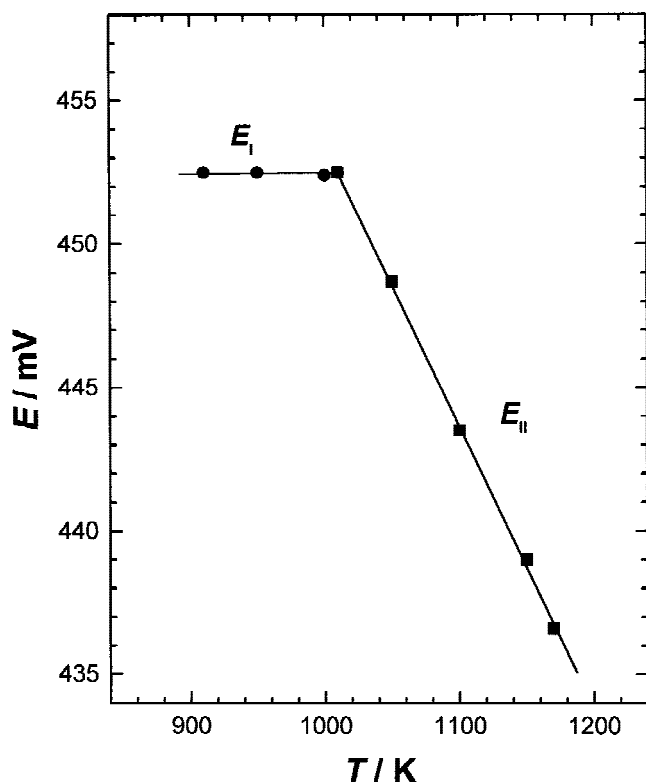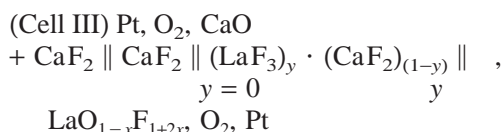$$E_I/\text{mV} = 453.3 - 7.6 \times 10^{-4}\,T/\text{K}\ (\pm0.1)\quad . \quad (3)$$

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

$$E_{II}/\text{mV} = 552.1 - 0.0986\,T/\text{K}\ (\pm0.43)\quad . \quad (4)$$

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)$_{(1-y)}$ ‖ ,
$\quad\quad\quad\quad y = 0 \quad\quad\quad\quad y$
LaO$_{1-x}$F$_{1+2x}$, 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, $(a_{\text{La}_2\text{O}_3}/a^2_{\text{LaF}_3})$, 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_{LaF_3}) at 1150 K. The point of inter-

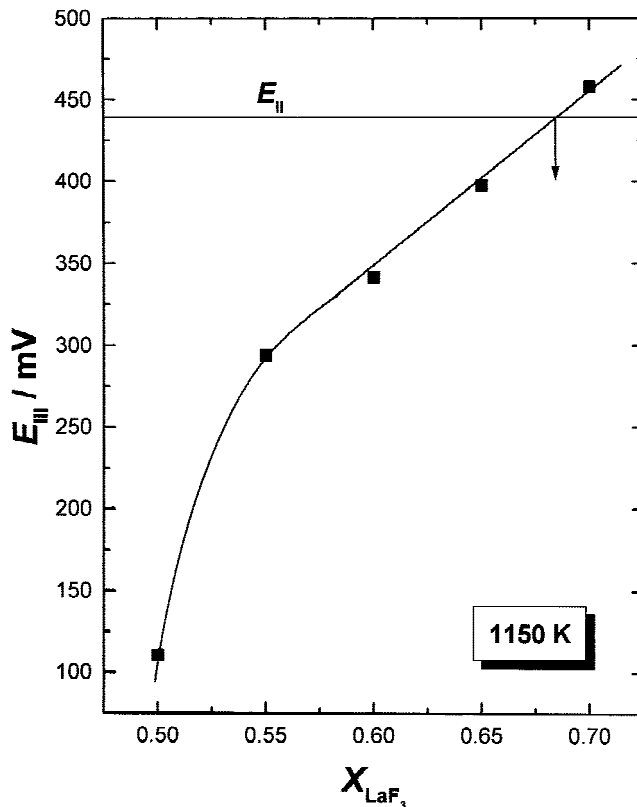FIG. 4. Temperature dependence of the reversible EMF of cells I and II.

FIG. 5. Superimposition of the EMF of cell II on the EMF of cell III as a function of composition (X_{LaF_3}) of the lanthanum oxyfluoride solid solution at 1150 K.

section of the EMFs defines the composition of the oxy-fluoride phase in equilibrium with the phase mixture Ga$_2$O$_3$ + 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.
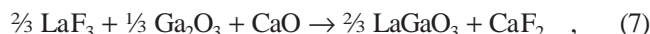
The electrochemical reaction at the working electrode on the right-hand side of cell I can be written as

$$\tfrac{2}{3}\ LaF_3 + \tfrac{1}{3}\ Ga_2O_3 + \tfrac{1}{2}\ O_2 + 2\ e^- \rightarrow \tfrac{2}{3}\ LaGaO_3 + 2\ F^- \quad . \tag{5}$$
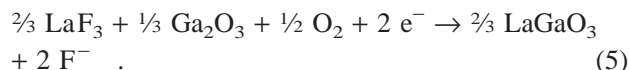
The corresponding reaction at the reference electrode on the left-hand side of cell I can be represented as

$$CaO + 2\ F^- \rightarrow CaF_2 + \tfrac{1}{2}\ O_2 + 2\ e^- \quad . \tag{6}$$
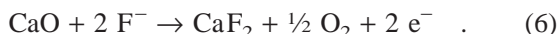
When the oxygen partial pressure is the same over both electrodes, the EMF of cell I is related to the standard Gibbs energy change for the virtual cell reaction

$$\tfrac{2}{3}\ LaF_3 + \tfrac{1}{3}\ Ga_2O_3 + CaO \rightarrow \tfrac{2}{3}\ LaGaO_3 + CaF_2 \quad , \tag{7}$$

$$\begin{aligned} \Delta G^0_{(7)}/J\ mol^{-1} &= -2FE_I/1000 \\ &= -87\ 473 + 0.15\ T/K\ (\pm 20) \quad . \end{aligned} \tag{8}$$

For the reaction

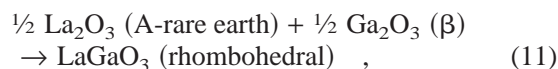$$CaF_2 + \tfrac{1}{3}\ La_2O_3 \rightarrow CaO + \tfrac{2}{3}\ LaF_3 \quad , \tag{9}$$

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

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

By combining Reactions (7) and (9), one obtains the reaction that represents the formation of rhombohedral LaGaO$_3$ from β–Ga$_2$O$_3$ and La$_2$O$_3$ with A-rare-earth oxide structure:

$$\begin{aligned} \tfrac{1}{2}\ La_2O_3\ (A\text{-rare earth}) + \tfrac{1}{2}\ Ga_2O_3\ (\beta) \\ \rightarrow LaGaO_3\ (\text{rhombohedral}) \quad , \end{aligned} \tag{11}$$

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

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 LaGaO$_3$.
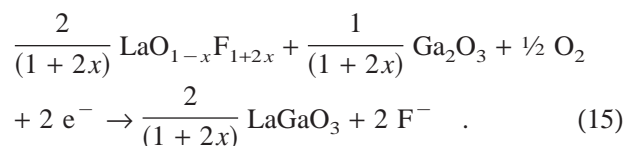
The electrochemical reaction at the working electrode on the right-hand side of cell II can be written as
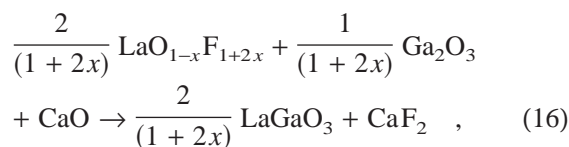
$$\frac{2}{(1 + 2x)}\ LaO_{1-x}F_{1+2x} + \tfrac{1}{2}O_2 + 2\ e^-$$
$$\rightarrow \frac{1}{(1 + 2x)}\ La_2O_3 + 2\ F^- \quad . \tag{13}$$
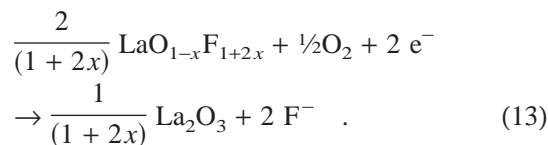
The activity of La$_2$O$_3$ at the electrode is defined by the dissociation of LaGaO$_3$ (two-phase equilibria involving LaGaO$_3$ and Ga$_2$O$_3$):

$$\frac{2}{(1 + 2x)}\ LaGaO_3 \rightarrow \frac{1}{(1 + 2x)}\ Ga_2O_3$$
$$+ \frac{1}{(1 + 2x)}\ La_2O_3 \quad . \tag{14}$$
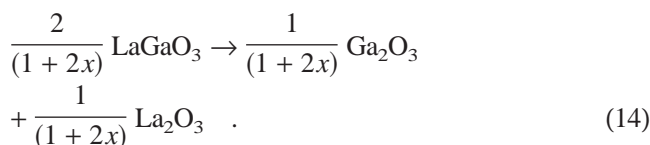
The overall reaction at the working electrode, obtained by combining Eqs. (13) and (14), is

$$\frac{2}{(1 + 2x)}\ LaO_{1-x}F_{1+2x} + \frac{1}{(1 + 2x)}\ Ga_2O_3 + \tfrac{1}{2}\ O_2$$
$$+ 2\ e^- \rightarrow \frac{2}{(1 + 2x)}\ LaGaO_3 + 2\ F^- \quad . \tag{15}$$

Basically, the lanthanum oxyfluoride phase converts the activity of La$_2$O$_3$ established by the phase mixture LaGaO$_3$ + Ga$_2$O$_3$ 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

$$\frac{2}{(1 + 2x)}\ LaO_{1-x}F_{1+2x} + \frac{1}{(1 + 2x)}\ Ga_2O_3$$
$$+ CaO \rightarrow \frac{2}{(1 + 2x)}\ LaGaO_3 + CaF_2 \quad , \tag{16}$$

$$\begin{aligned} \Delta G^0_{(16)}/J\ mol^{-1} &= -2FE_{II}/1000 \\ &= -106\ 540 + 19.03\ T/K\ (\pm 85) \quad . \end{aligned} \tag{17}$$

The Gibbs energy of mixing of LaO$_{1-x}$F$_{1+2x}$ solid solution relative to its component oxide (La$_2$O$_3$) 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 LaGaO$_3$ from Ga$_2$O$_3$ and La$_2$O$_3$, represented by Reaction (11):

$$\Delta G^o_{(11)}/J\ mol^{-1} = -46\ 220 + 7.74\ T/K\ (\pm 1500) \quad , \tag{18}$$

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.

J. Mater. Res., Vol. 15, No. 12, Dec 2000

2841

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 La_2O_3 and LaF_3 with composition in the binary system La_2O_3–LaF_3 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 La_2O_3 corresponding to the phase mixture Ga_2O_3 + LaGaO₃. The value of the Gibbs energy of formation is equal to half the chemical potential of La_2O_3: $\Delta G^{\circ}_{(11)} = \frac{1}{2}\Delta\mu_{La_2O_3}$. 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
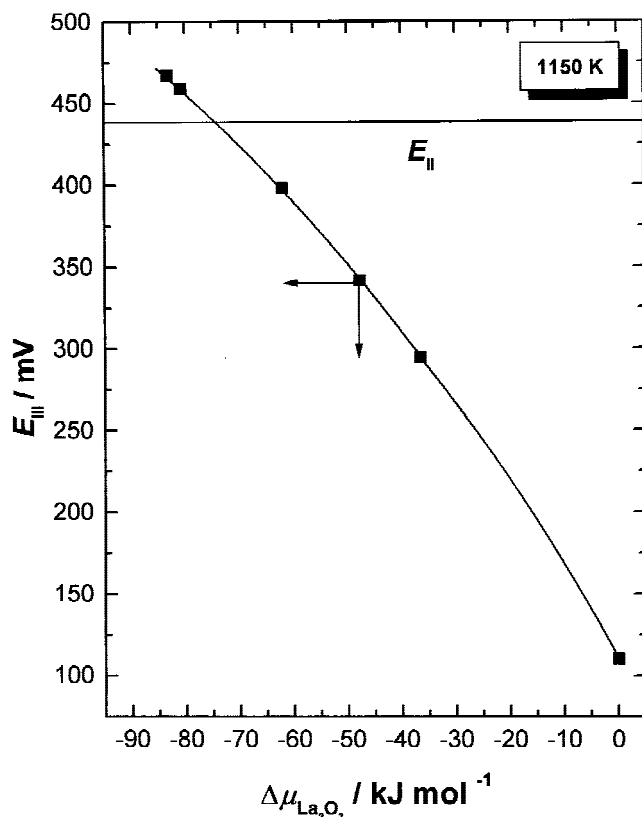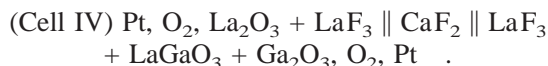
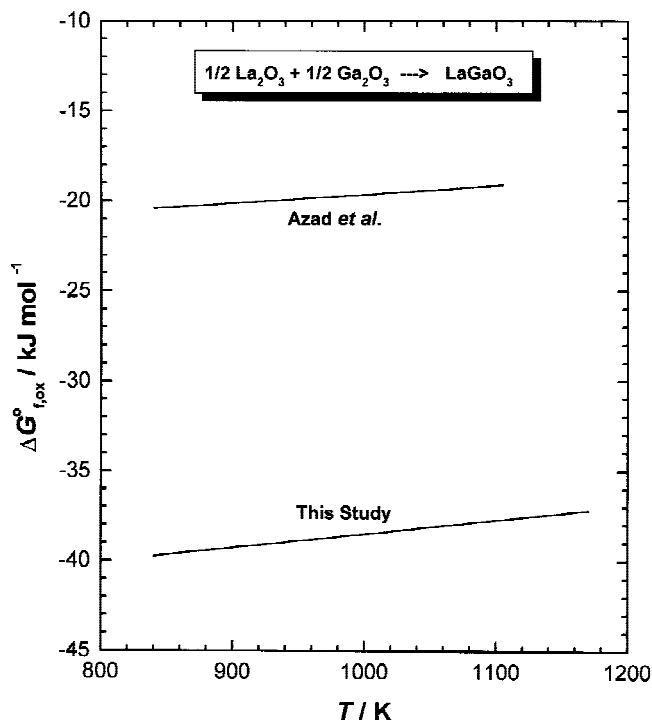(Cell IV) Pt, O₂, La_2O_3 + LaF_3 ‖ CaF_2 ‖ LaF_3 + LaGaO₃ + Ga_2O_3, O₂, Pt .

FIG. 7. Comparison of the Gibbs energy of formation of LaGaO₃ obtained in this study with that reported by Azad *et al.*[4]

FIG. 6. EMF of cell III as a function of the relative chemical potential of La_2O_3 in the lanthanum oxyfluoride solid solution $LaO_{1-x}F_{1+2x}$. The value of $\Delta\mu_{La_2O_3}$ in the phase mixture LaGaO₃ + Ga_2O_3 is defined when $E_{II} = E_{III}$.

Their reference electrode consisted of a mixture of LaF_3 and La_2O_3 in approximately equal mass ratio. At high temperature, this would have resulted in a single-phase oxyfluoride solid solution characterized by $X_{LaF_3} = 0.625$ (or $x = 0.182$). According to the results of this study, LaF_3 is also not stable at their working electrode at $T > 1010$ K; it would have equilibrated with the other phases Ga_2O_3 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 $X_{LaF_3} = 0.625$. 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 La_2O_3 and Ga_2O_3 at a mean temperature of 1040 K; $\Delta H^{\circ}_{f(ox)}$/kJ mol⁻¹ = −46.23 (±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

LaGaO$_3$ from the elements computed from the results of this study using the Neumann–Kopp rule is $\Delta H^{\mathrm{o}}_{\mathrm{f}(298.15)}$/ kJ mol^{-1} = −1488.25 (±5.5). The enthalpies of formation of Ga$_2$O$_3$ and La$_2$O$_3$ 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 LaGaO$_3$ from oxides; $\Delta S^{\mathrm{o}}_{\mathrm{f(ox)}}$/ kJ mol^{-1} K^{-1} = −7.75 (±4.4). Assuming that the heat capacity of LaGaO$_3$ is the sum of the heat capacities of La$_2$O$_3$ and Ga$_2$O$_3$, the standard entropy of LaGaO$_3$ at 298.15 K can be estimated as $S^{\mathrm{o}}_{\mathrm{f}(298.15)}$/J mol^{-1} K^{-1} = 98.38 (±5). It would be useful to measure the heat capacity of LaGaO$_3$ 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 LaGaO$_3$ in the temperature range from 910 to 1170 K. The value of y in the composition-graded (LaF$_3$)$_y$ · (CaF$_2$)$_{1-y}$ polycrystalline solid electrolyte was varied from 0 near the reference electrode, consisting of a mixture of CaO + CaF$_2$, 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$_2$O$_3$ in the two-phase region LaGaO$_3$ + Ga$_2$O$_3$ in the binary system La$_2$O$_3$–Ga$_2$O$_3$. Under pure oxygen gas, the equilibrium fluoride phase at the working electrode converts the activity of La$_2$O$_3$ 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.

REFERENCES

1. T. Ishihara, H. Matsuda, and Y. Takita, J. Am. Chem. Soc. **116,** 3801 (1994).
2. M. Feng and J.B. Goodenough, Eur. J. Solid State Inorg. Chem. **31,** 663 (1994).
3. M. Mizuno, T. Yamada, and T. Ohtake, Yogyo-Kyokai-Shi, **93,** [6] 295 (1985).
4. A.M. Azad, R. Sudha, and O.M. Sreedharan, Mater. Res. Bull. **26,** 97 (1991).
5. W.H. Zachariasen, Acta Crystallogr. **4,** 231 (1951).
6. D.B. Shinn and H.A. Eick, Inorg. Chem. **8,** 232 (1969).
7. K. Niihara and S. Yajima, Bull. Chem. Soc. Jpn. **45,** 20 (1972).
8. Y. Kanke and A. Navrotsky, J. Solid State Chem. **141,** 424 (1998).
9. K.T. Jacob, N. Dasgupta, H. Näfe, and F. Aldinger, J. Am. Ceram. Soc. (in press).
10. K.T. Jacob, N. Dasgupta, and Y. Waseda, J. Am. Ceram. Soc. **81,** 1926 (1998).
11. R.W. Ure Jr., J. Chem. Phys. **26,** 1363 (1957).
12. J. Delect, R.J. Heus, and J.J. Egan, J. Electrochem. Soc. **125,** 755 (1978).
13. K. Ono, T. Fujimura, and J. Moriyama, J. Jpn. Inst. Met. **42,** 469 (1978).
14. S. Mukhopadhyay and K.T. Jacob, J. Electroanal. Chem. **395,** 107 (1995).
15. S. Mukhopadhyay and K.T. Jacob, J. Electrochem. Soc. **140,** 2629 (1993).
16. S. Mukhopadhyay and K.T. Jacob, Metall. Mater. Trans. A **25A,** 173 (1994).
17. S. Mukhopadhyay and K.T. Jacob, in *Proceedings of the Second International Symposium on Ionic and Mixed Conducting Ceramics,* edited by T.A. Ramanarayanan, W.L. Worrell, and H.L. Tuller (Electrochemical Society, Pennington, NJ 1994), pp. 106–126.
18. K.T. Jacob and S. Mukhopadhyay, J. Electrochem. Soc. **142,** 161 (1995).
19. *Thermochemical Properties of Inorganic Substances,* 2nd ed., edited by O. Knacke, O. Kubaschewski, and K. Hesselmann (Springer-Verlag, Berlin, 1991), Vols. I and II.
20. K.T. Jacob and J.H.E. Jeffes, High Temp.-High Press. **4,** 177 (1972).