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Thermodynamic Properties of Lanthanum Aluminate, $LaAlO_3$*

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CaF_2, MgF_2 and BaF_2 have very low electronic conduction, suitable for study of the thermodynamics of double compounds with very low oxygen pressure [1, 2]. Therefore, they have been used as a solid electrolyte for the determination of free energies of formation of compounds in the Ca–Si–O [3], Ca–Nb–O [4], Mg–Al–O [5], Sr–Al–O [6] and Ba–Zr–O [7] systems.

The thermodynamic stability of $LaAlO_3$ is important for metallurgy and material science. The phase diagram of the binary system of La_2O_3–Al_2O_3 has been investigated above 1400 °C [8]: there are two stable compounds, $LaAlO_3$ and $LaAl_{12}O_{18}$. The phase relationship has not been established below this temperature. The thermodynamic properties of the two compounds have not been reported.

The purpose of this work was to study the free energy of formation of $LaAlO_3$ in the temperature range of 1023 to 1223 K using a CaF_2 single crystal as the solid electrolyte. From experiments it has been found that $LaAlO_3$ exists in equilibrium with Al_2O_3, but $LaAl_{12}O_{18}$ does not exist in equilibrium with Al_2O_3 at the experimental temperature. It was also found that La_2O_3 can react with LaF_3 to form LaOF. According to this information, the following galvanic cell was used:

$$\text{Pt, } O_2(g)|La_2O_3, LaOF|CaF_2|LaOF, LaAlO_3, Al_2O_3|O_2(g)\text{Pt}$$

The half-cell reaction on the left-hand side is

$$La_2O_3 + 2F^- = 2LaOF + \tfrac{1}{2}O_2 + 2e \qquad (1)$$

and the reaction on the right-hand side is:

$$Al_2O_3 + \dagger LaOF + \tfrac{1}{2}O_2 + 2e = 2LaAlO_3 + 2F^- \qquad (2)$$

Combining the two half-cell reactions, the virtual cell reaction becomes:

$$La_2O_3(s) + Al_2O_3(s) = 2LaAlO_3(s) \qquad (3)$$

The e.m.f of the galvanic cell is related to the standard free energy of formation of $2LaAlO_3$ from La_2O_3 and Al_2O_3 by

$$\Delta_f G^\circ = -2FE \qquad (4)$$

In the cell reaction all the components are assumed to be in their standard states; with these conditions it is necessary to operate the cell at one atmosphere of pure oxygen [3].

Experimental

Materials

La_2O_3 (99.99%) was sintered for 10 h at 900 °C. Al_2O_3 (99.999%) was sintered for 24 h at 1400 °C. LaF_3 was prepared by digesting La_2O_3 in hydrochloric acid (AnalaR) and then adding hydrofluoric acid (AnalaR); the purified LaF_3 powder was sintered for 24 h at 1000 °C. LaOF was prepared by sintering for 24 h at 1000 °C with equimolar quantities of La_2O_3 and LaF_3 mixture powder.

$LaAlO_3 + Al_2O_3$ two-phase mixture was prepared by sintering a quantity of La_2O_3 and Al_2O_3 with the weight ratio 1:1 at 1400 °C for 30 h.

CaF_2 single crystals (15 × 5 mm) were obtained from the Institute of Optical Research, Academia Sinica. Crystals were clear all.

Electrodes

The mixture of La_2O_3 and LaOF was finely ground and pressed to pellets of 15 × 4 mm (4.8 t/cm^2 power) and sintered for 24 h at 1000 °C. The mixture of LaOF, $LaAlO_3$ and Al_2O_3 (approximate LaOF:Al_2O_3:$LaAlO_3$ = 2:2:1 molar ratio) was ground and pressed as above and sintered at 1000 °C for 30 h.

Apparatus

Cells involving only solids were assembled by pressing together platinum discs with leads and pellets of the electrodes next to the CaF_2 single crystal electrolyte.

To enable the oxygen to pass easily through the interface of the electrode and the CaF_2 crystal electrolyte, a slit was cut in the electrode pellets.

The cell was placed in a quartz tube, which was put in an alumina tube in an electrical furnace with a twin wire wound non-inductively, and Pt–PtRh (10%) thermocouples were used for both temperature measurement and control. The temperature was controlled with an accuracy of ±0.5 °C.

A slow stream of oxygen was continuously passed through a column of KOH to absorb CO_2 and through two columns of silica gel and two columns of phosphorous pentoxide to absorb water vapor. It was then

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divided into two paths, which were maintained at equal flow rates with a microneedle valve and a capillary flowmeter, respectively, and then entered into the quartz tube from each side. The presence of moisture was avoided in order to eliminate the possible side reaction: $CaF_2 + H_2O \rightarrow CaO + 2HF$.

The cell was slowly heated to higher temperatures at the beginning in order to attain the easy equilibrium later.

The e.m.f. was measured with a Keithley 610C solid state electrometer ($10^{14}\ \Omega$) and high-input digital voltmeter as well as precise potentiometer e.m.f. measurements were continued for several days at each constant temperature. The e.m.f. values were steady after 72 h for the first temperature experiment, and less than that for another; e.m.f. values obtained were reproducible to better than ±0.1 mV. The reversibility of the electrode processes was ascertained in each case by momentarily polarizing the electrodes and observing that the original e.m.f. was restored using an X–Y recorder. Steady e.m.f. values could not be obtained below 970 K because of the sluggishness of the reaction, nor above 1220 K because of the vaporization of the electrolyte.

Results

The e.m.f. values of the cell at different temperatures are listed in Table I.

TABLE I. e.m.f. Values of the Cell

T (K)	E (mv)	T (K)	E (mv)
1096.2	73.72 ± 0.05	1219.3	123.93 ± 0.02
1117.0	82.05 ± 0.02	1101.7	80.09 ± 0.03
1137.4	91.24 ± 0.01	1122.1	89.96 ± 0.03
1158.0	99.42 ± 0.03	1140.6	92.55 ± 0.04
1178.4	107.72 ± 0.02	1162.9	99.40 ± 0.03
1198.8	115.84 ± 0.02	1182.8	108.46 ± 0.03
1202.8	117.13 ± 0.03	1222.3	127.28 ± 0.02
1182.4	106.82 ± 0.02	1203.4	118.05 ± 0.03

The e.m.f. values obtained at various temperatures are shown in Fig. 1.

Using a least-squares method, the equation for the variation of e.m.f. with temperature was obtained as

$$E = -353.08 + 0.39T \qquad (5)$$

Using eqn. (4) the $\Delta_f G^\circ$ ($2LaAlO_3$) values obtained at different temperatures are shown in Fig. 2.

Using eqns. (4) and (5) the equation for the variation of $\Delta_f G^\circ$ ($LaAlO_3$) with temperature can be represented as

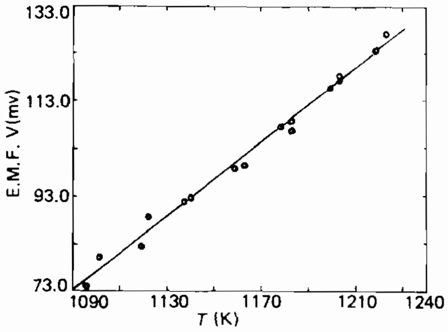

Fig. 1. Dependence of e.m.f. on temperature.

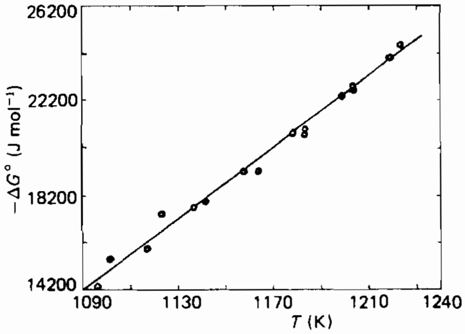

Fig. 2. Dependence of $\Delta_f G^\circ$ ($2LaAlO_3$) on temperature.

$$\Delta_f G^\circ (LaAlO_3) = 34160 - 37.81T \pm 180J \qquad (6)$$

and the correlation coefficient of the linear equation is equal to 0.994.

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