

# A high-temperature solid-state potentiometric sensor for nitrogen based on ceramic $\text{LaAl}_{12}\text{O}_{18}\text{N}$

T. E. WARNER, D. J. FRAY

*Department of Mining and Mineral Engineering, University of Leeds, Leeds LS2 9JT, UK*

A. DAVIES

*Cookson Technology Centre, Sandy Lane, Yarnton, Oxford OX5 1PF, UK*

The nitrogen-sensing properties of  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  are described for the first time. Positive e.m.f. measurements at high temperature across the cells  $\alpha\text{-Nb(N)}$ ,  $\beta\text{-Nb}_2\text{N}$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{LaAl}_{12}\text{O}_{18}\text{N} | \text{LaAl}_{11}\text{O}_{18}$  (or  $\text{LaAl}_{12}\text{O}_{18}\text{N}$ )  $| \text{LaAl}_{12}\text{O}_{18}\text{N}$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\beta\text{-Nb}_2\text{N}$ ,  $\gamma\text{-Nb}_4\text{N}_3$ , were in agreement with  $P_{\text{N}_2}(\beta\text{-Nb}_2\text{N}, \gamma\text{-Nb}_4\text{N}_3) > P_{\text{N}_2}(\alpha\text{-Nb(N)}, \beta\text{-Nb}_2\text{N})$  for the idealized stoichiometric cell reaction  $\gamma\text{-Nb}_4\text{N}_3 + 2\alpha\text{-Nb(N)} \rightarrow 3\beta\text{-Nb}_2\text{N}$ , thus demonstrating the nitrogen-sensing property of these cells. The e.m.f. for a variety of cells with electrodes containing  $\beta\text{-V}_2\text{N}$ ,  $\beta\text{-Nb}_2\text{N}$ ,  $\beta\text{-Ta}_2\text{N}$  and “ $\text{Ti}_2\text{N}$ ”, were consistent with the predicted equilibrium nitrogen partial pressures.

## 1. Introduction

Our attention has been drawn recently to nitrogen-doped materials with either the  $\beta/\beta''$ -alumina or magnetoplumbite type structures (especially those incorporating a higher valence mobile cation), with a view to exploiting their physical properties in nitrogen-sensing devices [1]. In 1988, Wang *et al.* [2] discovered a series of lanthanide aluminium oxide nitride compounds of stoichiometry  $\text{LnAl}_{12}\text{O}_{18}\text{N}$  and showed these to exhibit the magnetoplumbite-type structure. The introduction of a nitrogen atom into the sub-structure of the spinel blocks within the unit cell appears to have a stabilizing effect, resulting in the formation of  $\text{GdAl}_{12}\text{O}_{18}\text{N}$  which, in its undoped form ( $\text{GdAl}_{11}\text{O}_{18}$ ), does not exist [2]. Subsequent work in 1991 by Sun *et al.* [3] on the subsolidus phase relationships in the Ln–Al–O–N systems, revealed that  $\text{LnAl}_{12}\text{O}_{18}\text{N}$  coexists with  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{Al}_3\text{O}_3\text{N}$  at 1973 K (see Fig. 1).

None of the above studies presents results of any electrical measurements. The high-temperature electrical conductivity of  $\text{LaAl}_{11}\text{O}_{18}$  and  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  were investigated and reported by us elsewhere [4]. Here, we report for the first time, the nitrogen-sensing characteristics of  $\text{LaAl}_{12}\text{O}_{18}\text{N}$ , which acts simultaneously as a high-temperature solid electrolyte and a nitrogen-sensing phase.

## 2. Experimental procedure

Ceramic discs and powders of  $\text{LaAl}_{11}\text{O}_{18}$  and  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  were supplied by the Cookson Technology Centre, Oxford. For details of synthesis and phase analysis, the reader is referred to Warner *et al.* [4].

Ceramic discs of  $\text{LaAl}_{11}\text{O}_{18}$  or  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  were used as the  $\text{La}^{3+}$  electrolyte. Composite metal nitride electrodes were prepared by sintering, under an argon atmosphere, an appropriate mass ratio mixture of metal powder, e.g. niobium (Aldrich 99.9%), and metal nitride, e.g. NbN (Goodfellow 99%), with minor amounts of  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  (to enhance the electrolyte contact). E.m.f. measurements were performed with a stacked pellet sequence of electrodes and electrolyte, using a Keithley 614 electrometer with a grounded reference lead.

This stacked electrochemical cell was held within a high-purity alumina rig which was placed upon boron nitride spacers in a graphite tube and held within the working tube of a Lenton 1600 tube furnace with a flowing argon atmosphere. The graphite tube was earthed to shield inductive noise whilst providing a low *in situ* oxygen content (p.p.m., via the carbon/carbon monoxide couple) which is necessary for the stability of  $\text{LaAl}_{12}\text{O}_{18}\text{N}$ .

## 3. Results and discussion

$\text{LaAl}_{12}\text{O}_{18}\text{N}$  was shown by us recently to exhibit ionic ( $\text{La}^{3+}$ ) conductivity [4]. This, in conjunction with being an appropriate quasi binary compound, makes it an excellent candidate (along with other  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  compounds) for a high-temperature nitrogen-sensing electrolyte without the need for an auxiliary nitrogen-sensing phase.

$\text{LaAl}_{12}\text{O}_{18}\text{N}$  can be considered as the quasi binary compound  $\text{LaN} \cdot 6\text{Al}_2\text{O}_3$  within the Al–La–N–O quaternary system. In the specific case in which  $\text{LaAl}_{12}\text{O}_{18}\text{N}$  is accompanied by an excess of  $\alpha\text{-Al}_2\text{O}_3$  and an oxygen partial pressure below that for the

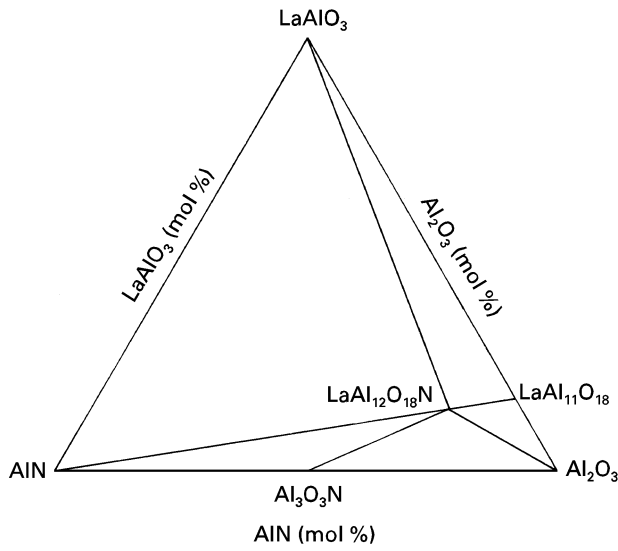
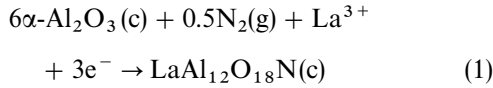


Figure 1 An isothermal section for the AlN–Al<sub>2</sub>O<sub>3</sub>–LaAlO<sub>3</sub> quasi ternary system at 1973 K, adopted from Sun *et al.* [3].

chemical oxidation of LaAl<sub>12</sub>O<sub>18</sub>N, this system can, in theory, sense nitrogen (e.g. dinitrogen gas) through the following electrochemical equilibrium reaction



This relates to the electrochemical cell

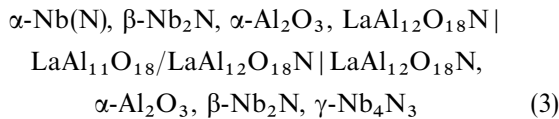
ionic La<sup>3+</sup> transport →

Pt, N<sub>2</sub> | LaAl<sub>12</sub>O<sub>18</sub>N, α-Al<sub>2</sub>O<sub>3</sub> | N<sub>2</sub>, Pt

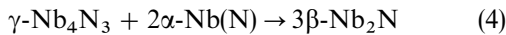
← [N] “virtual” atomic nitrogen transport (2)

such that the cell, when in closed circuit (with  $P'_{\text{N}_2} \neq P_{\text{N}_2}$ ), results in a counter transport of La<sup>3+</sup> ions and “virtual” nitrogen atoms.

To demonstrate this phenomenon, two all-solid-state electrochemical cells (one with LaAl<sub>11</sub>O<sub>18</sub> electrolyte and the other with LaAl<sub>12</sub>O<sub>18</sub>N electrolyte) with niobium nitride electrodes of different but fixed equilibrium partial pressures of dinitrogen gas, were constructed as follows



Adopting the idealized stoichiometries for α-Nb(N), β-Nb<sub>2</sub>N and γ-Nb<sub>4</sub>N<sub>3</sub> leads, as a first approximation, to the cell reaction



Thus, the standard cell e.m.f.,  $E_{\text{cell}}^\circ$ , can be expressed in terms of

$$3FE_{\text{cell}}^\circ = \Delta G_f^\circ(\gamma\text{-Nb}_4\text{N}_3) + 2\Delta G_f^\circ[\alpha\text{-Nb}(\text{N})] - 3\Delta G_f^\circ(3\beta\text{-Nb}_2\text{N}) \quad (5a)$$

or

$$6FE_{\text{cell}}^\circ = RT \ln_e \left[ \frac{P_{\text{N}_2(\text{eqm})}(\beta\text{-Nb}_2\text{N}, \gamma\text{-Nb}_4\text{N}_3)}{P_{\text{N}_2(\text{eqm})}(\alpha\text{-Nb}(\text{N}), \beta\text{-Nb}_2\text{N})} \right] \quad (5b)$$

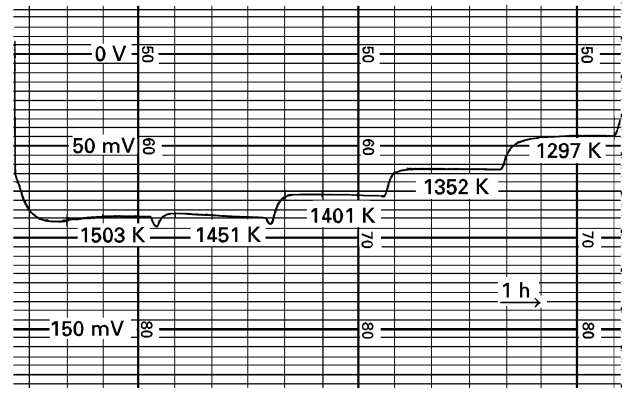


Figure 2 A succession of e.m.f. traces as a function of time for various temperatures as generated by the solid-state nitrogen activity cell under an argon/graphite atmosphere: α-Nb(N), β-Nb<sub>2</sub>N, α-Al<sub>2</sub>O<sub>3</sub>, LaAl<sub>12</sub>O<sub>18</sub>N | LaAl<sub>12</sub>O<sub>18</sub>N | LaAl<sub>12</sub>O<sub>18</sub>N, α-Al<sub>2</sub>O<sub>3</sub>, β-Nb<sub>2</sub>N, γ-Nb<sub>4</sub>N<sub>3</sub>.

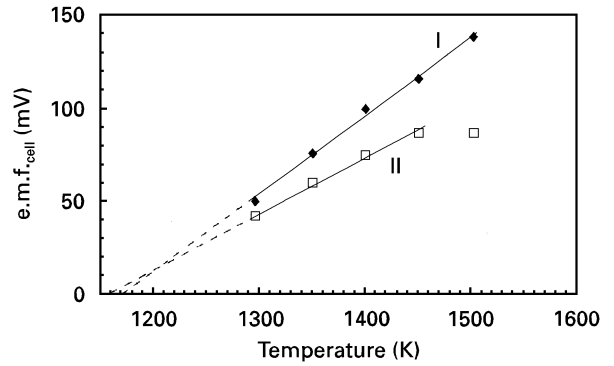


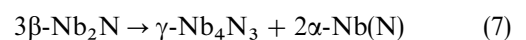
Figure 3 Plots of e.m.f. as a function of temperature for the nitrogen activity cells under an argon/graphite atmosphere: (I) α-Nb(N), β-Nb<sub>2</sub>N, α-Al<sub>2</sub>O<sub>3</sub>, LaAl<sub>12</sub>O<sub>18</sub>N | LaAl<sub>11</sub>O<sub>18</sub> | LaAl<sub>12</sub>O<sub>18</sub>N, α-Al<sub>2</sub>O<sub>3</sub>, β-Nb<sub>2</sub>N, γ-Nb<sub>4</sub>N<sub>3</sub>, and (II) α-Nb(N), β-Nb<sub>2</sub>N, α-Al<sub>2</sub>O<sub>3</sub>, LaAl<sub>12</sub>O<sub>18</sub>N | LaAl<sub>12</sub>O<sub>18</sub>N | LaAl<sub>12</sub>O<sub>18</sub>N, α-Al<sub>2</sub>O<sub>3</sub>, β-Nb<sub>2</sub>N, γ-Nb<sub>4</sub>N<sub>3</sub>.

Because at any relevant temperature

$$\begin{aligned} &P_{\text{N}_2(\text{eqm})}(\beta\text{-Nb}_2\text{N}, \gamma\text{-Nb}_4\text{N}_3) \\ &> P_{\text{N}_2(\text{eqm})}(\alpha\text{-Nb}(\text{N}), \beta\text{-Nb}_2\text{N}) \end{aligned} \quad (6)$$

a positive cell e.m.f. is predicted.

Fig. 2 shows the e.m.f. (*t*) traces from such measurements. The fast response observed upon changing the temperature (and hence the nitrogen activity) is highly encouraging. The electrodes, nevertheless, take a little longer to reach equilibrium, but then stay stable over several hours. Fig. 3 shows equilibrium EMFs as a function of temperature for both cells. Their polarity and order of magnitude are consistent with the above predictions, and therefore suggest that the cell e.m.f. is responding to changes in nitrogen activity. The lower e.m.f.s obtained with cell II may be within the realms of experimental error, or may be attributed to a minor contribution of electronic and/or oxide ion conductivity within the LaAl<sub>12</sub>O<sub>18</sub>N phase. But, interestingly, both cells when extrapolated to zero e.m.f. indicate a eutectoid at  $1165 \pm 5$  K in the Nb–N system, corresponding to the reaction



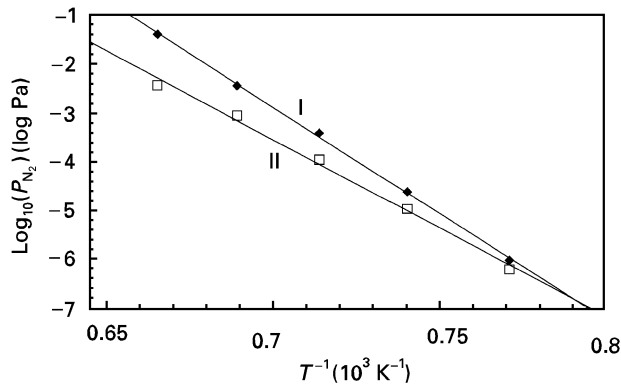
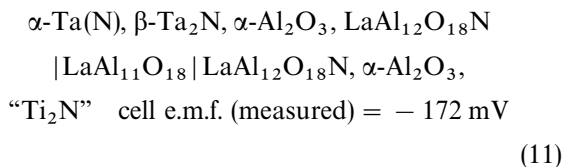
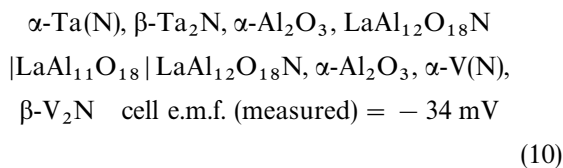
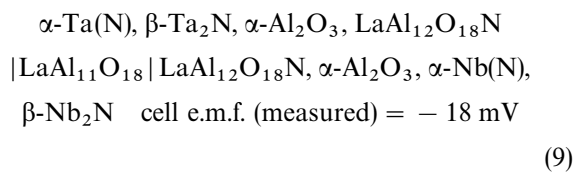
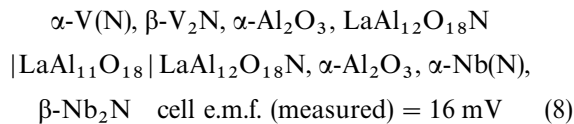


Figure 4 Plots of logarithmic nitrogen partial pressure as a function of inverse temperature for the nitrogen activity cells under an argon/graphite atmosphere: (I)  $\alpha$ -Nb(N),  $\beta$ -Nb<sub>2</sub>N,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, LaAl<sub>12</sub>O<sub>18</sub>N|LaAl<sub>11</sub>O<sub>18</sub>|LaAl<sub>12</sub>O<sub>18</sub>N,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\beta$ -Nb<sub>2</sub>N,  $\gamma$ -Nb<sub>4</sub>N<sub>3</sub>, and (II)  $\alpha$ -Nb(N),  $\beta$ -Nb<sub>2</sub>N,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, LaAl<sub>12</sub>O<sub>18</sub>N|LaAl<sub>12</sub>O<sub>18</sub>N|LaAl<sub>12</sub>O<sub>18</sub>N,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\beta$ -Nb<sub>2</sub>N,  $\gamma$ -Nb<sub>4</sub>N<sub>3</sub>.

A recent phase diagram for the Nb–N system [5] provides only speculative information below approximately 1550 K, such that a comparison of phase relationships cannot be made at present.

An alternative way of displaying the data of Fig. 3 is by adopting the expression for the temperature dependence of the nitrogen partial pressure for the phase Nb<sub>2</sub>N as given by Fromm and Gebhardt [6] ( $\log(P_{N_2}/\text{torr}) = 12.6 - 28400 T^{-1}$ ). This enables the cell e.m.f. data to be transformed to yield the nitrogen partial pressure for the equilibrium assemblage, Nb<sub>4</sub>N<sub>3</sub> + Nb<sub>2</sub>N (see Fig. 4).

In order to investigate the e.m.f. response to different nitrogen partial pressures, the e.m.f. of the following electrochemical cells were measured at  $1451 \pm 5$  K under argon



For phase relationships relating to the composition “Ti<sub>2</sub>N”, the reader is referred to the recent Ti–N phase diagram given by Lengauer [7]. Thermodynamic data given by Fromm and Gebhardt [6] were used to

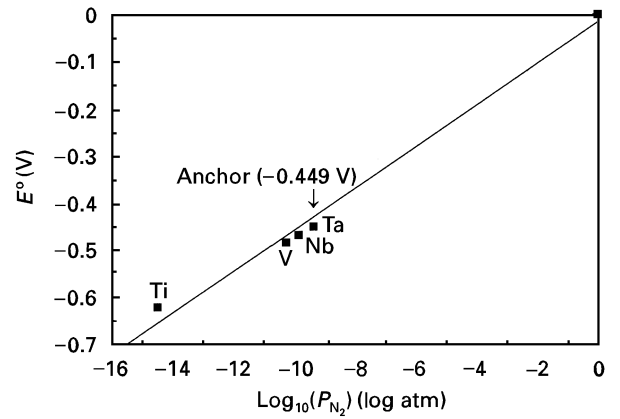


Figure 5 A plot of the standard cell e.m.f. as a function of  $\log_{10}(P_{N_2}/\text{atm})$  for various metal/di-metal nitride assemblages at  $1453 \pm 5$  K, taking  $P_{N_2}$  (Ta<sub>2</sub>N, Ta) as an anchor value with respect to 1 atm nitrogen partial pressure.

calculate the corresponding equilibrium nitrogen partial pressure at 1451 K for each of the various metal/metal nitride assemblages used. The e.m.f. measurements quoted above were then recalculated in terms of the standard reference state for nitrogen ( $P_{N_2}(\text{g}) = 1 \text{ atm}$ ), taking  $\log_{10} P_{N_2(\text{atm})}(\text{Ta}_2\text{N, Ta})_{\text{eqm}} = -9.36$  at 1451 K as an anchor value [6]. These e.m.f.s were plotted as a function of  $\log_{10}(P_{N_2}/\text{atm})$  including the origin, as shown in Fig. 5. The accuracy of this plot is dependent partly upon the reliability of the thermodynamic data given by Fromm *et al.* [6]. Nonetheless, these data are in excellent agreement with Nernstian-type behaviour over at least five decades of nitrogen partial pressure. The number of equivalent moles of electrons associated with the cell reaction is calculated from the gradient of the plot as 6.46, which is in good agreement with the theoretical value of 6 (namely 2 mol N<sup>3-</sup>). Both of these features provide evidence for the nitrogen-sensing ability of this device.

#### 4. Conclusion

Ceramic LaAl<sub>12</sub>O<sub>18</sub>N has been shown to act simultaneously as an electrolyte and a nitrogen-sensing phase at high temperature in a low-oxygen concentration atmosphere. This has been demonstrated over a range of nitrogen partial pressures and temperature. The e.m.f.s for the various electrochemical cells studied are consistent with a predominantly ionic (La<sup>3+</sup>) conduction within LaAl<sub>11</sub>O<sub>18</sub> and LaAl<sub>12</sub>O<sub>18</sub>N. Preliminary potentiometric measurements with niobium nitride electrodes, suggests the existence of a eutectoid at  $1165 \pm 5$  K corresponding to  $3\beta\text{-Nb}_2\text{N} \rightarrow \gamma\text{-Nb}_4\text{N}_3 + 2\alpha\text{-Nb(N)}$ .

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