PII: S0955-2219(99)00123-5

Defect Structures and Nonstoichiometry in Lanthanum Hexa-aluminate

Jae-Gwan Park* and A. N. Cormack

New York State College of Ceramics at Alfred University, Alfred, NY 14802, USA

Abstract

A number of defect structures and non-stoichiometries possible in lanthanum hexa-aluminate (LHA) have been investigated, by using computer-based atomistic simulation techniques. It has been possible to discriminate energetically between alternative models. Our calculations suggest that LHA will not form an ideal β-alumina-type stoichiometric phase $LaAl_{11}O_{18}$, but most likely a magnetoplumbite (MP)-type nonstoichiometric phase $La_{0.83}Al_{11.83}O_{19}$, which is essentially identical to the "vacancy model" phase proposed by Iyi et al. (J. Solid State Chem., 1984, 54, 70, 123). Our calculations also reveal that the defect complex in this phase is composed of a vacancy pair (V_{La} and V_{Al}) on the mirror plane, and a pair of Al Frenkel-like defects formed doubly (rather than singly) above and below the center of the vacancy pair. It is suggested that a nonstoichiometric phase $LaAl_{11.67}O_{19}$, which has also an MP-type structure with aluminum vacancies, may coexist with the most likely phase, especially when the Al/La ratio of the system is about 13 to 14. It is revealed that, in this nonstoichiometric phase, the aluminum vacancies prefer the central spinel block 2a sites to other sites. It is also quite possible to form solid solutions between these two MP-type LHA phases. Our calculation results indicate that the 'O_{La}' defect may be improbable in LHA system. It is also revealed that there is a great possibility of existence of metastable phases; it is seen, however, that β-type or β/MP-mixed-type structured phases are less stable than MP-type phases. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: defect structures, $LaAl_{11}O_{18}$, non-stoichiometry, simulation.

*To whom correspondence should be addressed at permanent address: Materials Science and Technology Division, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 130-650, Korea.

## 1 Introduction

Lanthanum hexa-aluminate (LHA), with an ideal stoichiometry $LaAl_{11}O_{18}$, belongs to a family of materials with diverse technological applications; hexa-aluminates containing alkali, alkaline earth, and lanthanide elements have been widely investigated in particular as superionic conductors,[1] luminescent and laser materials,[2] high-temperature combustion catalysts[3] and radioactive waste disposal hosts.[4] LHA, in particular, is used as a coating for alumina fibres in ceramic matrix composites.[5,6] One of the principal reasons for this usefulness lies in their crystal structures, which are layer structures based on the magnetoplumbite or beta-alumina structures.

In addition to its importance as an engineering material, LHA is of intrinsic scientific interest because of its inherent defect structure. This arises because its molecular stoichiometry, $LaAl_{11}O_{18}$, is incompatible with the stoichiometries of either of its putative parent structures, $MAl_{11}O_{17}$ (β-alumina) or $MAl_{12}O_{19}$ (magnetoplumbite). The structures of both of these compounds consist of spinel-like blocks separated by mirror planes containing the large cations. The unit cell structures of the β-alumina (β) and hexa-aluminate magnetoplumbite (MP) are shown in Fig. 1. The major difference between the two structures lies in the composition and site occupancy in these mirror planes, which are close-packed in MP but not in β. Although MPs and βs are structurally very similar (both have the same space group $P6_3/mmc$), it is the differences between them that dominate and lead to their rather different properties. The phase equilibria and crystal chemistry of these complex-structured hexa-aluminates show a considerable variation as a function of composition.

A further complicating factor in the case of LHA is its reported non-stoichiometry. In the binary system La_2O_3-Al_2O_3, the 'β-type compound' (ideal composition $LaAl_{11}O_{18}$) was first identified by Roth and Hasko.[7] Most of the subsequent
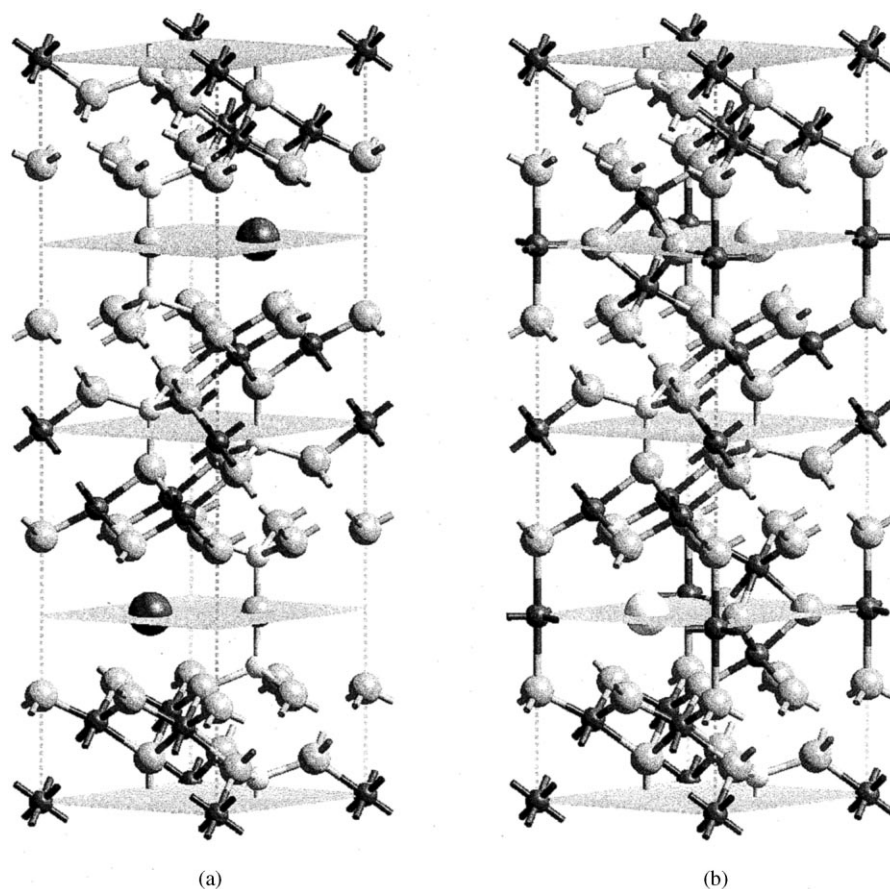
Fig. 1. Unit cells of the two parent structures of hexaaluminates, (a) Na β-alumina and (b) M^{2+} aluminate magnetoplumbite (Na = large black spheres; M^{2+} = large white spheres; O = medium size grey spheres; Al[6] = small black spheres; Al[4] = small white spheres; Al[5] = small black spheres in the mirror planes in (b); (004) Miller plane family is shown).

studies[8–14] on the phase diagram of this lanthanum hexa-aluminate (LHA) system, reported the ideal stoichiometric phase (Al/La = 11) or phases in a stoichiometric range of Al/La ratio from 11 to 12. Brisi et al.[14] proposed a nonstoichiometry of $La_{1-x}Al_{11+2/3+x-y}O_{19-3y/2}$. Stevels and Verstegen[15] first considered LHA to have a distorted MP-type structure with a stoichiometry of $La_{1-x}Al_{11+2/3+x}O_{19}$, based on X-ray diffraction data. Later, mainly based on the luminescence data, Stevels[16–18] proposed an MP-type structure model with a non-stoichiometry of $La_{1-x}Al_{11+2/3+5x/3}O_{19+x}$, in which part of the lanthanum sites are occupied by oxygen ions: the O_{La} defect. On the other hand, based on powder diffraction and fluorescence data, Dexpert-Ghys et al.[19,20] considered this compound to be composed of both β-type and MP-type structural units, the ratio of which depended on the composition, ranging in Al/La ratio of 11 to 14·2: The structure was thought to be β-type for the lower alumina contents, gradually changing to an MP-type for higher alumina contents. However, Iyi et al.[21] further confirmed that the structure of LHA corresponded to an MP structure (no possibility for β-like structural units in their specimen was ascertained), using single crystal diffraction data. In order to explain its nonstoichiometry, they proposed

two types of defect models, a 'vacancy model' and an 'interstitial oxygen model'. The latter, characterized by the O_{La} defect, is conceptually identical with the model proposed by Stevels.[16–18] Iyi et al.[21] adopted the vacancy model giving rise to a stoichiometry of $La_{0.833}Al_{11.833}O_{19}$, based on the results of structural refinement and chemical analysis. It has been reported that neodymium[22] and praseodymium[23] also form hexa-aluminates isostructural to this LHA phase. Gasperin et al.[24] reported that LHA adopts an MP structure with the refined stoichiometry of $La_{0.85}Al_{11.55}O_{18.6}$.

In this paper, as part of our work on the defect solid state chemistry of hexa-aluminates, we aim to elucidate further the defect structures and non-stoichiometry in LHA, by using computer-based atomistic simulation techniques, and show how these theoretical techniques may be used to obtain information about them.

The atomistic lattice simulation techniques in this work are based on the Born model of the solid as we have used and described previously.[25] In brief, the ionic solid is treated as a collection of point ions with short-range forces acting between them. The lattice interactions, as defined through interatomic pair potentials, are calculated explicitly and ions are relaxed to zero force using a second

derivative Newton–Raphson minimization procedure. The electronic polarization effects of the lattice are taken into account by means of the Dick–Overhauser shell model.[26] The potential model parameters used in this study are taken from the compilation of Lewis and Catlow[27] and the works of Butler *et al.*[28] and Catlow,[29] and are listed in Table 1. For details of the techniques, see Ref. 30.

2 Results

2.1 Structural models

It will be readily appreciated that a wide variety of possible defect structures may be accommodated in this ternary material, leading to a range of nonstoichiometries; for example Al-excess, La-poor, O-excess, etc. The defect structures may be classified in a number of ways. We have chosen the following: Firstly, we distinguish between β-type, MP-type and mixed β-MP-type structures according to the mirror plane structures. Then we consider defects on the various sublattice, i.e. defects on Al, La, and O sites, as well as interstitial defects. Details of the defect structural models and their simulation results are available elsewhere.[30]

The β-alumina structure used in this study, as a reference point for the input models, is an idealized modification of the structure of sodium β-alumina, which was reported by Peters *et al.*[31] The large cation and the oxygen in the mirror plane are assumed to be only at the 2d Beevers–Ross (BR) site and at the 2c site, respectively.[31] The composition of the mirror plane in this structure, referred to as the β-type, is $[LaO]^+$; note that it is charged, requiring compensating species elsewhere in the structure. The reference structural model for the MP structure is the structure of strontium aluminate magnetoplumbite ($SrAl_{12}O_{19}$), reported by Lindop *et al.*[32] The nomenclature of the crystallographic atomic sites [such as Al(2)] in the models is after that of Lindop *et al.*[32] The composition of

the MP-type mirror plane is $[LaAlO_3]^\times$. A number of supercells, such as a $\sqrt{3}\mathbf{a} \times \sqrt{3}\mathbf{a} \times \mathbf{c}$ triple cell, a $2\mathbf{a} \times 2\mathbf{a} \times \mathbf{c}$ quadruple cell, and a $3\mathbf{a} \times 2\mathbf{a} \times \mathbf{c}$ hexacell, were employed to simulate the different nonstoichiometries with various defect structural models, but in a perfect lattice structure.

For stoichiometric LHA, $LaAl_{11}O_{18}$, we found that the mixed β/MP-type phase would be most likely. The energetically most favored structure of this phase had ideal β-type and MP-type mirror planes alternating in the $\mathbf{c}$ direction, with aluminum vacancies (one per the basic cell) at the central spinel block Al(1) 2a sites to provide the electroneutrality. However, as discussed later, these structures are less stable than the non-stoichiometric ones, which are indicated with the prefix 'ns-', both in Table 2 and later in the text.

For nonstoichiometric LHA, our calculations (summarised in Table 2) predicted that β-type and mixed β/MP-type structures would be thermodynamically unstable with respect to MP-type phases. The lanthanum vacancy model, ns-MP-V_{La}, has the ideal MP structure except for V_{La} at every third 2d site. It was found that the V_{La} defect prefers not to be associated with any V_{Al}-Al_i Frenkel-like relaxation perpendicular to the mirror plane. The aluminum vacancy model, ns-MP-V_{Al}, has the ideal MP structure except for aluminum vacancies, two per the triple supercell. The lowest energy aluminum vacancy is found to be at the Al(1) 2a site in the middle of the spinel block.

In the lanthanum–aluminum vacancy model phase, ns-MP-$V_{La}V_{Al}$, whose stoichiometry corresponds to that proposed by Iyi *et al.*[21] as the 'vacancy model', a lanthanum vacancy (at 2d site) is coupled with an aluminum vacancy at its adjacent 2b mirror plane site. Our results showed that this coupled mirror plane vacancy pair, V_{La} and V_{Al}, is stabilized by two (not a single) pairs of aluminum Frenkel-like defects (V_{Al} and Al_i). The pairs are formed by relaxation of the Al ions from the spinel block 12k sites just above and below the

Table 1. Interatomic potential parameters used in this study

a. Short-range parameters for potential form $V(r) = A\exp(-r/\rho) - Cr^{-6}$

Interaction	A(eV)	$\rho(A)$	C(eVA)
La–O	1644·98	0·36196	0·000
Al–O	1474·40 [1334·31][a]	0·30059	0·000
O–O	22764·20	0·14910	17·890

b. Shell parameters

Interaction	Shell charge	Spring constant
La (core)–La (shell)	3·000	99 999·99
Al (core)–Al (shell)	3·000	99 999·99
O (core)–O (shell)	−2·207	27·29

[a]Value A in this bracket is appropriate for Al ions in a tetrahedral site.

Table 2. Equilibrated lattice energies of the model LHA phases and related oxides

Model	Chemical formula		Lattice energy[a]	
	Supercell	Basic cell	Supercell	Basic cell
LHA-β-MP	$La_8Al_{88}O_{144}$	$La_2Al_{22}O_{36}$	−7486·21	−1871·55
ns-MP-V_{La}[b]	$La_4Al_{72}O_{114}$	$La_{1.33}Al_{24}O_{38}$	−5966·68	−1988·89
ns-MP-V_{Al}	$La_6Al_{70}O_{114}$	$La_2Al_{23.33}O_{38}$	−5934·19	−1978·06
ns-MP-$V_{La}V_{Al}$	$La_{10}Al_{142}O_{228}$	$La_{1.67}Al_{23.67}O_{38}$	−11903·68	−1983·95
ns-MP-$O_{La}V_{Al}$	$La_7Al_{95}O_{153}$	$La_{1.75}Al_{23.75}O_{38.25}$	−7980·10	−1995·03
ns-β-MP-I	$La_6Al_{94}O_{150}$	$La_{1.5}Al_{23.5}O_{37.5}$	−7836·17	−1959·04
ns-β-MP-II	$La_5Al_{69}O_{111}$	$La_{1.67}Al_{23}O_{37}$	−5790·25	−1930·08
ns-β-MP-III	$La_5Al_{67}O_{108}$	$La_{1.67}Al_{22.33}O_{36}$	−5628·83	−1876·28
ns-β-MP-IV	$La_6Al_{90}O_{144}$	$La_{1.5}Al_{22.5}O_{36}$	−7516·99	−1879·25
ns-β-MP-V	$La_7Al_{91}O_{147}$	$La_{1.75}Al_{22.75}O_{36.75}$	−7653·98	−1913·50
ns-β-MP-VI	$La_6Al_{88}O_{141}$	$La_{1.5}Al_{22}O_{35.25}$	−7359·19	−1839·80
Aluminum oxide		Al_2O_3		−158·78
Lanthanum oxide		La_2O_3		−124·14
Lanthanum monoaluminate		$LaAlO_3$		−141·87

[a]Energies in eV per formula unit.
[b]The prefix ns- refers to non-stoichiometric compounds.

center of the vacancy pair to mirror plane region. The defect complex V_{La}–V_{Al}–2(V_{Al}–Al_i), combining the mirror plane vacancy pair with the stabilizing pairs of the Al Frenkel-like defects, is favored energetically over the complex with a single Al Frenkel-like pair. Iyi et al.[21] considered the former as type 2 and opted for this, without much conclusive evidence, over the latter considered as type 1. It is also revealed that the defect complex (one per the triple supercell) prefers to occur, randomly, in the two mirror plane regions rather than to be crowded in one region, keeping the other a perfect MP-type structure.

We have also examined defect structure containing O_{La} species since these were suggested earlier by Stevels.[16–18] This is an unusual defect since oxygen and lanthanum are oppositely charged species. We previously found O_{La} by itself to be unstable with respect to separate V_{La} and O_i defects in lanthanum magnesium hexa-aluminate.[33] In the present ns-MP-$O_{La}V_{Al}$ phase, the stoichiometry and defect mechanism of which correspond also to those designated by Iyi et al.[21] as the 'interstitial oxygen model', we found that a lower energy configuration occurred when the oxygen was displaced from the La site into an interstitial site. That is, the 2d position is an unstable one for the oxygen ion. Further calculations again showed that an even lower energy results when the oxygen is placed at the center of the spinel block (in an interstitial position). In this case, the mirror planes contain the defect complex V_{La}–V_{Al}–2(V_{Al}–Al_i) (one per the quadruple supercell) described above.

2.2 Relative stability of LHA phases
In the previous section, the most likely structures to be adopted by either the stoichiometric or non-stoichiometric phases were identified. In this section, we report on their relative stability. Thus the question addressed is whether LHA should be stoichiometric or non-stoichiometric. Considering their formation energies, obtained from the calculated lattice energies, answers this question.

The equilibrated lattice energies (each of which is the lowest in a particular compositional model) for the various models described previously are given in Table 2, together with those of related oxides, $LaAlO_3$, La_2O_3, and Al_2O_3. (The input structure of lanthanum mono-aluminate was that reported by Derighetti et al.[34] having the space group $R\bar{3}c$.)

Table 3 shows the formation reaction enthalpies for the diverse compositional model phases of LHA and remnant lanthanum mono-aluminate, $LaAlO_3$, obtained from the calculated lattice energies. The reactants are the binary oxide mixture (La_2O_3 and $11Al_2O_3$), whose composition constitutes the ideal stoichiometric LHA phase (Al/La = 11). The calculated enthalpies show that all the MP-type nonstoichiometric phases are energetically more favored than the (lowest energy) stoichiometric phase (LHA-β/MP) as well as all of the β/MP-mixed-type nonstoichiometric phases. Furthermore, it is also found that the model phase ns-MP-$V_{La}V_{Al}$ is most likely to be formed, even when the starting material has the composition of the ideal phase. The second-most favorable phase seems to be the ns-MP-V_{Al}.

Having seen that LHA prefers to adopt MP-type structures rather than possess β-type or mixed-β/MP type structures, the next question to be faced is whether these are stable against decomposition to other phases with different stoichiometries.

The relative thermodynamic stability between the LHA phases (especially, relative to the two most likely phases, ns-MP-$V_{La}V_{Al}$ and ns-MP-V_{Al}) can

be more clearly revealed, when we compare their decomposition reaction enthalpy.

The enthalpies of decomposition of the LHA phases, to a mixture of the ns-MP-V_{Al} phase and a compensating oxide, or to a mixture of the ns-MP-$V_{La}V_{Al}$ phase and a compensating oxide (or to a mixture of the two phases, ns-MP-$V_{La}V_{Al}$ and ns-MP-V_{Al}) are listed in Table 4. The decomposition enthalpy is the same as the difference between the enthalpies of the two reactions forming the decomposing phase and the decomposed phases, respectively, from a binary oxide mixture constituting the decomposing phase. We can see in the table that only the ns-MP-$V_{La}V_{Al}$ phase is thermodynamically stable against decomposition and that all the other phases have a thermodynamic tendency to decompose to a mixture of the (most stable) ns-MP-V_{La}-V_{Al} phase and a compensating oxide.

3 Discussion

The results reported in the previous section show that LHA would be non-stoichiometric; that is to say that its composition will depart from the ideal $LaAl_{11}O_{18}$. We can ascribe this to the incompatibility of the ideal stoichiometry and that of the ideal MP structure ($MAl_{12}O_{19}$). It is clearly more beneficial to conform to the crystallographic structure than to maintain molecular stoichiometry. This means

Table 3. Reaction enthalpies for formation of the model LHA phases and compensating $LaAlO_3$ from a binary oxide mixture constituting the ideal phase, calculated with the simulated lattice energies

Reactants	Products	Reaction enthalpy (eV)	LHA phase formed (Al/La)
$La_2O_3 + 11Al_2O_3$	$La_2Al_{22}O_{36}$	$\Delta E = -0.83$	LHA-β-MP (11)
$La_2O_3 + 11Al_2O_3$	$(20La_4Al_{70}O_{114} + 56LaAlO_3)/68$	$\Delta E = -1.02$	ns-MP-V_{La} (18)
$La_2O_3 + 11Al_2O_3$	$(20La_6Al_{70}O_{114} + 8LaAlO_3)/64$	$\Delta E = -1.45$	ns-MP-V_{Al} (11.67)
$La_2O_3 + 11Al_2O_3$	$(10La_{10}Al_{142}O_{228} + 32LaAlO_3)/66$	$\Delta E = -1.65$	ns-MP-$V_{La}V_{Al}$ (14.20)
$La_2O_3 + 11Al_2O_3$	$(20La_7Al_{95}O_{153} + 36LaAlO_3)/88$	$\Delta E = -0.99$	ns-MP-$O_{La}V_{Al}$ (13.57)
$La_2O_3 + 11Al_2O_3$	$(20La_6Al_{94}O_{150} + 56LaAlO_3)/88$	$\Delta E = -0.51$	ns-β-MP-I (15.67)
$La_2O_3 + 11Al_2O_3$	$(20La_5Al_{69}O_{111} + 28LaAlO_3)/64$	$\Delta E = -0.80$	ns-β-MP-II (13.80)
$La_2O_3 + 11Al_2O_3$	$(20La_5Al_{67}O_{108} + 24LaAlo_3)/62$	$\Delta E = +0.05$	ns-β-MP-III (13.40)
$La_2O_3 + 11Al_2O_3$	$(20La_6Al_{90}O_{144} + 48LaAlO_3)/84$	$\Delta E = -0.11$	ns-β-MP-IV (15)
$La_2O_3 + 11Al_2O_3$	$(20La_7Al_{91}O_{147} + 28LaAlO_3)/84$	$\Delta E = +1.05$	ns-β-MP-V (13)
$La_2O_3 + 11Al_2O_3$	$(20La_6Al_{88}O_{141} + 44LaAlO_3)/82$	$\Delta E = -0.33$	ns-β-MP-VI (14.67)

Table 4. Reaction enthalpies of decomposition of the LHA phase (per basic cell) to a mixture of the phase ns-MP-V_{Al} or ns-MP-$V_{La}V_{Al}$ and a compensating oxide, or to a mixture of the two phases[a]

Reaction of decomposition	Reaction enthalpy (eV)
LHA-β-MP $\rightarrow (5/16)V_{al} + (1/8)LA$	$\Delta E = -0.62$
LHA-β-MP $\rightarrow (10/33)V_{La}V_{Al} + (16/33)LA$	$\Delta E = -0.82$
$(1/3)$ns-MP-$V_{La} \rightarrow (2/9)V_{Al} + (38/9)A$	$\Delta E = -0.51$
$(1/3)$ns-MP-$V_{La} \rightarrow (4/15)V_{La}V_{Al} + (38/15)A$	$\Delta E = -0.22$
$(1/3)V_{Al} \rightarrow (32/99)V_{La}V_{Al} + (38/99)LA$	$\Delta E = -0.22$
$(1/3)V_{La}V_{Al} \rightarrow (5/18)V_{Al} + (19/9)A$	$\Delta E = +0.36$
$(1/4)$ns-MP-$O_{La}V_{Al} \rightarrow (7/24)V_{Al} + (5/3)A$	$\Delta E = -0.41$
$(1/4)$ns-MP-$O_{La}V_{Al} \rightarrow (1/3)V_{La}V_{Al} + (1/12)LA$	$\Delta E = -0.74$
$(1/4)$ns-MP-$O_{La}V_{Al} \rightarrow (11/152)V_{Al} + (5/19)V_{La}V_{La}$	$\Delta E = -0.69$
$(1/4)$ns-β-MP-I $\rightarrow (1/4)V_{Al} + 3A$	$\Delta E = -0.85$
$(1/4)$ns-β-MP-I $\rightarrow (3/10)V_{La}V_{Al} + (11/10)A$	$\Delta E = -1.17$
$(1/3)$ns-β-MP-II $\rightarrow (5/18)V_{Al} + (16/9)A$	$\Delta E = -0.58$
$(1/3)$ns-β-MP-II $\rightarrow (32/99)V_{La}V_{Al} + (5/99)LA$	$\Delta E = -0.91$
$(1/3)$ns-β-MP-II $\rightarrow (5/114)V_{Al} + (16/57)V_{La}V_{Al}$	$\Delta E = -0.88$
$(1/3)$ns-β-MP-III $\rightarrow (5/18)V_{Al} + (13/9)A$	$\Delta E = -1.46$
$(1/3)$ns-β-MP-III $\rightarrow (31/99)V_{La}V_{Al} + (10/99)LA$	$\Delta E = -1.76$
$(1/3)$ns-β-MP-III $\rightarrow (5/57)V_{Al} + (13/57)V_{La}V_{Al}$	$\Delta E = -1.70$
$(1/4)$ns-β-MP-IV $\rightarrow (1/4)V_{Al} + (5/2)A$	$\Delta E = -1.25$
$(1/4)$ns-β-MP-IV $\rightarrow (3/10)V_{La}V_{Al} + (3/5)A$	$\Delta E = -1.57$
$(1/4)$ns-β-MP-V $\rightarrow (7/24)V_{Al} + (7/6)A$	$\Delta E = -2.55$
$(1/4)$ns-β-MP-V $\rightarrow (7/22)V_{La}V_{Al} + (7/44)LA$	$\Delta E = -2.84$
$(1/4)$ns-β-MP-V $\rightarrow (21/152)V_{Al} + (7/38)V_{La}V_{Al}$	$\Delta E = -2.75$
$(1/4)$ns-β-MP-VI $\rightarrow (1/4)V_{Al} + (9/4)A$	$\Delta E = -1.01$
$(1/4)$ns-β-MP-VI $\rightarrow (3/10)V_{La}V_{Al} + (7/20)A$	$\Delta E = -1.33$

[a]$V_{Al} = La_6Al_{70}O_{114}$: ns-MP-$V_{Al}$; $V_{La}V_{Al} = La_5Al_{71}O_{114}$: ns-MP-$V_{La}V_{Al}$; $A = Al_2O_3$; $LA = LaAlO_3$.

increasing the oxygen content so that there are no oxygen vacancies or interstitials in the close-packed MP oxygen sublattice.

Consequently, there must be additional cations introduced into the structure to maintain electroneutrality. Our results indicate that these will be predominantly Al cations, so that one particular non-stoichiometric composition, with Al/La ratio 14.2 will be formed no matter what the initial overall composition of the reactants. Thus, even if one starts with a stoichiometric mixture (Al/La = 11), the LHA phase dominating the products will have a ratio of Al to La of 14.2, along with some other phases to conserve the initial composition of the reactants. It should be noted that the number 14.2 for the Al/La ratio is not completely arbitrary. It arises because of the need to introduce cation vacancies into the structure to retain overall electro-neutrality with respect to the MP structure and the oxygen content. There must be two cation vacancies per six MP formula units. Our results indicate that these will be the V_{La}-V_{Al} pair, which is stabilised by the Frenkel-like Al relaxation. Thus removing 1/6 of each of an Al and La cation per MP formula unit changes the Al/La ratio to 14.2.

However, in view of the magnitude of the enthalpies, we cannot exclude the possibilities of the occurrence of some other LHA phases (especially, the ns-MP-V_{Al} phase) as metastable ones. Existence of metastable phases during solid state reactions in LHA system was seen experimentally by Ropp and Libowitz[13] through the variability of their X-ray diffraction patterns.

For example, the possibility of coexistence of the two MP-type phases, ns-MP-$V_{La}V_{Al}$ (Al/La = 14.20) and ns-MP-V_{Al} (Al/La = 11.67) is demonstrated in Table 5, where the enthalpies of reactions forming the two MP-type phases and compensating oxides from mixtures of binary oxides with various Al/La ratios, are listed.

We can see in the table that, regardless of the starting composition, the ns-MP-$V_{La}V_{Al}$ phase (and a remnant oxide) is most likely to be formed. However, when the Al/La ratio of the starting material is 13.6 or 14, the differences in enthalpies, between the reaction forming a mixture of the two MP-type phases and the two reactions forming the ns-MP-$V_{La}V_{Al}$ phase (and a remnant oxide), are very small (< 0.05 eV). This small energy difference indicates that any of these reactions is likely to occur. It is possible that one of the three reactions may be more favored for unknown reasons (for instance, possibly for kinetic reasons). In other words, the product phases may vary from sample to sample even with the same starting composition. It is also possible that all the product phases (the two MP-type LHA phases, $LaAlO_3$, and La_2O_3) of

Table 5. Enthalpies of reactions forming the two most likely LHA phases, ns-MP-V_{Al} and ns-MP-$V_{La}V_{Al}$, and related oxides, from mixture of binary oxides with various Al/La ratios[a]

Reactant	Product	Reaction enthalpy (eV)
L + 10A	(9/32)V_{Al} + (5/16)LA	$\Delta E = -1.39$
L + 10A	(3/11)$V_{La}V_{Al}$ + (7/11)LA	$\Delta E = -1.57$
L + 11A	(5/16)V_{Al} + (1/8)LA	$\Delta E = -1.45$
L + 11A	(10/33)$V_{La}V_{Al}$ + (16/33)LA	$\Delta E = -1.65$
L + (35/3)A	(1/3)V_{Al}	$\Delta E = -1.49$
L + (35/3)A	(32/99)$V_{La}V_{Al}$ + (38/99)LA	$\Delta E = -1.71$
L + (35/3)A	(70/213)$V_{La}V_{Al}$ + (38/213)L	$\Delta E = -1.58$
L + 12A	(1/3)V_{Al} + (1/3)A	$\Delta E = -1.49$
L + 12A	(11/38)V_{Al} + (1/19)$V_{La}V_{Al}$	$\Delta E = -1.55$
L + 12A	(1/3)$V_{La}V_{Al}$ + (1/3)LA	$\Delta E = -1.74$
L + 12A	(24/71)$V_{La}V_{Al}$ + (11/71)L	$\Delta E = -1.62$
L + 13A	(1/3)V_{Al} + (4/3)A	$\Delta E = -1.49$
L + 13A	(3/19)V_{Al} + (4/19)$V_{La}V_{Al}$	$\Delta E = -1.72$
L + 13A	(4/11)$V_{La}V_{Al}$ + (2/11)LA	$\Delta E = -1.82$
L + 13A	(26/71)$V_{La}V_{Al}$ + (6/71)L	$\Delta E = -1.76$
L + 13.6A	(1/3)V_{Al} + (29/15)A	$\Delta E = -1.49$
L + 13.6A	(3/38)V_{Al} + (29/95)$V_{La}V_{Al}$	$\Delta E = -1.82$
L + 13.6A	(21/55)$V_{La}V_{Al}$ + (1/11)LA	$\Delta E = -1.87$
L + 13.6A	(136/355)$V_{La}V_{Al}$ + (3/71)L	$\Delta E = -1.84$
L + 14A	(1/3)V_{Al} + (7/3)A	$\Delta E = -1.49$
L + 14A	(1/38)V_{Al} + (7/19)$V_{La}V_{Al}$	$\Delta E = -1.89$
L + 14A	(13/33)$V_{La}V_{Al}$ + (1/33)LA	$\Delta E = -1.90$
L + 14A	(28/71)$V_{La}V_{Al}$ + (1/71)L	$\Delta E = -1.89$
L + 15A	(1/3)V_{Al} + (10/3)A	$\Delta E = -1.49$
L + 15A	(2/5)$V_{La}V_{Al}$ + (4/5)A	$\Delta E = -1.92$

[a] $V_{Al} = La_6Al_{70}O_{114}$; $V_{La}V_{Al} = La_5Al_{71}O_{114}$; A = Al_2O_3; L = La_2O_3; LA = $LaAlO_3$.

the three reactions may coexist as a mixture in a batch.

This point seems to explain partly, at least, the reason why the lattice parameters for the 'β-type' LHA phase were not reproducible from specimen to specimen at the same composition in the experiment of Roth and Hasko.[7] Fritsche and Tensmeyer[11] attributed the non-reproducibility of the lattice parameters to a degree of solid solubility. It is quite possible that the two MP-type LHA phases form solid solutions since they are structurally very similar. In this respect, it would also be necessary to take account of the possibility that the system will follow the reaction paths forming various metastable LHA phases.

In Iyi et al.'s experiment,[21] the Al/La ratio of clear part of the grown crystal was determined to be about 14.4 by wet chemical analysis, when the starting material had the composition of Al/La = 13.6, resulting in a small amount of $LaAlO_3$ inclusions in the grown boules. Furthermore, their result of structural refinement was consistent with the 'vacancy model' which is essentially the same as the ns-MP-$V_{La}V_{Al}$ model in this study. This experimental result suggests that the third reaction for the starting Al/La ratio of 13.6, given in Table 5, actually occurred in their specimen. Even though the ns-MP-V_{Al} phase was not detected in their

Table 6. Comparison of the simulated positional parameters of typical cations in the mirror plane region of ns-MP-$V_{La}V_{Al}$ model, with the X-ray parameters (from Ref. 18)

Atom	Site	#/cell	Measured coordinates		Difference	Calculated coordinates		#/cell
La(1)	2d	0·98	x	0·6667	0·0000	x	0·6667	1
			z	0·2500	0·0000	z	0·2500	
La(2)	6h	0·69	x	0·718	0·0018	x	0·7162	2/3
			z	0·2500	0·0000	z	0·2500	
Al(5)	4e	1·70	x	0·0000	0·0139	x	−0·0139	5/3
			z	0·2389	0·0023	z	0·2412	
Al(6)	12k	0·58	x	0·839	0·0132	x	0·8522	2/3
			z	0·186	0·0008	z	0·1852	

experiment, our calculations suggest that the ns-MP-V_{Al} phase (or its solid solution with the ns-MP-$V_{La}V_{Al}$ phase) would be coexistent in the boules. If the two LHA phases do coexist without a third phase, the mixture is expected to be composed of about 20 mol% of ns-MP-V_{Al} phase and about 80 mol% of ns-MP-$V_{La}V_{Al}$ phase.

On the other hand, the feasibility of the ns-MP-$V_{La}V_{Al}$ model is also confirmed by the fact that the calculated structural parameters, especially for the cations in the mirror plane region agree with the experimental parameters reported by Iyi *et al.*[21] Table 6 lists the equilibrated parameters for the La ions, the interstitial Al ions of the Frenkel-like defects, and the Al ions ideally positioned on the mirror plane, compared with their X-ray refined parameters, showing good agreement between them. The equilibrated parameters in the $2\mathbf{a} \times 3\mathbf{a} \times \mathbf{c}$ supercell are converted to the ones in the basic cell (and averaged to the equivalent site assigned in the X-ray refinement when the ions are slightly off-positioned from the site), in order to compare with the experimental basic cell parameters.

Consequently, despite the possibility of the coexistence with the ns-MP-V_{Al} phase, the most stable and prominent phase in LHA system seems to be the ns-MP-$V_{La}V_{Al}$ phase.

It is also shown in Tables 3 and 4 that the interstitial oxygen model phase [ns-MP-$O_{La}V_{Al}$ (Al/La = 13·57)] is less stable thermodynamically than the other vacancy model MP-type phases. This result suggests that interstitial oxygen is not preferable to cation vacancy in charge compensation for the substitution of M^{2+} with La^{3+} in the MP structure.

4 Conclusions

We have examined a number of defect structures and stoichiometries possible in LHA, using computer-based atomistic simulation techniques. It has been possible to discriminate energetically between alternative models. Our calculation results also provide an insight into the diverse structural and compositional behaviors observed in LHA system.

We suggest that LHA will not form an ideal stoichiometric phase $LaAl_{11}O_{18}$, but most likely an MP-type nonstoichiometric phase $La_{0.83}Al_{11.83}O_{19}$, (Al/La = 14·2) which is essentially identical to the "vacancy model" phase proposed by Iyi *et al.*[21] Our calculations also reveal that the defect structure in this phase prefers strongly the 'type 2' configuration suggested by them: the defect complex should be composed of a vacancy pair (V_{La} and V_{Al}) on the mirror plane, and a pair of Al Frenkel defects formed doubly (rather than singly) above and below the center of the vacancy pair. This defect complex, playing a decisive role in the structural stability of this phase, prefers to be evenly distributed among the mirror planes (on an average, one per every six basic cell units in a mirror plane).

It is suggested that a nonstoichiometric phase $LaAl_{11.67}O_{19}$, which has also an MP-type structure with aluminum vacancies, may coexist with the most likely phase, especially when the Al/La ratio of the system is about 13 to 14. It is revealed that, in this nonstoichiometric phase, the aluminum vacancies prefer the central spinel block 2a sites to other sites. It is also quite possible to form solid solutions between these two MP-type LHA phases.

It is also revealed by the calculated enthalpies of formation of various phases that there is a great possibility of existence of metastable phases. However, it may be claimed that β-type or β/MP-mixed-type structured phases are less stable than MP-type phases.

Our calculation results indicate that the 'O_{La}' defect, which has been proposed to interpret luminescence data in various MP-type structures, is improbable, at least, in LHA system; the interstitial oxygen prefers the central spinel block interstitial site to the vacant La site. Notwithstanding, a more likely configuration for the O_{La} defect is a complex with three Al Frenkel-like defects (two in the **c** direction, one in the mirror plane) around it, rather than the 'type 2' configuration (with interstitial oxygen at the vacant La site) suggested by Iyi *et al.*[21,22] It can also be concluded that 'interstitial oxygen' is not preferable to cation vacancy as charge compensation for the substitution of M^{2+} with La^{3+} in the MP structure.

Acknowledgements

References

1. Bruce, J. A. and Ingram, M. D., *Solid State Ionics*, 1983, **9/10**, 717.
2. Ravichandran, D., Roy, R., White, W. B. and Erdei, S., *J. Mat. Res.*, 1997, **12**, 819.
3. Machida, M., Eguchi, K. and Arai, H., *Chem. Lett.*, 1987, **1987**, 763.
4. Morgan, P. E. D. and Cirlin, E. H., *J. Am. Ceram. Soc.*, 1982, **66**, C114.
5. Morgan, P. E. D. and Marshall, D. B., *Mat. Sci. Eng.*, 1993, **A162**, 15.
6. Cinibulk, M., *Ceram. Sci. Eng. Proc.*, 1994, **15**, 721.
7. Roth, R. S. and Hasko, S., *J. Am. Ceram. Soc.*, 1958, **41**, 146.
8. Bondar, I. A. and Vinogradova, N. V., *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1964, **5**, 737 (Engl. Transl.).
9. Rolin, M. and Thanh, P. H., *Rev. Int. Hautes Temp. Refract.*, 1965, **2**, 175.
10. Godina, N. A. and Keler, E. K., *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1966, **1**, 18 (Engl. Transl.).
11. Fritsche, E. T. and Tensmeyer, L. G., *J. Am. Ceram. Soc.*, 1967, **50**, 167.
12. Mizuno, M., Berjoan, R., Coutures, J. P. and Foex, M., *Yogyo Kyokaishi*, 1974, **82**, 631.
13. Ropp, R. C. and Libowitz, G. G., *J. Am. Ceram. Soc.*, 1978, **61**, 473.
14. Brisi, C., Abbattista, F. and Vallino, M., *Rev. Int. Hautes Temp. Refract.*, 1980, **17**, 331.
15. Stevels, A. L. N. and Verstegen, J. M. P. J., *J. Lumin.*, 1976, **14**, 207.
16. Stevels, A. L. N., *J. Electrochem. Soc.*, 1978, **125**, 588.
17. Stevels, A. L. N., *J. Lumin*, 1978, **17**, 121.
18. Stevels, A. L. N., *J. Lumin*, 1979, **20**, 99.
19. Dexpert-Ghys, J., Faucher, M. and Caro, P., *J. Solid State Chem.*, 1976, **19**, 193.
20. Dexpert-Ghys, J., Faucher, M. and Caro, P., *J. Solid State Chem.*, 1982, **41**, 27.
21. Iyi, N., Inoue, Z., Takekawa, S. and Kimura, S., *J. Solid State Chem.*, 1984, **54**, 70.
22. Iyi, N., Inoue, Z. and Kimura, S., *J. Solid State Chem.*, 1984, **54**, 123.
23. Haemers, T. A. M., IJdo, D. J. W., Groen, W. A., van Hal, H. A. M. and Helmholdt, R. B., *Mater. Res. Bull.*, 1993, **28**, 111.
24. Gasperin, M., Saine, M. C., Kahn, A., Laville, F. and Lejus, A. M., *J. Solid State Chem.*, 1984, **54**, 61.
25. Park, J.-G. and Cormack, A. N., *J. Solid State Chem.*, 1996, **121**, 278.
26. Dick, B. G. and Overhauser, A. W., *Phys. Rev.*, 1958, **112**, 90.
27. Lewis, G. V. and Catlow, C. R. A., *J. Phys. C*, 1985, **18**, 1149.
28. Butler, V., Catlow, C. R. A., Fender, B. E. F. and Harding, J. H., *Solid State Ionics*, 1983, **8**, 109.
29. Catlow, C. R. A., *Proc. Royal Soc.*, 1977, **A353**, 533.
30. Park, J.-G., Ph.D. Thesis, Alfred University, Alfred, New York, USA, 1995.
31. Peters, C. R., Bettman, M., Moore, J. W. and Glick, M. D., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **B27**, 1826.
32. Lindop, A. J., Matthews, C. and Goodwin, D. W., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1975, **B31**, 2940.
33. Park, J.-G. and Cormack, A. N., *J. Solid State Chem.*, 1997, **130**, 199.
34. Derighetti, B., Drumheller, J. E., Laves, F., Muller, K. A. and Waldner, F., *Acta Crystallogr.*, 1965, **18**, 557 .