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Structure and thermal behaviour of lanthanum aluminium nitrates

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Abstract

The structure of the new phase $LaAl(NO_3)_6.12H_2O$ has been determined from single-crystal diffraction data. The symmetry is trigonal [a=10.948(1) Å, c=16.802(2) Å, S.G. $R\bar{3}$] and the structure consists of discrete lanthanum and aluminium polyhedra. La atoms are surrounded by six bidentate nitrate groups in the form of an icosahedron and Al atoms are octahedrally coordinated to six water molecules. The remaining H_2O molecules are located in the holes of the structure, whose cohesion is ensured by hydrogen bonds. The thermal decomposition gives first the cubic phase $LaAl(NO_3)_6.6H_2O$ [a=12.301(1) Å, S.G. $P2_13$], whose structure has been solved from single-crystal diffraction data. The structure is also built from $La(NO_3)_6^{3-}$ anions and $Al(H_2O)_6^{3+}$ cations. The final decomposition product is $LaAlO_3$, which crystallises from an amorphous state at about 450°C. A study of the microstructure of $LaAlO_3$ from diffraction line broadening shows the presence of a significant amount of microstrains at 900°C. © 1998 Elsevier Science S.A.

Keywords: Lanthanum aluminium nitrate hydrate; Lanthanum aluminium oxide; Thermal decomposition; Structure determination; Microstructure

1. Introduction

Various nitrato-complexes of trivalent lanthanide with monovalent and divalent cations as counter-ions have been reported (see Ref. [1]). The interaction in solution of trivalent cations with rare earth nitrates seems more difficult since no related compounds have been described. Nevertheless, the synthesis of such phases would be of interest due to their potentiality as precursors of mixed oxides, e.g. lanthanum aluminate $LaAlO_3$ which is used in technological applications related to catalysis and to substrates for high-T_c superconducting cuprate thin films. Recently, we have described the thermal decomposition of neutral and basic lanthanum nitrates [2], in which some unexpected features were reported, e.g. the existence of two polymorphic phases of $La(NO_3)_3.4H_2O$ and the sensitivity of the oxide nitrate to carbon dioxide. These studies have been subsequently extended to mixed phases containing monovalent (K) and divalent (Ni) elements [3]. The extension to compounds containing a trivalent cation is investigated here, through nitrato complexes of lanthanum and aluminium. Two new phases have been synthesised, $LaAl(NO_3)_6.12H_2O$ and $LaAl(NO_3)_6.6H_2O$. The present study deals with the synthesis, the crystal structure determination from single-crystal diffraction data and the thermal behaviour of these new compounds, as well as with the microstructural properties of the final decomposition product $LaAlO_3$.

2. Experimental

2.1. Materials preparation

$LaAl(NO_3)_6.12H_2O$ and $LaAl(NO_3)_6.6H_2O$ were synthesised from different procedures:

(i) cubic-shaped single crystals were obtained from concentrated nitric acid solutions of $La(NO_3)_3.6H_2O$ (Prolabo) and $Al(NO_3)_3.9H_2O$ (Merck) in a stoichiometric ratio and partially evaporated at 40°C and 80°C, respectively.
(ii) polycrystalline $LaAl(NO_3)_6.6H_2O$ was prepared from the evaporation at 80°C of a melted mixture of $La(NO_3)_3.6H_2O$ and $Al(NO_3)_3.9H_2O$ in a molar ratio. This powder is hygroscopic and must be preserved under low water-vapour pressure. At room temperature, in air, it transforms rapidly into the dodecahydrate

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phase which, in turn, becomes progressively deliquescent.

The chemical formula $LaAl(NO_3)_6.6H_2O$ was found from the determination of the nitrate content by a Dewarda titration (obs. 56.2%; calc. 57.6%) and from the weight loss measured from thermogravimetry for the total transformation into $LaAlO_3$ (obs.72.5%; calc. 71.6%).

2.2. Thermogravimetry

Thermogravimetry (TG) analysis was carried out either with a Rigaku Thermoflex instrument or a McBain type thermobalance. The powdered samples of about 50 mg were spread evenly in large sample-holders to avoid mass effects. The experiments were performed, with a heating rate of $10°C\ h^{-1}$, in a stream of nitrogen or in vacuum.

2.3. X-ray diffraction

X-ray powder diffraction data were collected by means of a D500 Siemens powder diffractometer, equipped with an incident beam monochromator (Cu $K\alpha_1$ radiation, $\lambda = 1.5406$ Å). To prevent hydration, the samples were kept in nitrogen by using a tight sample holder. The patterns were scanned with a step length of $0.02°(2\theta)$. The peak positions were obtained with the pattern decomposition program PROFILE from Socabim, available in the software package DIFFRAC-AT supplied by Siemens.

For the single crystal diffraction study, a crystal was introduced in a capillary and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation). The intensities were collected at room temperature with a $\theta/2\theta$ scanning mode and corrected for Lorentz and polarization effects. Additional experimental details are given in Table 1. Absorption corrections were based on a ψ scan program. Atomic scattering factors were taken from the 'International Tables for X-ray Crystallography' [4]. Structures determination and refinement were carried out with the programs SHELXS and SHELXL [5,6]. The drawings of the structure were produced with the program POWDER CELL [7].

3. Structure determination

3.1. Powder pattern indexing

Indexing of the powder diffraction patterns was performed with the program DICVOL91 [8]. The first 20 lines were used with an absolute angular error of $0.03°(2\theta)$. The solution found was then used for reviewing the powder diffraction data available by means of the computer program NBS*AIDS83 [9]. The powder data have been submitted to the ICDD [10] for possible inclusion in the Powder Diffraction File. The results were as follows:

(i) $LaAl(NO_3)_6.12H_2O$: trigonal unit cell with the refined parameters $a = 10.948(1)$ Å, $c = 16.802(2)$ Å and $V = 1744(1)$ Å^3. The systematic absences were consistent with the space group $R\bar{3}$. The final figures of merit, taking into account space group constraints, were $M_{20} = 146$ and $F_{30} = 117(0.0066, 39)$. No chemically related isostructural material was found from the interrogation of the NIST CDF database [10].

(ii) $LaAl(NO_3)_6.6H_2O$: cubic unit cell with the refined parameters $a = 12.301(1)$ Å and $V = 1861(7)$ Å^3. The structure was solved with the space group $P2_13$. The final figures of merit, taking into account space group constraints, were $M_{20} = 32$ and $F_{30} = 46(0.0182, 36)$. It should be noted that cell parameter is close to that reported for the compound $CeMg(NO_3)_6.6H_2O$ ($a =$

Table 1
Crystallographic data

Chemical formula	$LaAl(NO_3)_6.12H_2O$	$LaAl(NO_3)_6.6H_2O$
Crystal dimension (mm)	$0.5 \times 0.3 \times 0.1$	$0.3 \times 0.3 \times 0.1$
Chemical formula weight ($g\ mol^{-1}$)	754.096	646.006
Calculated density ($g\ cm^{-3}$)	2.15	2.31
Crystal system	trigonal	cubic
Space group	$R\bar{3}$	$P2_13$
Cell parameters (Å)	$a = 10.948(1)$ $c = 16.802(2)$	$a = 12.301(1)$
V(Å^3)	1744(1)	1861(7)
Z	3	4
Radiation (Å)	0.7093	0.7093
Data collection	h: $0 \rightarrow 15$ k: $0 \rightarrow 15$ l: $\bar{26} \rightarrow 27$	h: $0 \rightarrow 19$ k: $0 \rightarrow 19$ l: $\bar{1} \rightarrow 19$
No. observations ($I > 3\sigma$ (I))	1711	1738
No. variables	60	98
R	0.025	0.064
$R\omega$	0.087	0.115
ω (where $P = (F_o^2 + 2F_c^2)/3$)	$1/[\sigma^2(F_o)^2 + (0.2716P)^2 + 21.1647P]$	$1/[\sigma^2(F_o)^2 + (0.1354P)^2 + 278.69P]$

Table 2
Atomic coordinates and atomic displacement parameters with their standard deviations for $LaAl(NO_3)_6.12H_2O$

Atom	*x*	*y*	*z*	U_{eq}
La	0.0	0.0	0.0	0.0164(1)
Al	0.3333	0.6666	0.1666	0.0195(2)
N1	0.7794(2)	0.7506(2)	0.1003(1)	0.0223(3)
O11	0.8370(2)	0.7305(2)	0.0403(1)	0.0297(3)
O12	0.8217(2)	0.8766(2)	0.1192(1)	0.0304(3)
O13	0.6861(2)	0.6505(2)	0.1379(1)	0.0354(4)
OW1	0.6447(2)	0.4618(2)	0.8985(1)	0.0280(3)
OW2	0.5168(3)	0.3813(3)	0.0351(1)	0.0493(5)

$U_{eq}=(1/3)\ \Sigma_i\ \Sigma_j\ U_{ij}a_i^*a_j^*a_{i.}a_j$.

12.570 Å) [11], though the valence of the cations is different.

3.2. Structure determination and refinement

(i) $LaAl(NO_3)_6.12H_2O$. The positions of one independent La atom and one Al atom were obtained from the direct methods. The remaining non-hydrogen atoms were derived from two difference Fourier maps. The list of interatomic distances showed that four of them corresponded to one independent nitrate group. It was assumed that the two remaining atoms were O atoms of water molecules. This result is in accordance with the chemical formula $LaAl(NO_3)_6.12H_2O$. The final values of *R* and *Rω* factors, including the refinement of anisotropic thermal parameters (0.025 and 0.087, respectively) were satisfactory. Final structural and atomic displacement parameters are given in Table 2 and selected bond distances in Table 3.

(ii) $LaAl(NO_3)_6.6H_2O$. The positions of the independent La and Al atoms were obtained from the direct methods. The remaining atoms were derived from two difference Fourier maps. The list of interatomic distances showed that eight of them corresponded to two independent nitrate groups, and the last two atoms to water molecules. This result is in agreement with the chemical formula $LaAl(NO_3)_6.6H_2O$. To improve the overall quality of the results, absorption corrections were applied and the final *R* and *Rω* factors were 0.064 and 0.115, respectively. Final structural and atomic displacement parameters are given in Table 4 and selected bond distances in Table 5.

Table 3
Selected bond distances (Å) and angles (°) for $LaAl(NO_3)_6.12H_2O$

Bond distances	
La–O11 (×6)	2.659(2)
La–O12 (×6)	2.645(2)
Al–OW1 (×6)	1.887(2)
N1–O11	1.264(3)
N1–O12	1.256(2)
N1–O13	1.233(3)
Angles	
O11–N1–O12	116.7(2)
O11–N1–O13	121.1(2)
O12–N1–O13	122.2(2)
Possible hydrogen bonds	
OW1–O13	2.912(3)
OW2–O11	2.868(3)

Table 4
Atomic coordinates and atomic displacement parameters with their standard deviations for $LaAl(NO_3)_6.6H_2O$

Atom	*x*	*y*	*z*	U_{eq}
La	0.25	0.75	0.25	0.0183(1)
Al	0.75	0.75	0.25	0.0161(4)
N1	0.0679(5)	0.9057(5)	0.1751(5)	0.0200(10)
O11	0.1455(5)	0.9404(4)	0.2324(5)	0.0280(11)
O12	0.0724(5)	0.8110(5)	0.1407(4)	0.0275(11)
O13	0.0055(4)	0.4703(5)	0.3458(6)	0.0299(12)
N2	0.4068(5)	0.8253(6)	0.0687(7)	0.0296(14)
O21	0.4362(5)	0.7623(6)	0.1472(5)	0.0335(14)
O22	0.1397(6)	0.5754(6)	0.1878(5)	0.0381(15)
O23	0.4631(6)	0.8435(6)	−0.0109(4)	0.0354(14)
OW1	0.6532(5)	0.8592(4)	0.3009(4)	0.0249(10)
OW2	0.6999(5)	0.6508(4)	0.3542(4)	0.0238(10)

$U_{eq}=(1/3)\ \Sigma_i\ \Sigma_j\ U_{ij}a_i{}^*a_j^*a_{i.}a_j$.

Table 5
Selected bond distances (Å) and angles (°) for $LaAl(NO_3)_6.6H_2O$

Bond distances	
La–O11 (×3)	2.679(5)
La–O12 (×3)	2.673(6)
La–O21 (×3)	2.628(6)
La–O22 (×3)	2.659(7)
Al–OW1 (×3)	1.877(5)
Al–OW2 (×3)	1.902(6)
N1–O11	1.262(8)
N1–O12	1.242(8)
N1–O13	1.231(7)
N2–O21	1.292(9)
N2–O22	1.245(9)
N2–O23	1.221(9)
Angles	
O11–N1–O12	118.3(6)
O11–N1–O13	117.0(6)
O12–N1–O13	124.7(7)
O21–N2–O22	114.9(8)
O21–N2–O23	123.5(7)
O22–N2–O23	121.4(8)
Possible hydrogen bonds	
OW1–O13	2.830(9)
OW1–O21	2.635(9)
OW2–O11	2.661(8)
OW2–O23	2.718(9)

4. Description and discussion

The two crystal structures are built from discrete $[La(NO_3)_6]^{3-}$ anions and $[Al(H_2O)_6]^{3+}$ cations, which are linked together by hydrogen bonds arising from (i) both 'free' water molecules and water molecules of the metal complex for $LaAl(NO_3)_6.12H_2O$, and (ii) water molecules of the metal complex for $LaAl(NO_3)_6.6H_2O$. Figs. 1 and 2 show the two unit cells. The La atoms are coordinated to twelve O atoms belonging to six bidentate nitrate groups, in the form of irregular icosahedra (Fig. 3 Fig. 3a and b). La–O distances are in the range 2.628–2.679 Å with average values 2.652 Å and 2.660 Å for the dodecahydrate and the hexahydrate compounds, respectively. These values are in good agreement with the results reported for similar polyhedra, e.g. in $La_2Mg_3(NO_3)_{12}.24H_2O$ [2.642–2.696 Å, aver. 2.670 Å] [12], [2.613–2.778 Å, aver. 2.676 Å] in $La_2K_3(NO_3)_9$ [3]. The Al atoms are bonded to six water molecules in the form of an octahedra $Al(H_2O)_6$. The Al–O distance is 1.887 Å in the dodecahydrate. They are 1.877 and 1.902 Å in the hexahydrate. These values agree with those reported for $Al(NO_3)_3.9H_2O$ (1.78–1.95 Å, average, 1.88 Å) [13].

The nitrate groups act as bidentate ligands. They belong to the class I_{2b} of the classification established by Leclaire [14]. In each nitrate groups, the distances from the N atom to the non-coordinated O atom are shorter (mean value: 1.225 Å) than the other distances (mean value: 1.26 Å). The O–N–O angles between the two coordinated O atoms are smaller (mean value: 116.6°) than the O–N–O angles involving a terminal atom (mean value: 121.6°).

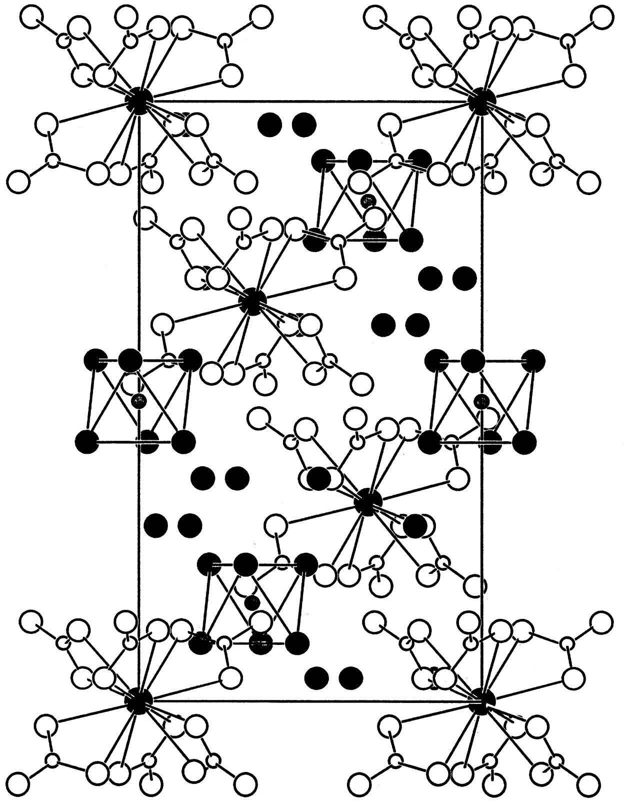

Fig. 1. Projection of the crystal structure of $LaAl(NO_3)_6.12H_2O$ along the *a* axis (*c* vertical), showing the packing of $La(NO_3)_6^{3-}$ and $Al(H_2O)_6^{3+}$ polyhedra (black circles are water molecules).

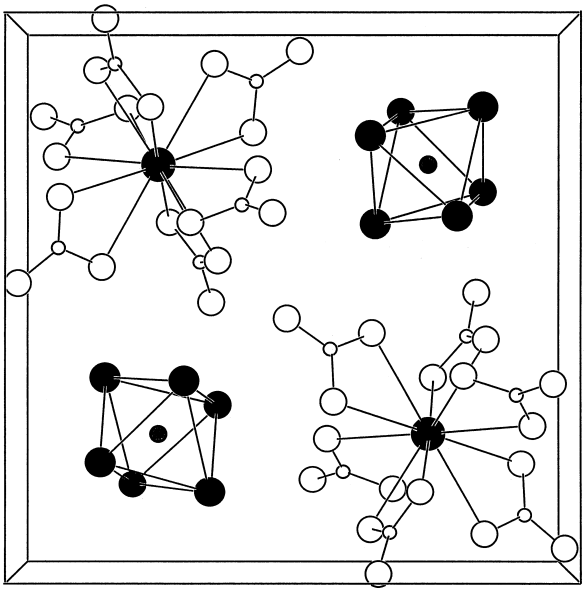

Fig. 2. Perspective view of the crystal structure of $LaAl(NO_3)_6.6H_2O$. (Only half the lanthanum and aluminium polyhedra are shown, the other polyhedra are omitted for clarity).

The cohesion of the two structures is ensured by hydrogen bonds (Tables 3 and 5) between the terminal oxygen atoms of the nitrate groups and the water molecules linked to Al atoms. Furthermore, in the hexahydrate phase, additional hydrogen bonds are established between the H_2O molecules and the O atoms of the NO_3 groups linked to La atom, and in the dodecahydrate compound, between the 'free' water molecules and O11 of the nitrate groups.

The structure of $LaAl(NO_3)_6.12H_2O$ can be described from sheets containing La icosahedra and 'free' water molecules alternating with sheets of $Al(H_2O)_6$ octahedra in the direction of the *c*-axis. The three-dimensional crystal structure of $LaAl(NO_3)_6.6H_2O$ can be described as deriving from a pseudo NaCl-type. It is built from a connection of $[La(NO_3)_6]^{3-}$ anions and $[Al(H_2O)_6]^{3+}$ cations. However, there is a translation of [1/4,1/4,1/4] of the polyhedra with respect to the NaCl structure-type. It has already mentioned there is a relationship between the cubic unit cells of $LaAl(NO_3)_6.6H_2O$ [$a=12.301(1)$ Å] and $Ce^{IV}Mg(NO_3)_6.6H_2O$ [$a=12.570$ Å] [11]. A refinement of the atomic positions of $LaAl(NO_3)_6.6H_2O$ was attempted from the positions reported for the cerium magnesium compound, but no reasonable solution was obtained, due to the difference of space groups. It is an example of false

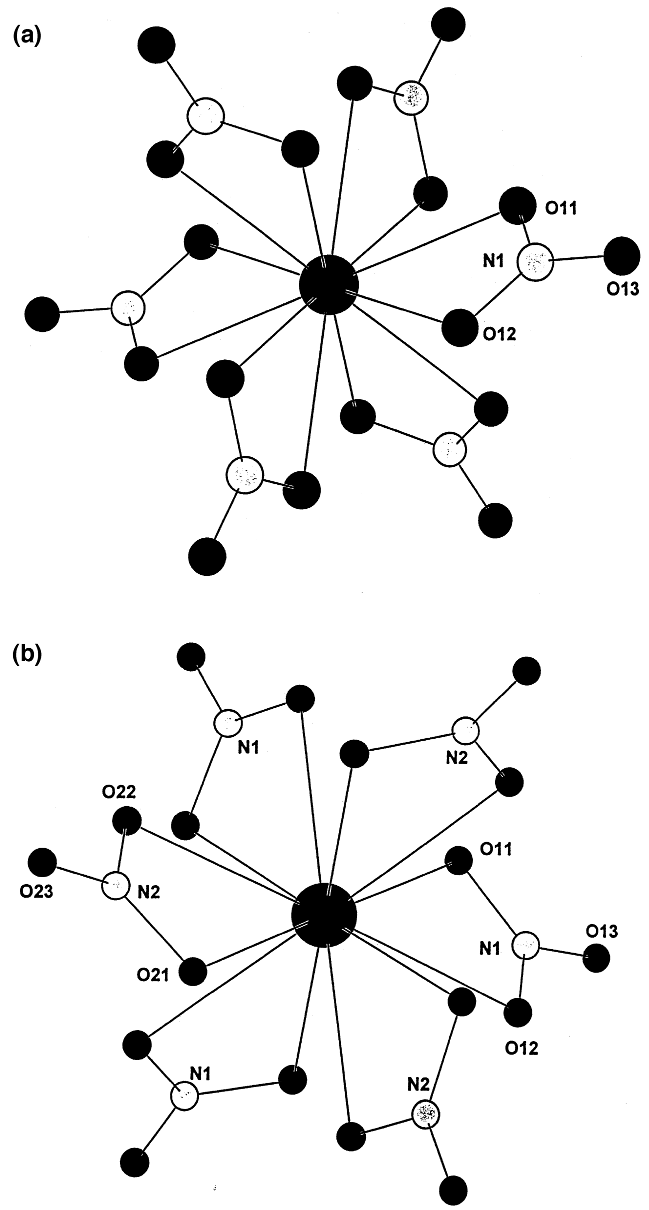

Fig. 3. Lanthanum polyhedra in (a) $LaAl(NO_3)_6.12H_2O$ and (b) $LaAl(NO_3)_6.6H_2O$.

isostructural relationship between two phases, which is a consequence of the different oxidation state of the metals.

5. Thermal behaviour

5.1. Thermal decomposition of $LaAl(NO_3)_6.12H_2O$

Fig. 4 displays the TG curves obtained in a nitrogen stream (curve a) and in vacuum (curve b). The dehydration of the precursor into $LaAl(NO_3)_6.6H_2O$ takes place at room temperature, according to the following reaction (observed weight loss: 14.1%, calculated: 14.3%):

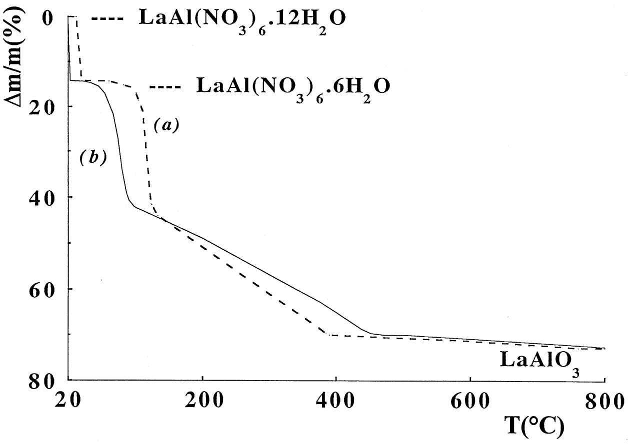

Fig. 4. TG curves for non-isothermal decomposition of $LaAl(NO_3)_6.12H_2O$. (a) in a stream of nitrogen; (b) in vacuum (heating rate: 10°C h^{-1}).

$$LaAl(NO_3)_6.12H_2O \rightarrow LaAl(NO_3)_6.6H_2O + 6H_2O_{(g)}.$$

The dehydration is followed by a rapid mass loss until a change in the curve slope, in both nitrogen or vacuum. In addition, in vacuum an inflexion point is observed on the TG curve at about 140°C. The corresponding weight loss is close to 43%, in accordance with the global composition $LaAlO(NO_3)_4$ (calc. 43.0%). The X-ray diffraction pattern of the solid obtained at this temperature revealed that this phase is ‘amorphous’. In the temperature range 140–400°C, a gradual weight loss until about 70% is observed. Probably due to the slow desorption of gases (NO, NO_2) from the highly divided hexagonal mixed oxide $LaAlO_3$ ($a=5.364$ Å, $c=13.11$ Å) formed, the final weight loss (72.5%) is only achieved at 700°C. It agrees well with the value 71.6% calculated from the reaction:

$$LaAl(NO_3)_6.12H_2O \rightarrow LaAlO_3 + 3(NO, NO_2, O_2)_{(g)} + 12H_2O_{(g)}.$$

X-ray powder diffraction patterns of the decomposition products collected at four temperatures are shown in Fig. 5. It shows that the crystallization of the mixed oxide occurs above 700°C.

5.2. Microstructure of lanthanum aluminium oxide

The microstructural properties of a sample of $LaAlO_3$, obtained at 900°C, was investigated from diffraction line-broadening analyses. The integral breadth (=peak area/peak intensity) of the diffraction lines in the angular range 20–150° (2θ) were extracted from the pattern decomposition technique with the program PROFILE, using a Voigt function to describe line shapes. Details on the procedure used have been reported elsewhere (see, for example, Refs. [15] and [16]). After correction for the instrumental contribution, using the Voigt method [15], the integral

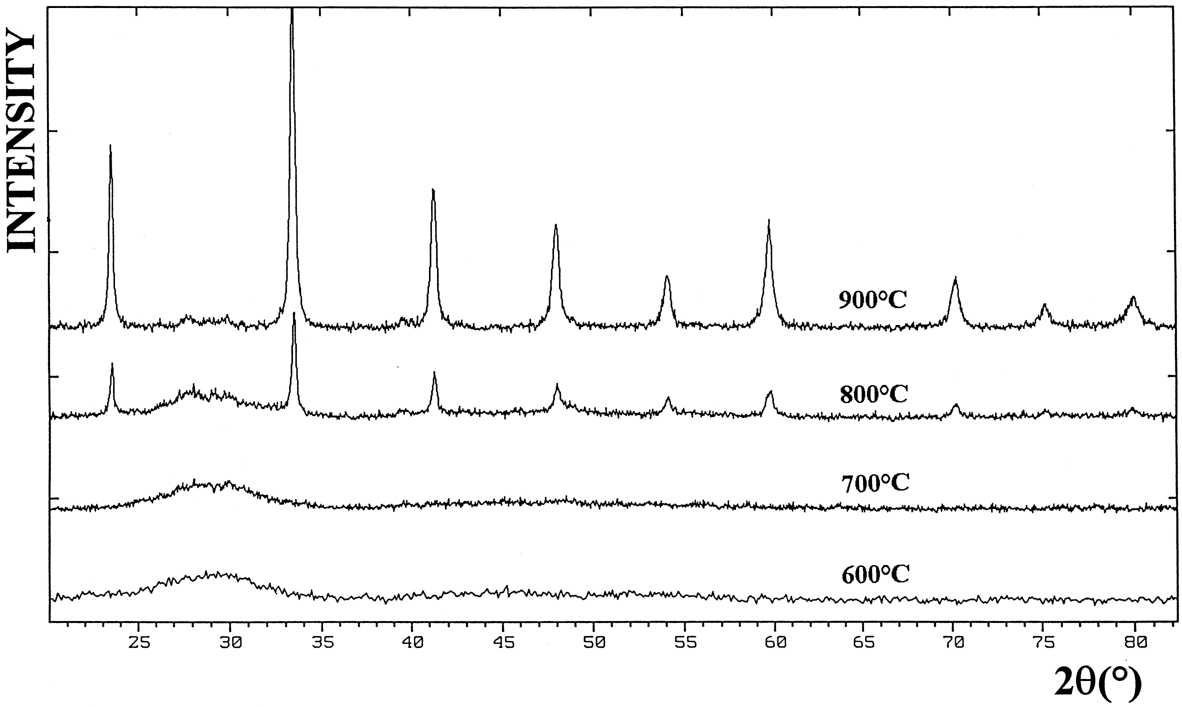

Fig. 5. X-ray powder diffraction patterns of $LaAlO_3$ at different temperatures.

breadths β_f^* ($=\beta_{2\theta}\cos\theta/\lambda$) expressed in reciprocal units were obtained. Their variation in reciprocal space, examined through a Williamson–Hall plot, β_f^* versus d^* ($=2\sin\theta/\lambda$), is shown in Fig. 6. Its is immediately apparent that there is a slight scatter in the values of β_f^* from a straight line with a significant positive slope. This result shows that the microstructure of $LaAlO_3$ is dominated by structural imperfections. Indeed, the mean apparent crystallite size calculated from the intercept is 2150 Å and the microstrain value derived from the slope is 0.0045, for the sample obtained at 900°C. It is worthwhile to note that a similar effect of line broadening dominated by structural imperfections was also reported for hexagonal La_2O_3 oxide obtained from the decomposition of neutral and basic lanthanum nitrates [2].

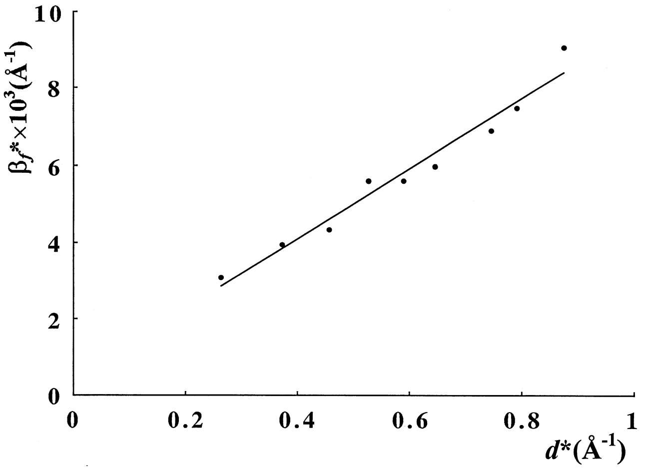

Fig. 6. Williamson–Hall plot of $LaAlO_3$ obtained at 900°C.

6. Conclusion

This study demonstrates that nitrato-complexes of lanthanum and aluminium can be formed. Two phases, $LaAl(NO_3)_6.12H_2O$ and $LaAl(NO_3)_6.6H_2O$, have been obtained and their crystal structure has been described. The structures are built from discrete $La(NO_3)_6^{3-}$ and $Al(H_2O)_6^{3+}$ ions. The final stage of the thermal decomposition of these phases leads to the mixed oxide $LaAlO_3$, which is characterised by structural imperfections.

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