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Low-Temperature Chemical Synthesis of Lanthanum Monoaluminate

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One of the promising candidates for ferroelectric substrate materials, lanthanum monoaluminate ($LaAlO_3$), was successfully synthesized by two separate chemical powder preparation techniques: (i) homogeneous precipitation from aqueous solutions containing urea (CH_4N_2O) in the presence of nitrate salts, and (ii) self-propagating combustion synthesis from aqueous solutions containing CH_4N_2O and the respective nitrate salts of lanthanum and aluminum. The submicrometer, spherical-like particles of the precursors were completely converted to pure $LaAlO_3$ at 850°C in the homogeneous precipitation route, and the same conversion temperature was observed to be 750°C, which becomes the lowest temperature ever reported for the powder synthesis of a pure $LaAlO_3$ phase. The materials were characterized by powder X-ray diffractometry, simultaneous thermogravimetric/differential thermal analysis, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Structural refinements by Rietveld analysis showed that $LaAlO_3$ was isostructural with $BaTbO_3$ and had the space group *R*-3*c*, in contrast to the previously assumed space group of *R*-3*m* for this phase. The atomic positions in the structure of $LaAlO_3$ were refined and presented for the first time, with respect to the present space group.

I. Introduction

LANTHANUM MONOALUMINATE, $LaAlO_3$, has been considered as an electrically insulating buffer layer in the form of single crystals or as thin films on substrates for the deposit of superconducting or ferroelectric materials.[1–4] Polycrystalline lanthanum aluminate has been prepared by the direct combination of the pure oxides La_2O_3 and Al_2O_3 at temperatures of $>$1550°C.[1,5–12] Preparation of $LaAlO_3$ from direct mixing and firing of the binary oxides has not been entirely satisfactory because of the difficulties encountered in ensuring complete oxide reaction and the introduction of impurities during the subsequent milling procedures and practices. Sung *et al*.[1] reported the full development of the $LaAlO_3$ phase only on heating the sample to 1600°C, and they needed to reheat the same sample to 1750°C for 3 h to form a polycrystalline disk to be used as a target for radio-frequency (rf) magnetron sputtering of $LaAlO_3$ thin films as buffer layers for 123 thin films on silicon wafers.

Synthesis of $LaAlO_3$ also was studied[13–15] by aqueous coprecipitation methods. When lanthanum and aluminum salts were coprecipitated from an ammonium carbonate solution, only partial lanthanum aluminate formation was observed at 900°C, with complete conversion occurring at temperatures $>$1300°C.[14] Similar results were reported by Vidsayagar *et al*.[13] and Krylov *et al*.[15] for "partial aluminate product formation" when soluble lanthanum and aluminum salts were precipitated with ammonium hydroxide followed by heat treatment in the temperature range of 1100°–1350°C.

In an attempt to prepare $LaAlO_3$ by an aerosol-furnace technique,[16] using water-soluble lanthanum and aluminum salts, products were formed at furnace temperatures of 900°–1500°C. In the runs with furnace temperatures of 1200°–1500°C, the formation of $LaAlO_3$ has been reported to be again only partial, and the samples still contained La_2O_3 and Al_2O_3. However, further annealing the aerosol-furnace samples at 1100°C also has been claimed in this report to lead to the complete conversion to $LaAlO_3$.

The possibility that fine-particle oxide ceramics could be produced using exothermic redox reactions between an oxidizer (metal nitrates) and a fuel (amides, hydrazides, etc.) has been reported.[17] This concept was demonstrated for the first time[18] by the rapid synthesis of fine-particle α-Al_2O_3 and related oxides such as metal aluminates, rare-earth orthoaluminates, and Ce^{3+}- or Cr^{3+}-doped aluminous oxides. The process involves the "combustion" of the corresponding metal nitrate plus either urea (CH_4N_2O) or carbohydrazide mixtures at 500° or 250°C, respectively, under normal atmospheric pressure.[17] The process yields foamy, voluminous, and fine oxide powders in $<$5 min. The combustion proceeds instantaneously, and energy savings have attracted much interest. This process also has been successfully used in the synthesis of $LaCrO_3$ and $Ba_2YCu_4O_8$ phases.[19,20]

In this paper, the production of $LaAlO_3$ powders from the starting lanthanum nitrate and aluminum nitrate water-soluble salts, via homogeneous precipitation with CH_4N_2O decomposition, is presented as one technique of powder synthesis. State-of-the-art ceramic-processing routes such as this one are characterized by numerous stringent requirements. A promising approach to successful processing may be to begin with a monosized, monodispersed powder to produce a uniform starting microstructure. Matijevic[21,22] has produced colloidal particles of uniform geometries, e.g., spheres, cubes, and disks, in the metal hydrous oxide systems. The decomposition of CH_4N_2O in aqueous solutions is accompanied by the slow and controlled supply of ammonia (NH_3) and carbon dioxide (CO_2) into the solution.[23] The smooth pH increase obtained by the decomposition of CH_4N_2O in unison with the steady supply of OH^- and CO_3^{2-} ions, typically lead to the precipitation of metal hydroxycarbonates of controlled particle morphology.[24–26] Homogeneous precipitation from aqueous solutions, in the presence of CH_4N_2O, has been used to produce monosized, spherical particles of basic lanthanide carbonates,[27] cerium oxide,[28] and $Y_3Al_5O_{12}$.[29]

In this study, homogeneous precipitation techniques similar to those described by Sordelet and coworkers[27,29] are applied to the synthesis of refractory $LaAlO_3$. The self-propagating combustion synthesis (SPCS) technique[17–20] also was used for the production of submicrometer powders of this phase. For better characterization of the structure, Rietveld analysis[30–33] is performed on the synthesized $LaAlO_3$ powder X-ray diffractometry (XRD) samples to determine the atomic parameters of the unit cell.

II. Experimental Procedure

The lanthanum source for this study was 99.9% pure oxide (Merck, Darmstadt, FRG). Stoichiometric amounts of lanthanum oxide (La_2O_3) after calcining for 6 h in air at 950°C, were

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Table I. Powder XRD Experimental Methods

Parameter	Value
Radiation type, source	X-ray, iron
Wavelength, λ, value used	1.936042 A ($K\alpha_1$)
λ discrimination	Diffracted beam, graphite, monochromatic
λ detector	Scintillation
Instrument description	
Division	1°
Record	0.3°
Instrumental profile breadth	0.10° 2θ
Temperature	24° ± 1°C
Specimen form	Side-loaded powder, packed for 2θ's
Range of 2θ	20°–110°
Specimen motion	None
Internal/external 2θ standard	Silicon (external)
Lattice parameter of 2θ standard	5.4315 A
2θ error correction procedure	Linear interpolation from nearest 2θ's of standard
Intensity measurement technique	Automated computer software (Rigaku Model DMax/B)
Peak heights error	~5%
Cell-refinement method	Least-squares (Appleman and Evans[34])

reacted with nitric acid (reagent grade, Merck) to form the desired 0.5*M* lanthanum nitrate stock solutions. Reagent-grade aluminum nitrate–9-hydrate (Riedel-De Haen AG, Seelze, Germany) was dissolved in distilled water to prepare the 0.4*M* aluminum nitrate stock solutions. Reagent-grade urea (CH_4N_2O; 99.5%, Riedel-De Haen AG) was used without further purification.

(1) Homogeneous Precipitation

A total of 50 mL of cation stock solutions (i.e., lanthanum nitrates and aluminum nitrates) was thoroughly mixed in a glass beaker. Distilled water (750 mL) containing 13.0 g of urea was then mixed with the above solution. The final clear solution was slowly heated to 95°C on a hot plate. Precipitation started in ~2 h with a "slight turbidity" in the clear solution, as the temperature did reach 90°C. Precipitates were aged for 4 h at 95°C on the hot plate under slow stirring. After aging, the precipitates in the opaque solution were separated from the mother liquor either by conventional filtration or centrifugation (at 2500 rpm) in polycarbonate bottles. The precipitates were washed once with water and then twice with isopropyl alcohol

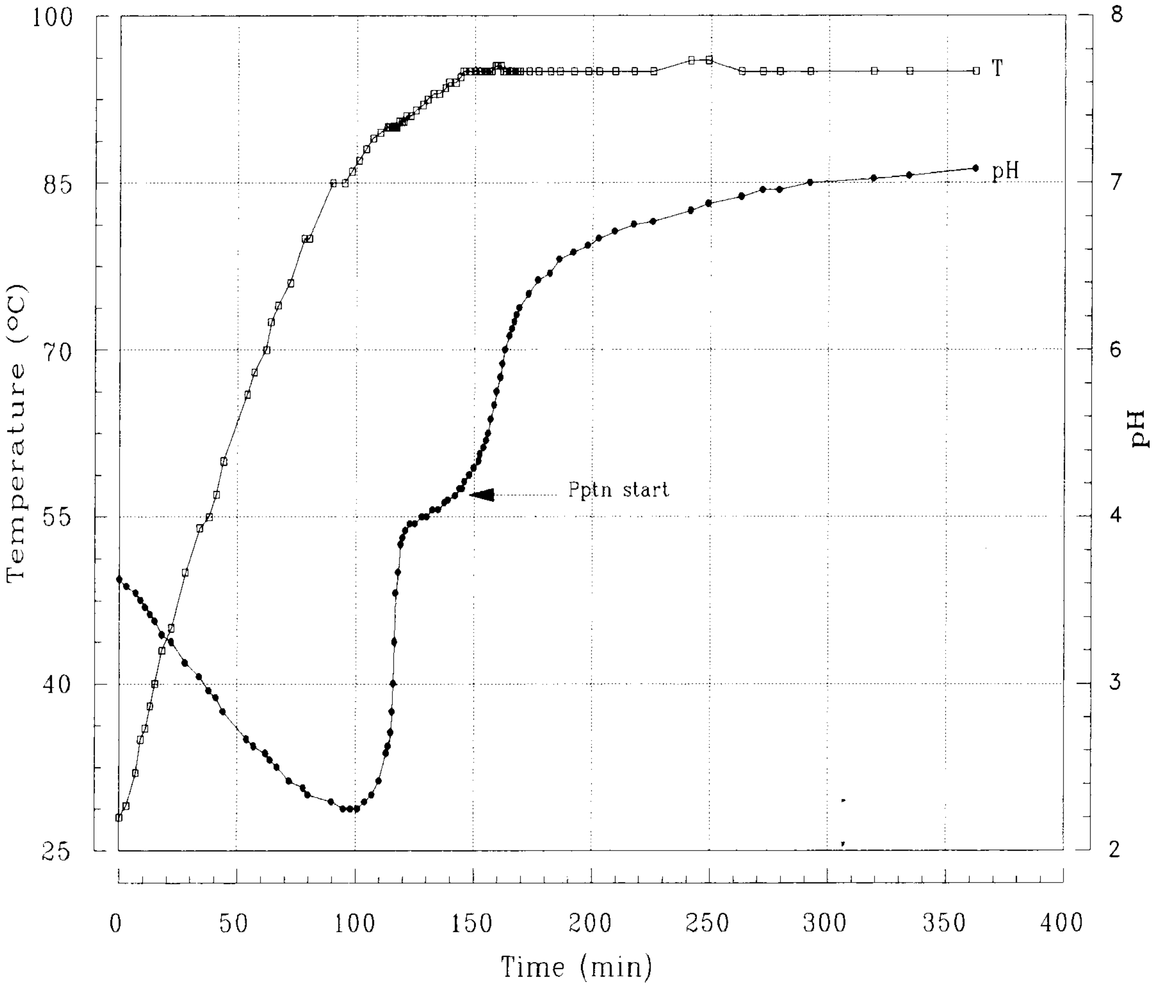

Fig. 1. Experimental traces of pH and temperature versus time obtained in the standard homogeneous precipitation process.

(reagent grade, Merck). The washed precipitates were oven-dried at 85°C overnight.

(2) Self-Propagating Combustion Synthesis (SPCS)

A total of 50 mL of the cations solution, taken from each of the nitrate stock solutions, in appropriate amounts, to give the stoichiometry of $LaAlO_3$, was mixed with a magnetic stirrer in an uncovered 100-mL-capacity glass beaker for 1 h at room temperature. CH_4N_2O (2 g) was then added to this solution. Following the dissolution of CH_4N_2O in the cations solution, the beaker contents were immediately transferred into a 250-mL-capacity Pyrex™ (Corning Glass Works, Corning, NY) beaker. The Pyrex beaker containing the liquid mixture was placed in a muffle furnace maintained at 510° ± 10°C. Initially, the mixture boils and undergoes dehydration followed by decomposition, with swelling and frothing, resulting in a foam that ruptures with a flame and glows to incandescence.[17] The entire combustion process was complete in $<$15 min. The product of combustion was a voluminous, foamy, and amorphous precursor. This foamy precursor was then ground in an agate mortar to a fine powder and calcined on an α-Al_2O_3 plate, in air, in the temperature range of 350°–1100°C for 6–24 h to yield the crystalline- and pure-$LaAlO_3$ phases.

(3) Powder Sample Characterization

Powder XRD patterns, for phase characterization and purity, were obtained for the dried precipitates, as well as for powders heat-treated at 350°–1050°C. A diffractometer (Model D-Max/B, Rigaku Co., Tokyo, Japan) was used with monochromated Fe$K\alpha$ radiation at the step size of 0.02° and the preset time of 1 s for phase-characterization purposes. The XRD data for Rietveld analysis were collected with a step size of 0.02° and preset time of 10 s in the 2θ range of 20°–110°. Further details of the XRD practices are depicted in Table I.

The characteristics of the thermal decomposition of the precipitates dried at 85°C overnight were monitored with simultaneous thermogravimetric/differential thermal analysis (TG/DTA) Netzsch GmbH, FRG). A 40–50 mg sample was heated to 1200°C in flowing air at a rate of 10°C/min. Particle-size and morphology characteristics of the $LaAlO_3$ samples were assessed from scanning electron microscopy (SEM) micrographs (Model JSM6400, JEOL, Tokyo, Japan). Prior to examination, the powder or pellet samples were sputter-coated with a layer of gold ~15 nm thick. Energy-dispersive X-ray spectroscopy (EDXS) (Kevex, Foster City, CA) was performed on the pelletized and sintered samples to acquire semiquantitative elemental-distribution information. A pure sample of 1.1 at.% neodymium-doped yttrium aluminum garnet (Nd:YAG) polycrystalline disk (quantitatively analyzed by the inductively coupled plasma (ICP) method prior to this study) was used as a standard material in the EDXS runs. The analysis was performed on the polished (0.1 μm diamond paste) surfaces of our samples. The EDXS information was believed to be accurate to ±3 at.%.

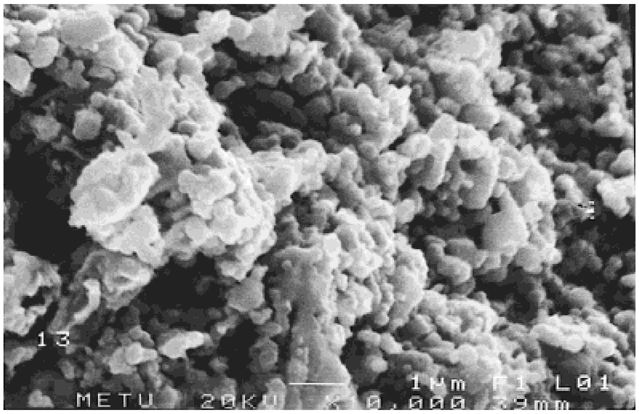

Fig. 2. SEM micrograph of the typical powders produced by the homogeneous precipitation process.

Table II. Powder XRD Pattern of $LaAl(OH(CO_3))_2$

hkl	d_{calc}	d_{obs}	I/I_0
110	5.6185	5.6090	20
101	4.3508	4.3540	100
200	4.2972	4.2976	54
111	3.7538	3.7527	80
210	3.7192	3.7194	78
120	3.4080	3.4078	50
211	2.9936	2.9935	25
021	2.9901	2.9905	90
121	2.8240	2.8239	22
220	2.8092	2.8080	22
310	2.6728	2.6728	45
002	2.5224	2.5222	41
301	2.4912	2.4917	18
221	2.4544	2.4538	40
311	2.3618	2.3620	53
202	2.1754	2.1749	21
400	2.1486	2.1482	26
230	2.1447	2.1449	20
212	2.0876	2.0879	56
022	2.0864	2.0860	56
410	2.0639	2.0640	30
122	2.0275	2.0273	41
231	1.9737	1.9733	27
222	1.8769	1.8772	22
330	1.8728	1.8732	34
040	1.8562	1.8564	15
312	1.8345	1.8348	16
421	1.7448	1.7450	10
041	1.7420	1.7422	15
240	1.7040	1.7045	21
510	1.6746	1.6748	3
402	1.6357	1.6359	6
241	1.6144	1.6141	5
412	1.5974	1.5972	18
520	1.5598	1.5597	6
431	1.5446	1.5444	10
213	1.5323	1.5325	13
332	1.5037	1.5035	24
042	1.4950	1.4948	5
521	1.4902	1.4903	3
142	1.4729	1.4727	6
223	1.4429	1.4431	4
600	1.4324	1.4322	8
313	1.4234	1.4231	5
530	1.4118	1.4117	4
250	1.4035	1.4035	9
512	1.3952	1.3954	5

III. Results and Discussion

(1) Homogeneous Precipitation

The formation of the solid phase in the glass aging beakers was governed by the controlled generation of hydroxide ions through the decomposition of urea. The decomposition behavior of urea appears to be dependent on the urea concentration, as well as other variables such as temperature and the presence and amounts of cations in the solution. The decomposition of urea and the progress of the precipitation was followed, as a function of temperature and pH, in the lanthanum nitrate- and aluminum nitrate-containing solutions. A typical plot of pH versus temperature and time is reproduced in Fig. 1. The initial drop in pH appears to be possibly due to the presence of acidic lanthanum cations in the solution and, although not directly suggested by the data of Fig. 1, the formation of the intermediate complex HCNO,[27] followed by an increase in the dissociation constant of water. The pH started to increase rather abruptly at ~85°C. A similar observation was given by Cornilsen and Reed,[24] in alumina precipitation in the presence of urea, that urea itself decomposes at ~80°C. This increase in pH coincided with the observation of slight turbidity in the solution as cations started to precipitate. An increase in pH was observed until the hydrolysis of cations was complete. On completion of the decomposition of urea, the pH of the solution leveled off at ~7 toward the boiling point and remained approximately the same during the rest of the aging period.

Figure 2 shows an SEM micrograph of a representative powder sample that was obtained from the centrifuged precipitates following the calcination at 900°C in a stagnant dry air atmosphere for 4 h. The precursor powders also had the same morphology. From this micrograph, the particles are not as uniform and well dispersed as to the proved ability of the urea method tested in other material systems (in the absence of the second cation),[27,28] but it still demonstrates that, although heavily agglomerated, submicrometer spherical particles of lanthanum monoaluminate can be produced by this technique.

The precipitates dried at 85°C in air were crystalline, and they displayed an orthorhombic crystal structure that was quite similar, in terms of their lattice parameters, to those of $YOH(CO_3)$ (ICDD[†] Powder Diffraction File card 30-1444) especially. Previous researchers also have confirmed[27] that the above outlined process, when applied to Y_2O_3 precipitation, produces $YOH(CO_3)$ precursors after aging. Although somehow premature at this stage, without having the quantitative chemical analysis data of the precursors, assuming that the samples have a stoichiometry and structure resembling those of other rare-earth hydroxycarbonates seems to be, at least, logical. The semiquantitative EDXS analysis of the dried precursors proved that lanthanum and aluminum were present in the samples. The XRD pattern of the precursor was refined and further generated with lattice parameter software,[34] and the unit cell was seen to be orthorhombic, having the possible space group *Pbnm* (62) with the refined ◦lattice parameters of a = 0.85945(6) ◦ nm (8.5945(6) A), b = 0.74247(6) nm (7.4247(6) A), c = 0.50449(4) nm (5.0449(4) A), and V = 0.32193(3) nm^3 (321.93(3) A^3); the estimated standard deviations in the last significant figure are given in parentheses. The powder XRD pattern of this new phase, with the "tentative" formula $LaAl(OH(CO_3))_2$, is given in Table II. However, this crystalline phase of the dried precursors disappeared completely on heating to ~300°C, as can be seen from Fig. 3, which displays a sequence of isothermal heatings at different and increasing temperatures to exhibit the pattern of phase evolution in $LaAlO_3$ precursors.

The XRD traces of the precursor phase began to display diffuse patterns with relatively broad peaks as the temperature was increased beyond 350°C. Few broad peaks in the 350°, 500°, and 600°C traces (6 h each, in dry air) were identified to resemble those of LaOOH (ICDD Powder Diffraction File card 19-656), in terms of the *d*-spacings and intensities. However, because our EDXS analysis showed the presence of lanthanum and aluminum in the precursors, these weak-intensity, broad

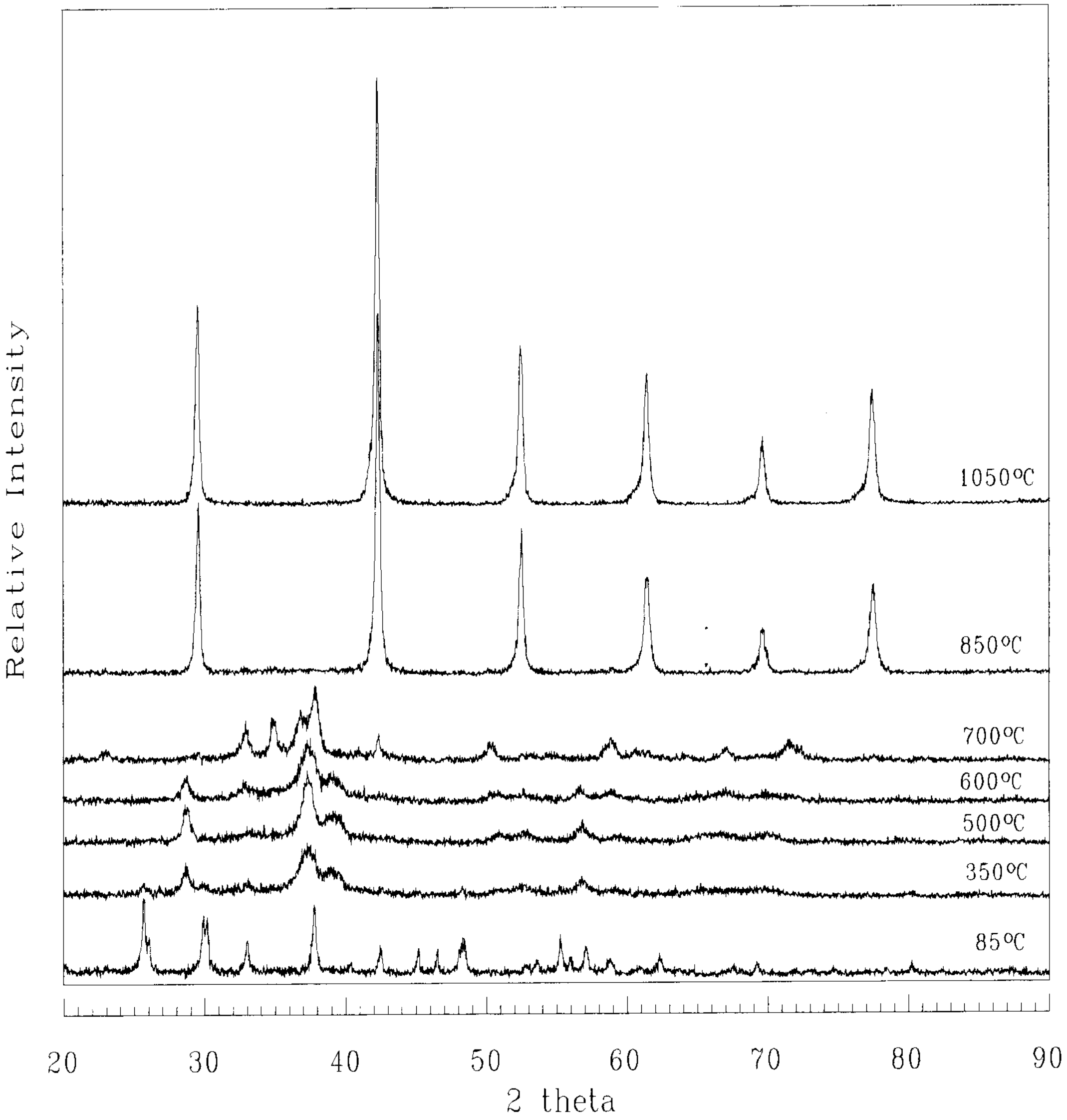

Fig. 3. Monitoring of the phase-evolution characteristics in $LaAlO_3$ precursor powders synthesized by homogeneous precipitation, via XRD.

[†] International Centre for Diffraction Data (formerly Joint Committee on Powder Diffraction Standards, JCPDS), Newtowne Square, PA.

peaks may supposedly belong to a new phase, such as $LaAl(OOH)_2$. This picture persisted, in terms of the XRD traces, at temperatures up to 700°C, at which we have detected the appearance of La_2O_3 (ICDD Powder Diffraction File cards 5-602 and 22-641). The conversion from an approximately amorphous bulk to completely crystalline $LaAlO_3$ occurred at 850°C. Further heating of the powder to 1050°C did not cause any degradation in the crystalline quality of the $LaAlO_3$ phase. These findings represent the achievement of a significant decrease (~250°C) in the synthesis temperature, as compared to the previous work on this material.

The simultaneous TG/DTA trace presented in Fig. 4, produced by using the same precursor powder (dried at 85°C following the centrifugal filtration) samples, provides a typical example on the "nonequilibrium" nature of this technique. However, it does show that the decomposition of the orthorhombic phase was completed by ~250°C. At higher temperatures, the reported temperatures by the DTA trace lag the actual thermal events, examined by isothermal heatings, by >150°C. This is exemplified to be especially so in the DTA-reported temperature of conversion to crystalline $LaAlO_3$ (992°C). On the other hand, the TG data provide more-reliable information on the nature of the reactions occurring. The TG data indicates a total weight loss of 34.2% occurs in the sample, which is too high for a simple hydroxide. Therefore, if one considers the following reactions to occur in a stepwise manner in the precursors,

$$LaAl(OH(CO_3))_2 \rightarrow LaAl(OOH)_2 + 2CO_2(g)$$

(27.51% weight loss)

$$LaAl(OOH)_2 \rightarrow LaAlO_3 + H_2O(g)$$

(7.77% weight loss)

and because the total weight loss in such a process would be 35.28%, the figure reported by the TG data would almost be in accord with the assumed scheme of processes leading to complete conversion to $LaAlO_3$.

(2) Self-Propagating Combustion Synthesis (SPCS)

The product of combustion was a voluminous and foamy amorphous precursor. This foamy precursor could easily be ground in an agate mortar to a fine white powder. The calcination and phase-evolution characteristics of these precursor powders were studied under isothermal heatings in air at different temperatures by powder XRD. The crystallization behavior of $LaAlO_3$ powder samples prepared by the combustion synthesis technique is given in Fig. 5. The crystallization of $LaAlO_3$ was noted to begin at temperatures as low as 650°C. Figure 5 shows that 750°C was the lowest temperature necessitated for the formation of phase-pure $LaAlO_3$ powders by the SPCS method. The advantage (lower temperature of crystallization of the desired phase) of the SPCS route over that of homogeneous precipitation is believed to remain in the fact that the temperatures spontaneously attained during the combustion process do instantaneously extend into the range of ~2000°C for extremely short periods of time, and this ensures obtaining an amorphous precursor powder body, which can later crystallize out the desired phase at a lower temperature. The EDXS analysis performed on all the samples displayed in Fig. 5 revealed that lanthanum and aluminum were present in exactly equal amounts, which is a fact that confirms the phase purity of these samples.

The $LaAlO_3$ powders synthesized by the SPCS route were uniaxially pressed into green pellets 1 cm in diameter and 3 mm

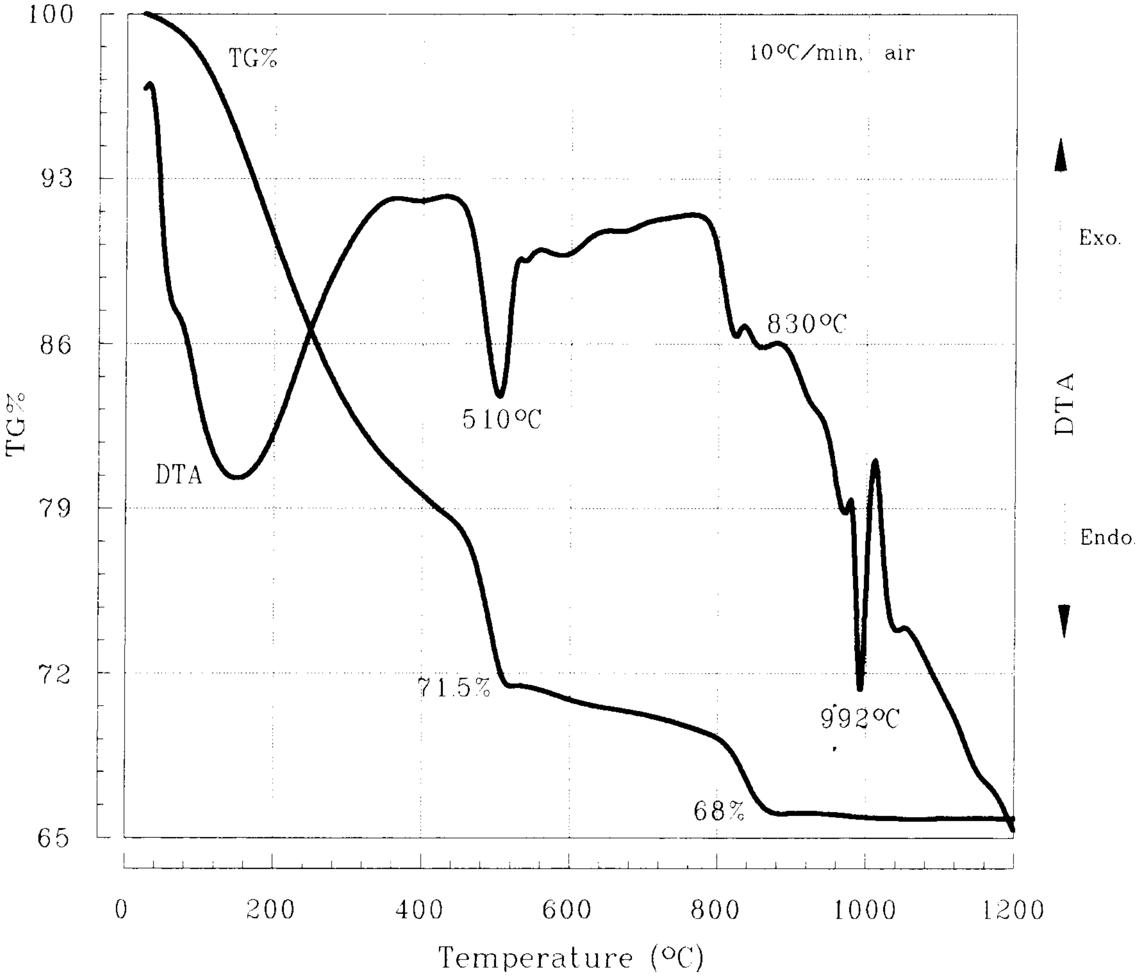

Fig. 4. Simultaneous TG/DTA traces of the precursor powders of the homogeneous precipitation process.

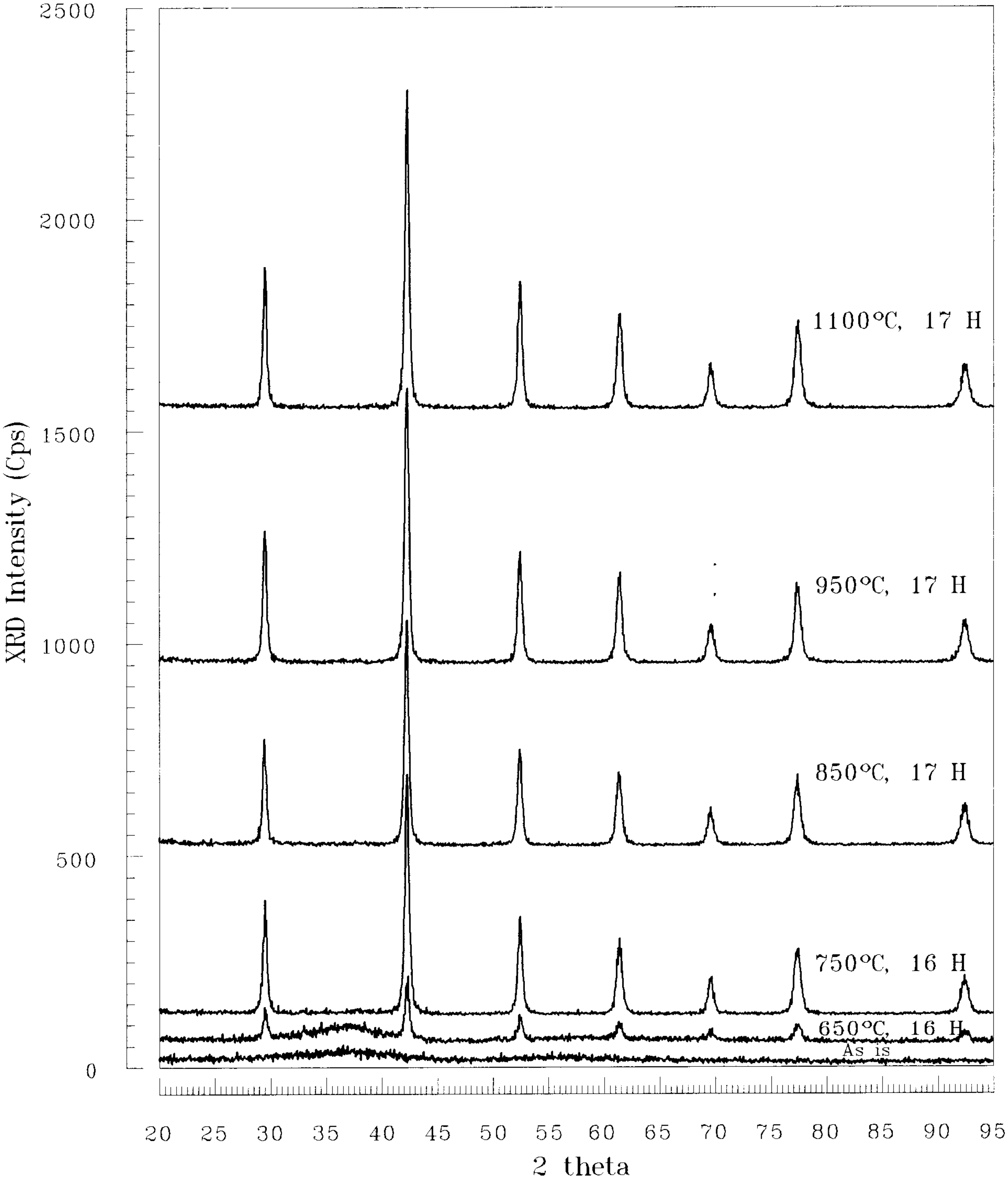

Fig. 5. Monitoring of the phase-evolution characteristics in $LaAlO_3$ precursor powders synthesized by self-propagating combustion synthesis, via XRD.

in thickness at a pressure of ~200 MPa in steel dies and sintered, in an air atmosphere, separately at 1350° and 1500°C for 6 h. The SEM micrographs of the top, flat surface of the pellet (1350°C) and fracture surface (1500°C) of these samples are given in Figs. 6(A) and (B), respectively. From the microstructure of the sample heated at 1350°C, this temperature apparently was simply insufficient for densification (~75%) to be achieved in the SPCS powders of $LaAlO_3$. On the other hand, the SEM micrograph of the fracture surface of the pelletized sample heated at 1500°C for 6 h (Fig. 6(B)) displays a significant amount of densification (>99% of the theoretical density), and recrystallization apparently occurs with final grain sizes not exceeding the micrometer level.

(3) Structural Refinements by Rietveld Analysis

Rietveld analysis[30,31] has been performed on the $LaAlO_3$ samples (produced by both techniques—homogeneous precipitation and SPCS) calcined at 1000°C in air for 17 h. Our initial purpose in applying this technique was mainly to check the crystallographic phase purity of our samples. After refining[32,33] the background, temperature, and positional parameters, the structure was found to be rhombohedral, with the hexagonal cell parameters a = 0.53619(1) nm (5.3619(1) A) and c = 1.31045(1) nm (13.1045(1) A); the estimated standard deviations in the last significant figure are given in parentheses. Also, the $LaAlO_3$ phase does not possess a tetragonal polymorph, as does its neighboring element, cerium, in the case of $CeAlO_3$.[12]

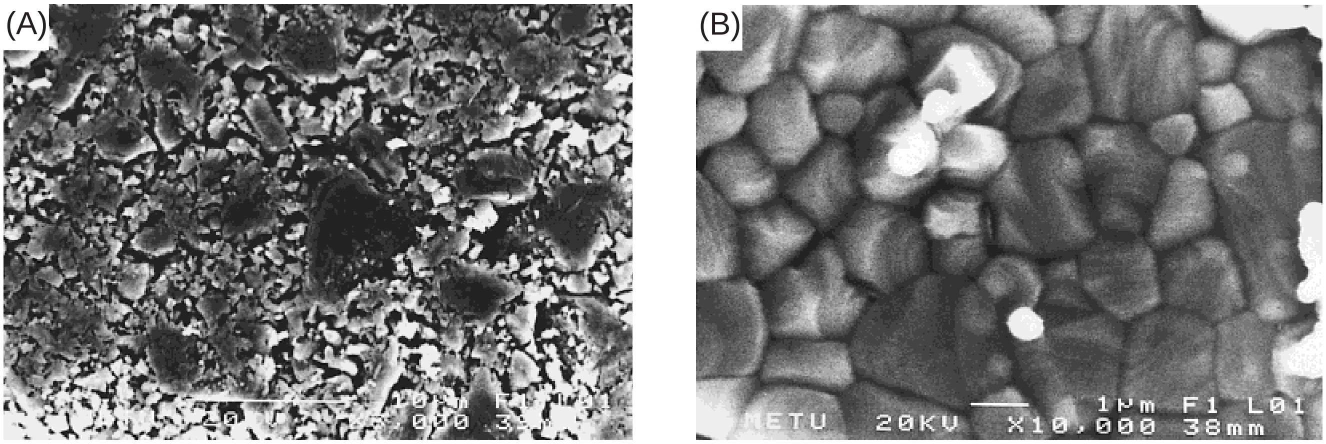

Fig. 6. SEM micrographs of the fracture surfaces of the pellets prepared using $LaAlO_3$ powders synthesized by self-propagating combustion synthesis at (A) 1350° and (B) 1500°C for 6 h.

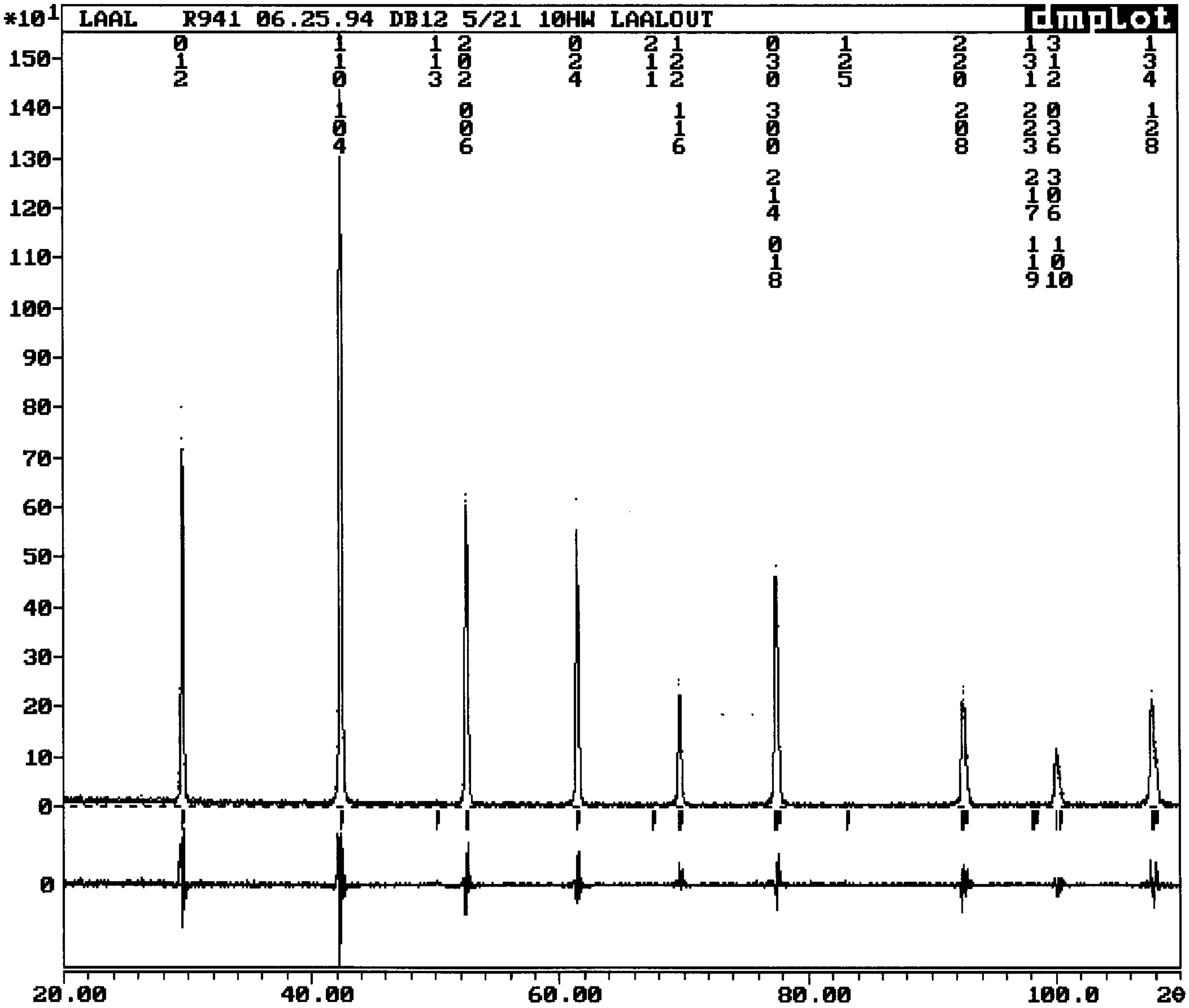

Fig. 7. Rietveld plot of $LaAlO_3$ precursor powders, from self-propagating combustion synthesis, calcined in air at 1000°C overnight. Indices with the hexagonal unit-cell settings are shown (*y*-axis is relative intensity, in counts per second (cps)).

The Rietveld plot of this study is reproduced in Fig. 7. The disagreement factor (R_{wp}) was 2.1% for the entire refinement. The lattice parameters were in agreement with the parameters asserted in ICDD Powder Diffraction File cards 9-0072 and 31-22 for $LaAlO_3$. However, in our analysis, the space group of this phase preferred the disordered R-3c (167) over R-3m (166), which was claimed in both of the previous studies leading to those ICDD file cards. This controversy is believed to originate from the early work of Geller and Bala,[6] in which the space group R-3m (166) was suggested to be the most probable space group for the rare-earth aluminates $PrAlO_3$ and $NdAlO_3$. In the more-recent studies of Denighetti *et al.*,[35] Scott,[36] Jacobson *et al.*,[37] and Banks *et al.*[38] on $LaAlO_3$, $NdAlO_3$, and $BaTbO_3$, however, the choice of the space group R-3c (167) was already reported to have a greater likelihood for these pseudo-perovskites. The significant structural differences between the two space groups could be summarized as follows: the R-3m structure would place aluminum ions at $-3m$ sites, lanthanum ions at $3m$ sites, and oxygen ions at m sites, whereas the R-3c structure would have aluminum ions at -3 sites, lanthanum ions at 32 sites, and oxygen ions at 2 sites.

The positional parameters of the $LaAlO_3$ structure were determined by Rietveld refinements. The atom positions in the hexagonal settings of the $LaAlO_3$ unit cell are as follows: 2 La^{3+}: 0 (0.25), 0 (0.25), 1/4 (0.25); 2 Al^{3+}: 1/3 (0.0), 2/3 (0.0), 2/3 (0.0); and 6 O^{2-}: 1/6 (−0.295), 1/3 (0.769), 7/12 (0.25). The positions in the rhombohedral settings are given in parentheses for the x, y, and z fractions, respectively. The rhombohedral unit cell of $LaAlO_3$ is drawn in Fig. 8. $LaAlO_3$ was found to be almost isostructural with the antiferromagnetic $BaTbO_3$.

IV. Summary

One of the rare-earth monoaluminates, $LaAlO_3$, was synthesized by two different chemical synthesis techniques: (i) from aqueous solutions containing NO_3^- as the supporting anion in the presence of CH_4N_2O by homogeneous precipitation, and (ii) from aqueous solutions containing the respective nitrate salts of the cations and CH_4N_2O by self-propagating combustion synthesis.

The decomposition of CH_4N_2O regulated the precipitation kinetics in homogeneous precipitation. This study has shown that preparing chemically homogeneous submicrometer particles of $LaAlO_3$ via aqueous precipitation techniques is possible. Nevertheless, the formed particles were heavily agglomerated. Precursors were crystalline and exhibited a unique orthorhombic structure that possibly belongs to a new phase with the tentative formula $LaAl(OH(CO_3))_2$. The hydroxycarbonate precursor powders decomposed to hydroxides in the temperature range of 250°–300°C and then converted at ~850°C to pure $LaAlO_3$ in a stepwise manner.

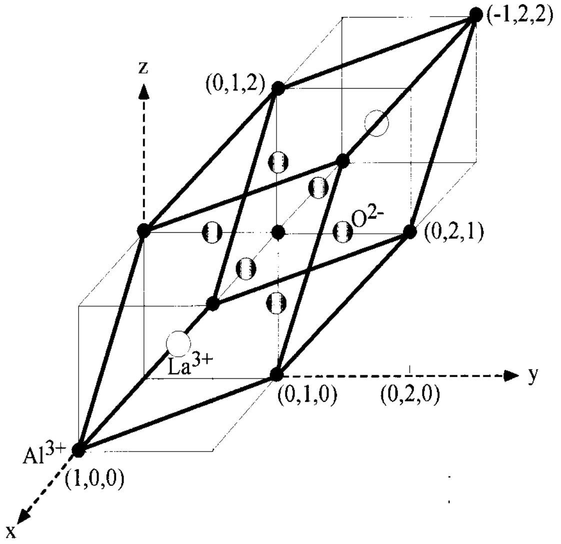

Fig. 8. Rhombohedral structure of the unit cell of $LaAlO_3$. Relation of the primitive rhombohedral cell (a = 5.355 A, α = 60.16°, space group of R-3c) to the perovskite cube is shown.

The second chemical synthesis technique, self-propagating combustion synthesis, that we used to produce $LaAlO_3$ powders yielded an amorphous precursor after the 500°C combustion step, which then can be converted into a pure crystalline phase at ~650°C by calcination in an air atmosphere for ~16 h. This temperature represents the lowest-ever synthesis temperature reported for one of the powders of refractory rare-earth monoaluminates.

The Rietveld structural analysis performed on the samples showed that the rhombohedral pseudo-perovskite $LaAlO_3$ did actually belong to the space group R-3c, in contrast to the assumed space group R-3m for this phase. Unit-cell parameters of the structure were refined and presented.

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