

A "Green Chemistry" Approach to the Synthesis of Rare-Earth Aluminates: Perovskite-Type LaAlO₃ Nanoparticles in Molten Nitrates

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Perovskite-type LaAlO₃ nanoparticles have been prepared by a facile, rapid, and environmentally friendly molten salts method using alkali metal nitrates as low-temperature fluxes. Starting from hydrated lanthanum and aluminum nitrates and alkali metal hydroxides, the proposed methodology consists briefly of two steps: a mechanically induced metathesis reaction followed by short firing at temperatures above nitrates melting points. The purpose of the first is twofold: on the one hand to generate in situ the alkali metal nitrate flux and on the other hand, to obtain a La and Al-containing precursor material suitable for the synthesis of bulk LaAlO₃ nanoparticles in molten nitrates. Different alkali metal nitrates and eutectic mixtures were used to analyze the influence of melt basicity in the reaction outcome. Single phase LaAlO₃ was obtained directly, without any purification step when using three molten media: LiNO₃, NaNO₃, and their mixture; using KNO₃ as flux either alone or as part of eutectic compositions, prevents complete conversion, and the title material is obtained mixed with additional crystalline phases such as lanthanum hydroxinitrates and carbonates. As-prepared LaAlO₃ powders are composed of loosely agglomerated nanoparticles with very fine crystallite size (32-45 nm). The present method reduces considerably previously reported synthesis time/temperatures for this material.

I. Introduction

HERE is a particular scientific and technological interest I worldwide in developing cleaner and more efficient methods for the synthesis and manufacturing of ceramic materials with well controlled properties, i.e., size, shape and crystal structure; thus, great emphasis is placed nowadays on the implementation of environmentally friendly procedures which could reduce or even avoid the use and generation of hazardous substances while minimizing waste production and energy consumption. This contribution presents a "green chemistry" approach for the nanoscale synthesis of a technologically important ceramic material, perovskite-type lanthanum ortho-aluminate LaAlO₃ (LAP); as many other rareearth aluminates, LAP shows excellent chemical and thermal stability (m.p. ~2110°C), mechanical durability and exploitable optical and electrical properties leading to a wide range of potential applications. Thus, LAP provides excellent lattice match and good matching for thermal expansion to many materials with perovskite structure and hence, is fre-

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quently used as a substrate and buffer layer for depositing high-temperature superconductor and ferroelectric thin films¹⁻ it has been also used as support for combustion catalysts or even as a catalyst itself for the oxidative coupling of methane and hydrogenation of hydrocarbons.⁵⁻⁷ Owing to its high quality factor ($Q_{\rm f}$) and relative permittivity ($\varepsilon_{\rm r}$) LAP is in addition a promising candidate for low loss microwave and dielectric resonance applications.^{8,9} Finally, with La³⁺ and/ or Al³⁺ partially replaced by Sr^{2+} and/or Mg^{2+} , respectively, LAP becomes a good oxygen ion-conducting material at low oxygen partial pressures and high temperatures changing to a mixed ionic and p-type electronic conductor at high oxygen pressures.¹⁰⁻¹² As many alumina-based ceramics, rare-earth aluminates are refractory materials and their synthesis is normally carried out by an energy intensive solidstate reaction, either by the conventional ceramic method at very high temperatures or by precipitation of a precursor material from solution and subsequent calcination with numerous grinding and firing cycles needed to obtain single phase samples. In addition, as La₂O₃ is very sensitive toward CO_2 and moisture, its exposure to atmospheric air frequently leads to hydroxylation and/or carbonation, the latter having a negative effect on reactivity because of the high decomposition temperatures of lanthanum carbonates. Thus, temperatures well above 1500°C are required to prepare bulk LAP powders when using fairly inert Al₂O₃ as Al-donor and La_2O_3 as the lanthanum source. Alternative methods such as sol-gel,^{13,14} high-energy mechanical milling using transient alumina as Al source,¹⁵ chemical coprecipitation^{16,17} or self-propagating combustion reaction^{18,19} to mention some, have successfully reduced the LAP synthesis temperatures to the 700°C-1000°C range. However, wet- and soft-chemistry methods applied to the synthesis of aluminum-containing species are in general time-consuming and very challenging because of the large number of Al^{3+} hydroxide and oxyhydroxide species existing in solution, each having specific physicochemical properties and demanding the optimization of many different experimental parameters such as pH, nature of starting chemicals, temperature or even, mixing procedures. To the best of our knowledge, a substantial reduction in the synthesis temperature below ~600°C has been only achieved by using an autoclave and high water vapor pressure (2–26 MPa) with the so-called "supercritical water fluid" method (SCWF); however, even after long soaking times under extreme conditions (24 h at 200°C and 18 h at 380°C), submicron LAP particles (200-300 nm size) were only obtained mixed with a large proportion of secondary phases.20 Herein we report a novel, facile, rapid, and cost-effective

Herein we report a novel, facile, rapid, and cost-effective method for the large-scale production of $LaAlO_3$ nanocrystals by combining a metathesis reaction and short firing at remarkably low temperature of 350°C. The proposed methodology compares favorably with previously suggested approaches for the synthesis of nanocrystalline LAP and

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might well be useful to prepare other perovskite and garnettype complex oxides based on Ln_2O_3 -Al₂O₃ combinations (Ln: lanthanides and yttrium) for optical, electronic, and structural applications.

II. Experimental Procedure

The starting materials used were obtained as follows: La (NO₃)₃·6H₂O (Aldrich, St. Louis, MO, 99.99%), Al (NO₃)₃·9H₂O (Aldrich, A.C.S. Reagent, 98 + %), NaOH (Aldrich, Reagent grade, 97%), LiOH·H₂O (Aldrich, A.C.S. Reagent, 98 + %), and KOH (Aldrich, A.C.S. Reagent, 85 + %). A typical experiment was conducted according to the following procedure shown schematically in Fig. 1: an equimolar mixture of hydrated lanthanum and aluminum nitrates was combined with an alkali metal hydroxide or hydroxides mixture, transferred to an yttria partially stabilized zirconia container (5.2 wt% Y2O3) together with 20 mm diameter YPSZ balls as grinding media and milled for 30 min in a planetary ball mill (Retsch GmbH, Haan, Germany) using a rotating disk speed of 350 rpm and a balls-to-powder mass ratio of 10:1. The amount of reactants was salt-balanced such that there were no alkali metals or nitrates excess according to the following equation (alkali metals/total nitrates molar ratio = 3/1):

 $\begin{array}{l} Al(NO_3)_3 \cdot 9H_2O + La(NO_3)_3 \cdot 6H_2O + 6AOH \\ \rightarrow LaAlO_3 + 6ANO_3 + 18H_2O \end{array}$

The resulting activated precursor material was dried 1 h at 120°C to reduce moisture and to minimize violent gas evolution on melting and finally loaded into alumina crucibles, fired in air 3 h at different temperatures using an electrical furnace (heating rate = $5^{\circ}C/min$) and cooled thereafter to room temperature. As-obtained solidified melts were suspended in distilled water to separate the alkali metal nitrate by-product from the water insoluble fraction which was then collected by filtration or centrifugation, dried 3 h at 120°C and characterized by different techniques. Thus, phase analysis was carried out using X-ray diffraction in a Philips X'Pert diffractometer (PANanalytical B.V., Almelo, Holland) using Ni-filtered CuKa radiation ($\lambda = 1.5418$ Å) in the 10°–80° (20) range (0.025°/s). Thermal stability of the as-prepared precursor materials was examined by simultaneously recording the thermogravimetric and differential thermal analysis curves in static air, in a Perkin-Elmer Pyris Diamond TG/DTA model (PerkinElmer, Inc, Waltham, MS) using a typical sample size of 15 mg and a heating rate of 5°C/min. Particles size distribution of the as-prepared nanopowders was examined by using a Horiba Partica LA-950V2 Laser Diffraction/Scattering Analyzer (HORIBA Instruments, Inc, Irvine, CA) after



Fig. 1. Flowchart illustrating the experimental procedure followed in this work.

ultrasonically suspending the solid (LAP index of refraction $n_D \approx 2$) in an aqueous solution containing TAMOLTM 960 (2.5 wt% of powder charge) as dispersing agent. The instrument is equipped with two different light sources, a 650 nm red laser diode and a 405 nm blue emitting diode (LED), and uses the Mie scattering theory to accurately measure particle size from 3 mm down to 10 nm. Powder microstructural characteristics were analyzed using scanning electron microscopy using a JEOL JSM6400 microscope (JEOL Ltd., Tokyo, Japan) equipped with an Oxford INCA 300 x-sight Energy Dispersive X-ray Spectrometer (Oxford Instruments, Abingdon, Oxfordshire, U.K.) and using high-resolution transmission electron microscopy using a Jeol-2000 FXII microscope equipped with an Oxford INCA 200 ×-sight EDS system. For the latter characterization, LAP powders were suspended in ethanol with ultrasonic agitation and drop cast onto a carbon-coated copper grid. The chemical composition of the as-prepared nanoparticles was determined using the microscopes by using energy dispersive analysis of X-rays and in bulk powders by X-ray fluorescence spectrometry using a 4 kW S4 Pioneer (Bruker AXS GmbH, Karlsruhe, Germany) sequential wavelength-dispersive X-ray fluorescence spectrometer (WDXFS).

III. Results and Discussion

A metathesis or displacement chemical reaction involves the exchange of atomic/ionic species between reactants to give stable products and has become in recent years an alternative route for the synthesis of important solid-state compounds²¹; because of Al³⁺ low reactivity in molten nitrates, in our case the purpose of using such reaction is twofold: on the one hand to generate in situ alkali metal nitrates, high-lattice energy by-products, and thus the driving force behind the metathesis reaction itself and at the same time the reaction media for molten salt synthesis; on the other hand to produce a suitable lanthanum and aluminum (La and Al)containing precursor material for the synthesis of LAP nanoparticles in molten nitrates. Molten salts synthesis (MSS) of ceramic materials is usually carried out by blending the appropriate inorganic precursor salts with a large excess of the desired flux and firing the mixture to the reaction temperature, above the flux melting point. Salts most commonly used as fluxes in MSS are selected amongst alkali and alkaline-earth metal hydroxides, nitrates, halides, carbonates or sulfates; low-cost nitrates and/or their eutectic mixtures are normally preferred because of their lower melting points (see Table I),²² their stability over a wide liquid temperature window (typically up to ~550°C) and their high water solubility which facilitates recovering of the target phase by simply washing the solidified melt with distilled water. As reaction media, molten nitrates behave as a Lux-Flood base²³ and thus, they are not only the non-aqueous solvents facilitating ion diffusion but also the sources of active species, i.e., oxide ions and/or oxygen atoms; reactivity in molten nitrates depend mainly upon reactants nature and basicity of the melt which regarding alkali metal nitrates, decreases as the size of the alkali metal cation increases (Li > Na > K).

This contribution will first present results obtained with individual hydroxides/nitrates and then with their eutectic mixtures, including at the end, a relevant discussion.

(1) Synthesis of LaAlO₃ in Molten Alkali Metal Nitrates

Figure 2 shows the XRD analysis of a mixture consisting of hydrated La and Al nitrates and lithium hydroxide, LiOH, at different stages of the experimental process together with the XRD patterns found in the JCPDS-ICDD databank as characteristic of rhombohedral LiNO₃ (PDF card no. 08-0466) and LaAlO₃ (PDF card no. 31-0022). To facilitate phase identification, each individual XRD pattern is normalized with respect to its most intense reflection. Since LiNO₃ is the

Table I.	Melting 1	Points of Some	Common Fluxes	Used in Molt	en Salt Synthesis
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Flux	NaNO.	NaOH	NaCl	Na-CO-	Na.80.
Malting paint (9C)	210	210	909	054	Na ₂ 50 ₄
Melting point (°C)	310	318	808	854'	884
Flux	LiNO ₃	KNO_3	$NaNO_3/LiNO_3 (46:54)^{\ddagger}$	$NaNO_3/KNO_3 (50:50)^{\ddagger}$	$LiNO_3/KNO_3 (41:59)^{\ddagger}$
Melting point (°C)	254	337	193	220	133.5
to un					

[†]Decomposition temperature.

[‡]Mol%.

only crystalline product clearly identified in the XRD pattern labeled in Fig. 2 as "Milled" and collected after 30 min, it is obvious that a mechanically induced metathesis reaction took place in the starting mixture in such a short milling time. There is in addition a series of broad and very low intensity reflections such as those centered around ~28°, ~39° and ~48° (2 θ) which were identified as belonging to hexagonal La(OH)₃ (PDF card no. 36-1481) suggesting the formation also of very fine or poorly crystalline particles of this material on milling; no sign of any crystalline aluminum species is apparently observed. To induce LiNO₃ melting, the as-prepared precursor material was first dried at 120°C, fired at 350°C, and analyzed again using XRD (pattern labeled as "Fired"). A new set of reflections marked in Fig. 2 with asterisks and identified as characteristic of the rhombohedral LAP target material, are clearly visible besides those characteristic of LiNO3: e.g., rhombohedral LAP most intense reflection of Miller indexes (110) at 33.41° (20). Finally, as shown at the top of the same figure (diffraction pattern named "Washed"), polycrystalline LAP was easily isolated after removing the soluble LiNO3 by-product by washing with distilled water. Since no additional crystalline phases (not even La(OH)₃) are apparently present, it might be assumed that both cations, aluminum and lanthanum, reacted completely in molten LiNO3 at a remarkably low temperature of 350°C. It was decided then to test the method just described with NaOH and KOH as promoters of the metathesis reaction instead of LiOH and thus, using NaNO₃ and KNO₃ as reaction media in the MSS step.

Figure 3 shows the XRD patterns obtained from a sample subjected to the same experimental procedure described above but by replacing LiOH by NaOH. The first conclusion



Fig. 2. X-ray diffraction patterns of the reaction mixture containing LiOH after milling (Milled), firing at 350° C (Fired) and removing the soluble LiNO₃ component (Washed). Reflections marked with diamonds and asterisks are those characteristic of La(OH)₃ and LaAlO₃, respectively. XRD patterns of LiNO₃ and LaAlO₃ found in the JCPDS-ICDD databank are also included as a reference.

LaAIO. Washed (a.u.) Fired ntensity Milled NaNO, 15 20 25 30 35 40 45 50 55 60 65 70 75 80 2 Theta(°)

Fig. 3. X-ray diffraction patterns of the reaction mixture containing NaOH after milling (Milled), firing at 350°C (Fired) and removing the soluble NaNO₃ component (Washed). Reflections labeled with asterisks are those characteristic of rhombohedral LaAlO₃. Reported XRD patterns of NaNO₃ and LaAlO₃ are also shown as a reference.

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to be drawn after examining the XRD pattern labeled as "Milled" is that as before, a metathesis reaction takes place on milling with sodium replacing both trivalent metals in their nitrates. In this case, NaNO₃ is the only crystalline phase present (PDF card no. 36-1474) and thus, both lanthanum and aluminum species are present as amorphous materials. After heating above NaNO₃ melting point, the XRD pattern ("Fired") still contains the reflections belonging to NaNO₃ but together with those characteristic of the LAP target material and marked with asterisks. No additional phases are evident after removing the nitrate by-product (XRD pattern labeled as "Washed") and thus, the procedure presented herein is also useful to obtain LAP powders at very low temperatures using an in situ generated NaNO₃ flux.

Figure 4 shows the evolution of a sample containing KOH when subjected to the same sequence of experiments. The presence of the characteristic reflections of orthorhombic KNO₃ (PDF card no. 05-0377) in the XRD pattern labeled as "Milled" confirms as well that milling induces a metathesis reaction; however, it is also evident the presence of a noticeable amount of La(OH)3 in the sample, in fact much larger than that when milling is carried out in the presence of the less basic LiOH or NaOH. Firing above the KNO₃ melting point (XRD pattern labeled as "Fired") yielded a mixture of LAP and KNO3 although the identification of the former is difficult because of overlapping reflections. Finally, a mixture of hexagonal La(OH)3 and rhombohedral LAP is obtained after washing with distilled water. Although as shown by XRD, the characteristic reflections of La(OH)₃ disappear almost completely on firing, they reappear again after washing because of dehydration/rehydration suggesting thus, the



Fig. 4. X-ray diffraction patterns obtained for the reaction mixture containing KOH after milling (Milled), firing at 390° C (Fired) and removing the soluble KNO₃ component (Washed). Reflections labeled with asterisks are those characteristic of LaAlO₃. Reported XRD patterns of La(OH)₃ and KNO₃ are also shown as a reference.



Fig. 5. Thermal analysis curves obtained for the products of the SSM reactions in mixtures containing LiOH (top), NaOH (middle) and KOH (bottom), after milling for 30 min.

presence of an important amount of unreacted La^{3+} (and thus, Al^{3+}) in the latter sample.

Figure 5 shows the thermogravimetric and differential thermal analysis curves of the precursor materials obtained after milling equimolar mixtures of hydrated La and Al nitrates with Li, Na, and K hydroxides which are in fair agreement with those previously published for the three alkali metal nitrates alone. Thus, the presence in each case of an intense endothermic event without weight loss at temperatures very close to those reported in literature as the melting points of the corresponding nitrates (see Table I), confirms that independently of the alkali metal hydroxide used, mechanical milling triggers a metathesis reaction in these systems. Furthermore, two additional endothermic events without associated weight losses found at ~130°C and ~275°C in the KOH- and NaOH-containing mixtures, respectively, are ascribed to KNO₃ and NaNO₃ polymorphic transformations. Thus, KNO₃ is known²⁴ to undergo a reversible transformation at ~130°C from the room temperature and atmospheric pressure stable orthorhombic form (form II) to a rhombohedral one (form I). As for NaNO₃, the transformation takes place at $\sim 275^{\circ}$ C from an ordered rhombohedral phase (form II) to a disordered one (form I).²⁴ The nature of the alkali metal ion does not seem to have almost any influence on the loss mass observed between room temperature and the nitrates melting points reaching between 7% and 9% of the initial weight as shown in the TGA curves; thus, similar losses are observed mostly in a single event detected at increasing temperature as the nitrate melting point increases: 185°C, ~200°C, and 237°C for the LiNO₃-, NaNO₃-, and KNO₃-containing systems, respectively. This weight loss is accompanied by an endothermic peak in the DTA curves of the first and latter precursors and is probably due to some dehydration process of the La and/or Al species formed initially on milling. An additional small endothermic event without weight loss is observed at ~297°C in the KNO3containing system.

Therefore, we have shown that rhombohedral LAP can be prepared at very low temperatures by using Li, Na, or K nitrates fluxes following the proposed methodology, although single phase samples were only obtained when using the more reactive Li and Na nitrate melts. As shown using XRD, hydroxides' basicity plays also an important role in the outcome of the process with the more basic KOH stabilizing La and Al hydroxides in the precursor material and thus, hindering the formation of the mixed oxide in the corresponding molten nitrate. It is important to mention at this point that our attempts to prepare the target material by just mixing an equimolar mixture of La(NO₃)₃·6H₂O and Al(NO₃)₃·9H₂O with commercially available alkali metal nitrates and firing above the latter melting points, proved to be unsuccessful evidencing the importance of the metathesis reaction when generating a suitable precursor material for the MSS step.

(2) Synthesis of LaAlO₃ in Molten Alkali Metal Nitrate Eutectics

In an attempt to reduce even further the synthesis temperature, it was decided to test also this methodology using alkali metal nitrate eutectics generated in situ through a metathesis reaction. Thus, an equimolar mixture of hydrated aluminum and lanthanum nitrates was mechanically blended with a mixture of two hydroxides, either LiOH/NaOH, LiOH/KOH or NaOH/KOH. Whereas the total alkali metals to nitrates molar ratio was maintained at 3 to 1 as described in Section II, each hydroxide was weighed out according to the corresponding nitrates eutectic composition, i.e., NaNO₃/LiNO₃ eutectic is 46:54 mol% and thus, NaOH/LiOH were added in a 46:54 mol% ratio. Figure 6 shows an XRD analysis of this particular sample selected as representative of the series at different stages of the process whereas Fig. 7 shows the thermal evolution of the precursor mixture obtained after milling for 30 min. The first important conclusion drawn from the XRD pattern of the sample that was only milled is that both hydroxides participated in the metathesis reaction since the characteristic reflections of lithium and sodium nitrates are clearly seen. In addition, La(OH)₃ is also found together with some other small reflections which we were not able to assign to a known material. The thermal analysis curves shown in Fig. 7 also support the idea of a complete metathesis reaction since there is an intense endothermic peak at 194°C which happens to be the melting temperature of the NaNO₃/LiNO₃ eutectic and no events are observed at the melting points of neither NaNO₃ nor LiNO₃. In addition, there is also another endothermic event at 176°C just before melting, which is accompanied by a small weight loss and might be related with the ones observed in the TGA curves of the three nitrates shown in Fig. 5. Thus, this precursor mixture was fired 3 h at two temperatures above the eutectic melting point (i.e., 250°C and 350°C) and the XRD patterns are also shown in Fig. 6. Interestingly and excluding those of

the nitrates fluxes, the characteristic reflections of the target material are already the most intense in the XRD pattern obtained after firing at incredibly low 250°C; however, there are also additional peaks indicating the presence of secondary phases such as lanthanum hydroxinitrates and carbonates suggesting that the experimental parameters used are not sufficient to promote the formation of single phase LAP powders. However, when the same precursor material is fired at 350°C, the XRD pattern contains only the reflections of both nitrates and the target LAP material which is then isolated as single phase after washing with distilled water. Similarly, no single phase LAP powders were obtained after milling the hydrated metal nitrates with mixtures of LiOH/KOH and NaOH/KOH in a weight proportion matching that of their eutectics and firing at different temperatures above their melting points but below 350°C. Figure 8 shows a comparison between the XRD patterns of samples prepared in the three eutectic compositions after firing at 350°C and removing the water soluble components. As it can be seen, the three milled precursors rendered LAP although when KNO₃ is present, reaction does not seem to be complete with unreacted lanthanum existing as a very small amount of carbonate or hydroxycarbonate.

(3) Crystallite Size and Particles Size Distribution

Powder samples prepared in LiNO₃, NaNO₃ and their eutectic mixture were further analyzed by using different techniques. The X-ray line broadening method was used to calculate the crystallite size of the as-prepared LAP nanopowders using the Scherrer formula:

$D = 0.9 \cdot \lambda / B \cdot \cos \theta_{\rm B}$

where *D* is the average crystallite size, *B* is the full width at half-maximum XRD peak (110) in radians, λ is the wavelength of the incident X-ray radiation and θ_B is the Bragg angle in radians. Results obtained were in the 32–45 nm range and are shown in Table II together with the particle size of the same samples determined using laser diffraction technique; Fig. 9(a) shows a typical graphic representation of such determination obtained for the sample prepared in molten LiNO₃/NaNO₃ eutectic selected as representative of the series. As shown, this sample presents a multimodal particle size distribution (PSD) with ~80% having an equivalent



Fig. 6. X-ray diffraction patterns of the reaction mixture containing LiOH and NaOH after milling (Milled), firing at 250°C and 350°C and removing the water soluble LiNO₃ and NaNO₃ components of the latter (Washed).

spherical diameter equal or below 100 nm (mode size 64.9 nm); there are also two additional peaks in the PSD graph, the first centered around 260 nm and the second corresponding to a much coarser group of particles located around 1.8 µm indicating the presence of large agglomerates of nanometric particles. Similar PSD results were obtained for the remaining samples prepared in LiNO₃ and NaNO₃ alone although as Table II shows, the flux with the lowest melting point of the three, leads also to a considerable reduction in the D90 size because of a decreasing fraction of large agglomerates. Figures 9(b)-(f), show SEM and TEM micrographs of some samples prepared in this work, before and after removing the water soluble components. As shown in (b), after firing and cooling down to room temperature, our samples consist of large grains with small brighter particles at their surface; EDS microanalysis carried out in conjunction with SEM confirmed the first ones to be the solidified alkali metal nitrate fluxes (NaNO3 in this case) whereas the second ones correspond to the LAP mixed oxide. SEM micrographs shown in (c) and (d) correspond to LAP powders prepared in LiNO₃ and NaNO₃, respectively, after removing the nitrate by-product whereas (e) and (f) are TEM micrographs of the latter sample. As shown, the samples are basically constituted by well crystallized LAP nanocrystals (La/Al atomic ratio as determined by EDS almost identical to the expected theoretical value within experimental errors) aggregated together to form loosely agglomerates of submicronic and more or less round shaped particles.



Fig. 7. Thermal analysis curves of the precursor obtained after milling an equimolar mixture of the hydrated La^{3+} and Al^{3+} nitrates, with a mixture of LiOH and NaOH.



Fig. 8. X-ray diffraction patterns of the reaction mixture containing LiOH/NaOH (top), LiOH/KOH (middle) and NaOH/KOH (bottom) after the SSM reaction, firing at 350°C and removing the water soluble components.



Fig. 9. (a) Size distribution data for LAP particles prepared in molten $LiNO_3/NaNO_3$; (b) SEM micrograph of the precursor prepared by milling hydrated La and Al nitrates and NaOH after firing at 350 showing a very large NaNO₃ particle covered by small LAP brighter particles; (c) and (d) SEM micrographs of the LaAlO₃ powders prepared in molten LiNO₃ and NaNO₃, respectively, after removing the water soluble components; (e) and (f) TEM micrographs showing LaAlO₃ nanocrystals prepared in molten NaNO₃.

Tabl	le II.	Crysta	allite an	d Partic	le Size of	f LAP	
Samples	Obtai	ied in 1	Molten	LiNO ₃ ,	NaNO ₃ ,	and T	Their
-		Eı	itectic I	Mixture			

Crystallite size	Mode size	D50	D90
(nm)	(nm)	(nm)	(nm)
35	64.3	68.4	324.9
32	62.4	65.1	327.8
45	64.9	68.8	223.2
	Crystallite size (nm) 35 32 45	Crystallite size (nm)Mode size (nm)3564.33262.44564.9	Crystallite size (nm) Mode size (nm) D50 (nm) 35 64.3 68.4 32 62.4 65.1 45 64.9 68.8

IV. Discussion

The proposed two-step methodology compares favorably with existing techniques for the synthesis of bulk LAP powders since neither La^{3+} nor Al^{3+} nitrates or hydroxides, allow obtaining the crystalline target material at such low temperatures. Thus, different attempts have been carried out to synthesize LAP powders by first melting and then dehydrating and firing equimolar mixtures of both hydrated metal nitrates^{25–27}; according to these reports, the crystallization of bulk LAP starts at a very high temperature, typically in the 700°C–1000°C range, although as-prepared samples still contain a large amorphous fraction and need further heating at temperatures higher than 1100°C to fully transform reactants into polycrystalline LAP and avoid the formation of the very stable corundum phase. The low reactivity of La and Al nitrates is probably caused by the complexity of their thermal decomposition mechanisms and the large number of possible intermediate species. Thus, $La(NO_3)_3 \cdot 6H_2O$ powders melt at ~56°C and then dehydrate and decompose on heating in a series of endothermic steps which yield an oxynitrate LaONO₃ at ~350°C and finally crystalline La_2O_3 at ~600°C.^{28,29} As the intermediate LaONO₃ is very reactive toward CO₂, a certain amount of La2O2CO3 is frequently produced when firing hydrated lanthanum nitrate in air requiring temperatures higher than 800°C to obtain pure La₂O₃. As for the hydrated aluminum nitrate $Al(NO_3)_3$ 9H₂O, its thermal decomposition does not give any stable anhydrous intermediate with the salt melting at ~80°C and dissociating below 400°C by the simultaneous dehydration and elimination of nitrogen oxides yields amorphous aluminum oxides and eventually if the temperature is high enough^{30,31} (>1000°C), crystalline Al₂O₃.

Similarly, La and Al hydroxides only decompose at relatively high temperatures and thus, are not suitable starting chemicals for the low temperature synthesis of LAP. Hence, thermal analysis studies of La(OH)₃ show³² two endothermic steps of mass loss at 386°C and 535°C, the first one rendering a lanthanum hydroxide oxide, LaOOH, and the second

the oxide La₂O₃. Attempts to prepare LAP powders by hydroxides homogeneous precipitation from solution lead to an amorphous precursor with temperatures higher than ~850°C needed to crystallize the target material.^{16,17}

Therefore, the synthesis temperature reported herein reduces considerably the lowest temperature ever used before for the preparation of single phase LAP powders using either metal nitrates or hydroxides as starting chemicals.

A survey of the literature published on previous attempts to synthesize either of the two oxides, La₂O₃ and Al₂O₃, LAP or similar aluminates by using MSS was not very encouraging. Thus, La(III) is a weak Lux-Flood acid apparently existing in molten nitrates as a very stable lanthanyl cation LaO^+ (or $La(OH)_2^+$) which is fairly inert and insoluble reacting only at high temperatures, or as La₂O₃ which according to the Lux-Flood theory is itself a base.23,33,34 Hence, lanthanum (III) chloride or hydrated lanthanum nitrate dissolves slowly in contact with molten nitrates to yield first a lanthanum oxide nitrate LaONO3 and then on further heating at higher temperatures (~650°C) and almost simultaneously with the thermal decomposition of the nitrate flux, the corresponding La₂O₃ oxide. Unfortunately, washing the reaction product with water always leads to crystalline La(OH)3 and thus, MSS does not compete favorably with other powder processing methods commonly used for the synthesis of bulk La₂O₃. As for aluminum (III), it behaves in molten nitrates as a very strong acid and depending on the Al source, precipitates as a different form of alumina^{23,35,36} thus, aluminum (III) chloride reacts in molten nitrates or nitrate eutectics to yield very fine and poorly crystalline α -alumina whereas the sulfate, Al₂(SO₄)₃, is much more stable with reaction starting at higher temperatures and rendering γ -alumina. In contact with molten NaNO₃, KNO₃ or their mixture hydrated aluminum nitrate yields an amorphous solid which as happens with La₂O₃, is easily hydrated during the washing step yielding crystalline bayerite Al (OH)₃; thus, hydrated Al-nitrate has not been considered an appropriate Al source for the synthesis of alumina by MSS.²

Although many lanthanum containing perovskites have been prepared in molten nitrates or nitrites,^{34,37,38} reaction temperatures are in general higher than 500°C because of La high reactivity toward the atmospheric components requiring more than often a purification step to remove lanthanum hydroxinitrates or carbonates and to obtain single phase samples. As for Al-containing mixed oxides, no previous reports have been found on their synthesis in molten nitrates. LAP powders have been already prepared, 39,40 by MSS using complex fluxes and at much higher temperatures than the ones presented herein; thus, LAP particles were obtained in the 630°C-800°C temperature range using a KF/KCl eutectic salt as reaction media (melting temperature ~610°C) through a dissolution/precipitation mechanism with both starting chemicals, La₂O₃ and Al₂O₃, dissolving in the flux and LAP particles precipitating from the liquid media after it became oversaturated. The same compound was also obtained by Kojima et al. at 650°C using alkali metal carbonate eutectics as fluxes and La₂(CO₃)₃ 8H₂O and α -Al₂O₃ as lanthanum and aluminum sources, respectively. Molten carbonate eutectic facilitates LAP formation by first dissolving the lanthanum species and then making possible La^{3+} diffusion to the reaction site, at the Al_2O_3 particles surface with the reaction mechanism including the formation of a La2O2CO3 intermediate. Using a N2 atmosphere decreased the reaction temperature to 500°C but only after prolonged soaking time (72 h). In any case, the as-prepared sample contained after washing, unreacted metal oxides and lanthanum oxycarbonates needing of a final purification step using concentrated HCl.

A thorough characterization of the La- and Al- containing precursor material obtained in our case after the metathesis reaction is still very much underway and would be the subject of a follow-up publication. At this point we could only speculate on the reaction mechanism but the fact is that the only chemical species which could be identified by XRD after milling besides the corresponding alkali metal nitrates, is poorly crystalline La(OH)₃; therefore, LAP is not formed on milling but in the melt probably from Al and La hydroxides or oxyhydroxides. In any case, by introducing a metathesis reaction and obtaining an activated precursor we were able to circumvent La and Al low reactivity in molten nitrates and achieve mixed oxide formation at astonishingly low 250°C as shown in Fig. 6(a).

One of the main concerns when using dry mechanical milling for obtaining ceramic materials is the probable contamination of the samples because of wearing and debris of the milling tools; however, the experimental settings used in this work (e.g., short milling time, YPSZ containers and balls, moderate rotating disk speed and hydrated metal nitrates of low melting points as starting chemicals) were selected to minimize this problem and ensure very low levels of zirconium inclusions. Thus, Zr content determined in different samples by WDXFS was always found to be below 0.4 wt% independently of the alkali metal hydroxide used to induce the metathesis reaction. Another possible source of chemical contamination arises during the molten salt synthesis with increasing levels of impurities (basically alkali metal cations) found when using higher temperatures and long firing times. Contamination also increases as the size of the alkali metal decreases with Li being very difficult to eliminate completely from the solids after reaction because of its facility to enter different crystal lattices. However, reaction parameters used in this case (low temperatures and short firing times) should help when minimizing the impact of this source of possible contaminants: e.g., chemical analysis in different samples prepared in NaNO3 indicates the content of Na⁺ lower than 0.6 wt%. The proposed methodology proved to be also highly reproducible with yields larger than 95% with respect to the amounts of La and Al nitrates initially weighed, repeatedly obtained. Finally, we believe it might be perfectly possible to prepare pure LAP samples below 350°C by for example, raising melts basicity and thus, oxide ions concentration and this is part of our continuing effort.

V. Conclusions

We have been able to obtain nanometric LaAlO₃ particles at very low temperatures by combining a metathesis reaction and molten nitrates as reaction media. The metathesis reaction fulfils two goals which are to obtain an appropriate La- and Al-containing precursor material and to generate in situ, the nitrate flux. Irrespective of the alkali metal nitrate flux used, our results show that LaAlO₃ nanoparticles are obtained when firing the precursor material at 350°C although single phase samples are only obtained in the more reactive (basic) fluxes. The proposed methodology has some outstanding advantages over existing techniques for preparing lanthanum ortho-aluminate powders. First, it is simple, rapid, and does not involve the use of expensive chemicals (e.g., alkoxides) and thus, the entire process is cost-effective. Secondly, the synthesis is at very low temperature and does not need any sophisticated or costly equipment nor special handling precautions because is carried out under normal atmosphere; although there is still some room for improvement, the yield is very high and the process might be easily adopted for technological applications. Third, the process is non toxic because it does not involve the use of organic solvents or any purification step often needed in MSS and consisting of washing with concentrated acid solutions. The process might be expanded to other perovskite and garnet-type rare-earth aluminates with important scientific and technological applications.

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