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Low temperature synthesis of microwave dielectric $LaAlO_3$ nanoparticles: effect of chloride on phase evolution and morphology

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Abstract

A novel chemical synthesis route has been developed to prepare $LaAlO_3$ from low cost inorganic precursors, by gelation–precipitation technique. Phase evolution, morphology, agglomeration and surface area were studied as a function of chloride content and heat treatment temperature. The samples containing chloride crystallized at 1100 °C with the formation of intermediate phases. The product was highly agglomerated and had low surface area. On the contrary, the as-synthesized chloride-free samples crystallized directly to pure $LaAlO_3$ perovskite phase at 600 °C, which is the lowest crystallization temperature achieved so far. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of chloride-free samples reveal very fine clusters of nanosized spherical particles. The as synthesized and calcined chloride-free samples have a high surface area and are thermally stable upto 1600 °C without decomposition.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; D. Perovskites; E. Substrates; Phase evolution

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1. Introduction

Lanthanum aluminate ($LaAlO_3$) has a permittivity of 23, a $Q \times f$ of 65,000 and a negative τ_f of $-44 \times 10^{-6}\,^{\circ}C$ [1], suitable for applications in dielectric resonators. $LaAlO_3$ has also been widely used as a substrate for depositing superconducting thin films for microwave devices since it provides a high quality factor and excellent lattice and thermal expansion matching to Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O superconductors [2,3]. Due to its high surface area and catalytic activity, $LaAlO_3$ has also been used as catalyst for oxidative coupling of methane. However, for practical applications it is necessary to reduce the sintering temperatures of $LaAlO_3$ ceramics from 1400–1600 °C, so that it can be co-sintered with low-melting conductors to produce multilayered miniaturized devices. This can be achieved by using fine particle sized homogenous powders and/or low melting glass additions.

$LaAlO_3$ prepared by conventional solid-state reaction of oxides at high temperature (1500–1700 °C) [4,5] has large particle sizes, limited chemical homogeneity and low sinterability. Various low temperature chemical routes have been tried namely sol–gel [6], urea decomposition [7], self propagating combustion synthesis [8], coprecipitation of hydroxides [9], polymerization route [10], mechanochemical route [11], citrate combustion route [12], PVA evaporation route [13], etc. The major drawback of most of these chemical routes was that full $LaAlO_3$ phase formation was observed only above 1100 °C and the as-synthesized particles were highly agglomerated. In this study, we report an easy, inexpensive, and reliable method to synthesize $LaAlO_3$ powders, which not only crystallizes at low temperature retaining a high surface area, but also could be sintered to near full density at low temperatures, thus giving improved microwave dielectric properties.

2. Experimental

2.1. Powder preparation

High purity lanthanum chloride ($LaCl_3 \cdot xH_2O$, IRE Ltd., India) and anhydrous aluminum chloride ($AlCl_3$, E-Merck,

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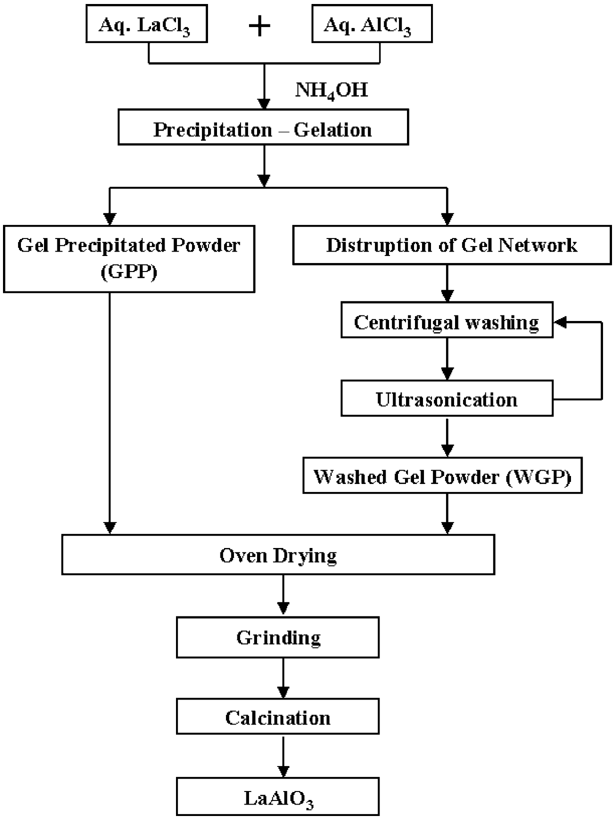


Fig. 1. Flowchart of the powder preparation process.

India) were used as precursors. 0.5 M solutions of $LaCl_3$ and $AlCl_3$ were mixed in equimolar ratio. Dropwise ammonia solution (E-Merck, India) was added in excess into the mixed chloride solution whereby gelation followed by precipitation occurs. The transformed gel was oven dried for overnight, which upon grinding produced a fragile porous fluffy mass. Thus, prepared powders are henceforth referred to as gel precipitated powders (GPP). In another sequence, the precipitated-gel was disrupted with intense magnetic stirring followed by ultrasonication. The disrupted gel was centrifugally filtered at 5000 rpm for 10 min for six to eight times to wash off chlorides. The filtered mass was dried to get another batch of porous fluffy mass. These powders are hereby referred to as centrifugally washed gel powders (WGP). Fig. 1 shows the block diagram of the powder preparation process in this work.

2.2. Powder characterization

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were performed at a heating rate of 10 °C/min with alumina as reference (Model TG/DTA 32, Seiko, Japan). The chloride content of the as-synthesized and heat treated samples were analyzed. The phase analysis was done by powder X-ray diffraction (XRD) method (Model No. PW 1730, Philips, Holland), using Cu Kα radiation ($\lambda = 1.54056$ Å) operating at 30 kV and 25 mA, and a scan rate (2θ) of 2°/min. Based on XRD line broadening at half-maximum of the (1 1 2) peak ($d = 2.6804$ at $2\theta = 33.40°$), crystallite sizes in the calcined $LaAlO_3$ powders at various calcinations temperatures were estimated using the Scherrer equation [14]. Scanning electron microscopy (SEM, Leica Stereoscan 440, LEICA, England) and transmission electron microscopy (TEM, JEM 1200 EX, JEOL, Japan) was used to observe the particle and agglomerate size, morphology and the amount of agglomeration of the particles.

3. Results and discussion

3.1. Powder preparation

In the combined gel synthesis, on the addition of ammonia, the precipitated particles cross-link to form a gel structure, which is capable of arresting the remaining solvent, and the unprecipitated solutes get immobilized. Hence, the as-synthesized powder is a mixture of NH_4Cl, $Al(OH)_3$ and $La(OH)_3$, with some unprecipitated $LaCl_3$ and $AlCl_3$. This is confirmed by the large amount of chloride present in the as-synthesized GPP samples as shown in Table 1. In the second process, the intense magnetic stirring disrupts the gel and the immobilized unreacted solutes get precipitated during ultrasonication process. The NH_4Cl formed gets removed from the system during repeated centrifugal washing. The DTA–TG (not shown here) of the GPP and WGP samples show two endothermic peaks at 240 and 330 °C, which could be due to the dehydroxylation of $La(OH)_3$ and $Al(OH)_3$, respectively. However, the centrifugally washed gel powders showed a higher degree of endothermicity due to a greater hydroxide content. The TGA showed weight loss corresponding to the same temperatures. The TG of the as synthesized WGP sample showed a 30% weight loss and that the powders became loss free above 400 °C. In contrast, the GPP samples show a weight loss of more than 70%, most of it occurring below 400 °C, with a faint weight loss continuing till higher temperatures. due removal of residual chlorides.

Table 1
Chloride content of the powders prepared by the two routes at various heat treatment temperatures[a]

Temperature	GPP (wt.%)	WGP (wt.%)
As-synthesized	36.45	2.65
400 °C	5.30	1.18
600 °C	4.25	0.12
800 °C	2.16	–
1100 °C	1.85	–
1300 °C	0.2	–

[a] A dash (–) denotes that the chloride content was beyond the detection limits.

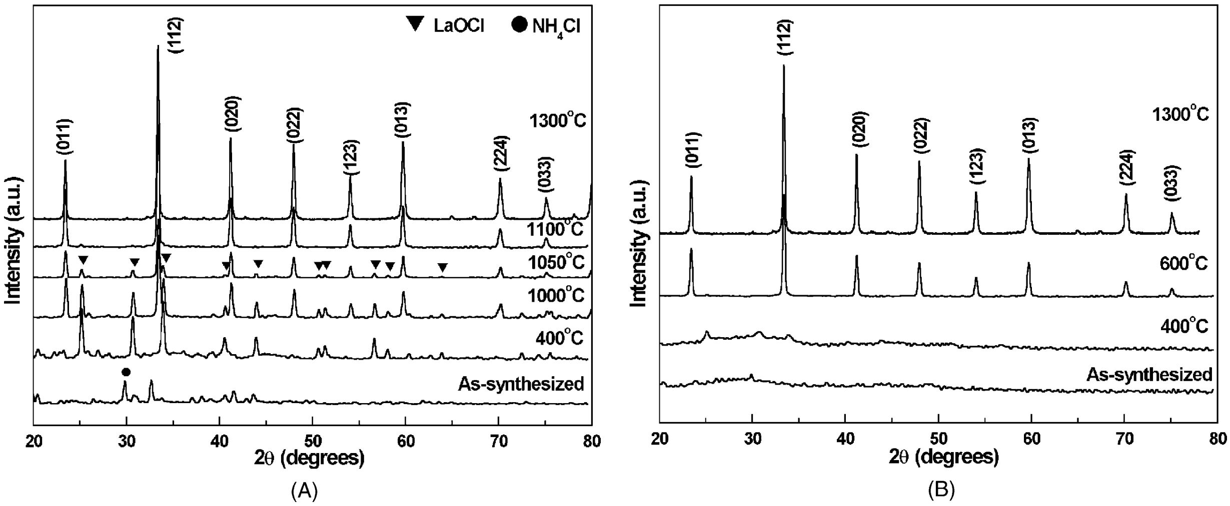


Fig. 2. XRD patterns of as-synthesized and calcined powders prepared by he two routes: (A) gel precipitated powders; (B) washed gel powders.

3.2. Effect of chloride on phase evolution

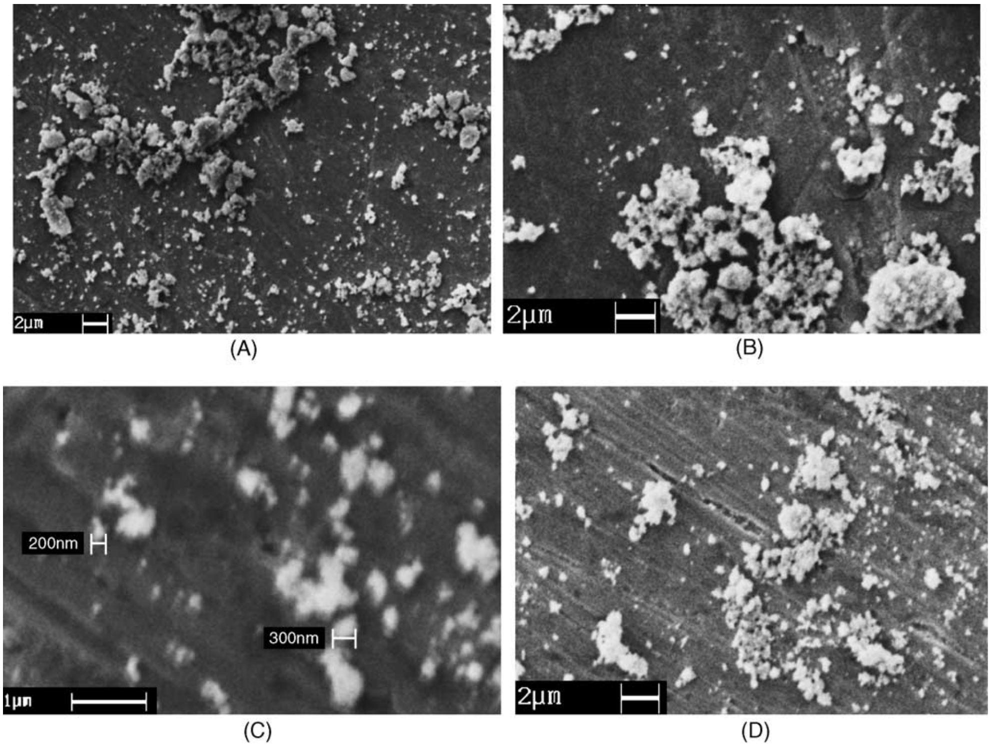
The as-synthesized GPP samples exhibited crystalline phases, e.g. NH_4Cl as shown in Fig. 2(A). However, the as-synthesized washed gel samples were fully X-ray amorphous and no peaks of ammonium chloride could be detected as seen in Fig. 2(B). This proves that the washed gel powders were quite free from chlorides, and repeated centrifugation—washing was effective in removing the chloride ions from the precipitate as confirmed from the analysis for chloride content (Table 1). The chloride content gradually decreases on heating the powders, which is due to the decomposition of unprecipitated $AlCl_3$ and some $LaCl_3$. The gel-precipitated samples calcined at 400, 600, 800 and 1000 °C, show the presence of an impurity phase lanthanum oxychloride, LaOCl (ICDD File card no. 08-0477) at all these temperatures, along with the lanthanum aluminate phase, $LaAlO_3$ above 800 °C. During heat treatment $LaCl_3$ forms the LaOCl phase, which then delays the $LaAlO_3$ phase formation. The complete $LaAlO_3$ phase formation was achieved in the sample calcined at 1100 °C, and there was no deterioration in the crystalline nature of the $LaAlO_3$ phase on heating it to 1600 °C.

On the contrary, the washed gel samples calcined at 400 °C were still amorphous, and no intermediate crystalline phase could be detected and at 600 °C full crystallization to $LaAlO_3$ phase takes place. To the best of our knowledge, this is the lowest temperature achieved so far, previous reported lowest value being 675 °C by Adak et al. [13]. In the present work, it is possible that the crystalline $LaAlO_3$ phase might have evolved from a completely homogeneous mixture of the metal hydroxides in the precipitated gel, which have brought down the crystallization temperature. Furthermore, the absence of peaks for either La_2O_3 or Al_2O_3 suggests that the stoichiometry of the metal ions is maintained in our chemical synthesis route. The measured lattice parameters ($a = 5.357$ Å, $a = 60.1^\circ$, $V = 108.951$ Å^3, space group R-3c) matches with the earlier reported values [15]. The crystallite sizes of powders calcined at 600, 1000, 1100 and 1300 °C were found to be 15, 25, 28 and 32 nm, respectively.

The surface area of powders calcined at 600 °C measured by BET method was found to be 45 m^2/gm, which is much higher than the earlier reported values [11,12] The particle size calculated from surface area, assuming spherical particles, was found to be ~23 nm (density of $LaAlO_3$ is 5.86 g/cm^3). The BET surface area of the WGP sample was measured to be ~72 m^2/g, and after heat treatment to 1300 °C for 4 h, it retained a high surface area of ~40 m^2/g, much greater than the earlier reported works. This retention of high surface area by $LaAlO_3$ is due to the lowering of crystallization temperature, as there is strong tendency for simultaneous grain growth when crystallization takes place at high temperatures, causing reduction in surface area.

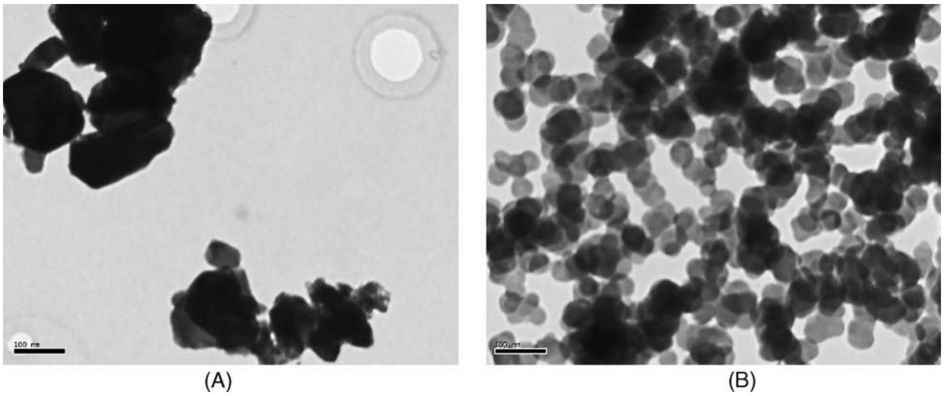
3.3. Effect of chloride on powder morphology

The SEM micrographs (Fig. 3) show that the GPP samples have an irregular powder morphology and are highly agglomerated, the average agglomerate size being about 0.5–2 μm. The agglomeration could be due to strong hydrogen bonding in the gel network, which is then difficult to remove in the subsequent stages. The agglomerate size further increases on heating it to 1300 °C as shown in Fig. 3(B). The WGP samples, on the contrary, show a better morphology than the GPP samples, have finer particles at the same calcination temperatures, the primary agglomerates being 200–300 nm in size. The TEM micrograph in Fig. 4(A) shows that the particles of gel-precipitated samples have got sintered and have irregular shape at the crystallization temperature of 1100 °C. On the contrary, the washed gel powders are almost spherical in shape and have a narrow size distribution with a particle size of 25–30 nm at the crystallization temperature of 600 °C as seen in Fig. 4(B). This regular morphology in the WGP samples is a result of



(A) (B) (C) (D)

Fig. 3. SEM micrographs of the powders calcined at 600 °C (A and C) and at 1300 °C (B and D). The micrographs (A) and (B) correspond to gel-precipitated samples whereas (C) and (D) correspond to washed gel powder samples.



(A) (B)

Fig. 4. TEM micrographs of the gel-precipitated powder calcined at 1100 °C (A) and washed gel powder calcined at 600 °C (B).

the ultrasonication of the precipitates, which provides sufficient energy to break the hydrogen bonds in the precipitate thus forming monodisperse nanopowder.

4. Conclusions

The low temperature phase formation in the precipitated chloride free powders is due to very small particle size of the precipitate and the absence of any intermediate phases during the heat treatment process, so that $LaAlO_3$ phase directly forms immediately after the dehydroxylation takes place. The SEM and TEM show that the washed gel powders have a regular and spherical morphology.

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