

Low temperature synthesis of spherical lanthanum aluminate nanoparticles

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Abstract

Lanthanum aluminate powders could be prepared by a novel ultrasonic assisted combined gel synthesis from metal chloride solutions with ammonia destabilization. The decomposition and crystallization behavior of the gel was studied by DTA/TGA. The washed and powdered gel was calcined at different temperatures and the phase evolution was studied by X-ray diffractometry. Phase pure lanthanum aluminate was obtained for powders calcined at a temperature as low as 600 °C for 4 h. NMR studies confirmed that the Al in the powders were octahedrally coordinated. SEM study revealed that the powders were uniformly distributed with occasional primary agglomerates. TEM micrographs show that the powders were spherical nanoparticles with sizes in the range of 25–40 nm.

Keywords: Lanthanum aluminate; Gel-precipitation; Ultrasonication; Nanoparticles

1. Introduction

The growth of satellite communications and cellular radio systems has led to a requirement for compact, stable and low cost filters. These are necessary to ensure that the transmitted signals are confined to closely defined allotted frequency bands, and to stop incoming signals from interfering with satisfactory performance of the communication systems. LaAlO₃ ceramics with its high quality factor (Q_{xf}), high dielectric constant (ϵ_r), and zero temperature co-efficient of resonant frequency (τ_f) is a promising material for the use of dielectric resonators and microwave device substrates. Single crystal LaAlO₃ 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 [1,2]. Due to its high surface area and catalytic activity, LaAlO₃ has also been used as catalyst for oxidative coupling of methane and hydrogenation and hydrogenolysis of hydrocarbons. However, there are some

technological constraints (e.g. high sintering temperature) for the use of LaAlO₃ especially for sophisticated purposes. For practical applications, it is necessary to reduce the sintering temperatures of LaAlO₃ ceramics from 1400–1600 °C to a lower value, 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 homogeneous powders and low melting glassy phase additives.

Conventionally, LaAlO₃ has been prepared by mixing the oxide powders, followed by solid-state reaction at high temperature (1500–1700 °C) [3–7]. This solid-state reaction process presents several drawbacks, such as high reaction temperature, large particle size, limited chemical homogeneity and low sinterability. Various low temperature chemical routes have evolved for preparing finer and homogeneous powders. Lux et al. [8] produced LaAlO₃ powders by aerosol synthesis (thermal decomposition of atomized mixed metal nitrate solutions). The LaAlO₃ obtained was not phase pure and contained unreacted La₂O₃ even after calcinations at 1500 °C. Vidyasagar et al. [9] obtained phase pure LaAlO₃ by co-precipitation method and subsequently calcining the powders at 950 °C for 12 h. Taspinar and Tas [10] observed crystallization of LaAlO₃ powders calcined at 850 °C for 17 h, prepared by homogeneous precipitation with urea decomposition. He also synthesized this material using

urea as a fuel and metal nitrates as the oxidants. Though the phase formation of LaAlO_3 occurred at $750\text{ }^\circ\text{C}$ for a prolonged calcination time, the pressed and sintered pellets could only show 75% densification because of highly agglomerated particle morphology. Sol-gel synthesis from La and Al isopropoxides, by Peshev et al. [11], shows phase pure LaAlO_3 at $900\text{ }^\circ\text{C}$ for 4 h.

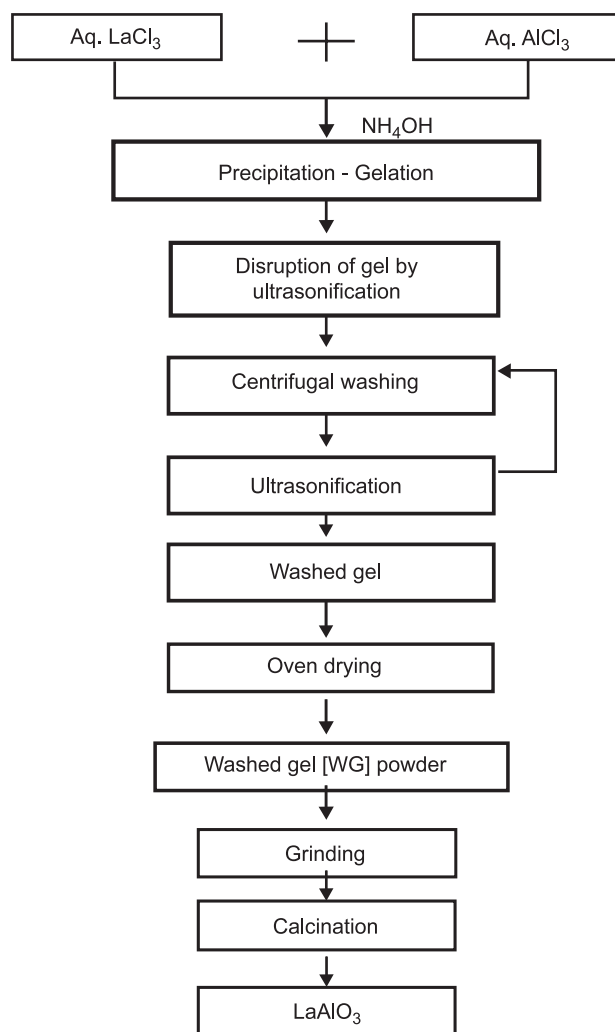
Several other low temperature methods have been tried for synthesizing LaAlO_3 powders, e.g. by in-situ polyesterification using citric acid and ethylene glycol [12], using hydrazine monohydrate solution [13], by ethylene di-amine tetra acetic acid (EDTA) gel method and by citrate combustion method with crystallization temperature varying between 700 and $900\text{ }^\circ\text{C}$ for different soaking periods. However, the lowest temperature for crystallization reported so far being $675\text{ }^\circ\text{C}$ in polyvinyl alcohol (PVA) evaporation route by Adak and Pramanik [14], whereas powders prepared with a lower PVA to nitrate ratio showed crystallization at higher temperatures.

The major drawback of most of these chemical routes was that the as-synthesized particles were highly agglomerated. In few cases a partial phase formation only could be observed. Moreover, the methods employed are relatively tedious and involve the use of expensive precursors. In this paper we report an easy, inexpensive, and reliable method to synthesize LaAlO_3 powders which not only crystallizes at low temperature, but also retains a high surface area (smaller particle size), which is all the more important for the intended applications of LaAlO_3 .

Combined Gel synthesis of ceramic powders has been reported for many systems like Mag-Al spinel [15], Alumina-Zirconia microcomposites [16]. The synthesized powders by this method have intimate and homogeneous mixing of cations resulting in low temperature phase formation and enhanced sinterability. Moreover, the process is simple, easy to control and could be carried out with low cost precursor as compared to other chemical methods. The present work discusses the synthesis of LaAlO_3 from respective metal chlorides by a combined gel precipitation. Any approach for a low temperature synthesis of a compound depends on the ability to combine the reactants of high reactivity so that the kinetics of compound formation is relatively fast. Ultrasonic irradiations have been applied in many mineral processing techniques, applied essentially to increase dissolution rates, increase of products, faster kinetics and reduced reagent consumption [17]. An additional step of ultrasonication of the gel-precipitated powders followed by centrifugal washing is included in addition to the conventional combined gel precipitation process.

2. Experimental

The experimental procedure is depicted in a flow sheet in Fig. 1. Separate solutions of LaCl_3 (IRE, India) and AlCl_3 (E-Merck, India) were prepared by mixing required amount



of salts with doubly distilled water. Then these two solutions were mixed in equimolar ratio and the resulting solution was magnetically stirred at $80\text{ }^\circ\text{C}$ to get a uniform solution of the two cations. The mixed chloride solution was then destabilized using as received ammonia solution (E-Merck). Upon addition of ammonia simultaneous precipitation and gelation occurred to form a continuous network structure through out the whole volume of the original solution, thereby ceasing the stirring action of the magnetic needle. The gel structure was disrupted with intense magnetic stirring and addition of excess ammonia. Then the precipitate was ultrasonically churned in a bath filled with distilled water followed by centrifugal washing at a frequency of 6000 rpm for 10 min . This process of ultrasonication and centrifugal washing was repeated 5–6 times for each batch of precipitated gel. The washed gel was then dried overnight to get a batch of porous fluffy mass. Lanthanum chloride and aluminum chloride solutions were gelled in separate beakers with addition of ammonia for studying the decomposition behavior of individual hydroxides of lanthanum and aluminum.

The thermal behavior of the washed gel, lanthanum hydroxide gel and aluminum hydroxide gel as well as synthesized powder was examined by thermogravimetry and differential thermal analysis (Model TG/DTA 32, Seiko, Japan) from room temperature to 800 °C, at a heating rate of 10 °C min⁻¹ with alumina as the reference.

X-ray diffractometer (Model PW 1730, Philips, Holland) was used for the phase analysis of the powders calcined at different temperatures using Cu-K α ₁ radiation ($\lambda=1.54056$ Å) at an accelerating voltage of 30 kV and a current of 25 mA, and a 2θ scan rate of 2 min⁻¹. The powder samples were mounted on a flat XRD plate and scanned at room temperature in the range $20 \leq 2\theta \leq 80$. X-ray line broadening technique was used to determine crystallite size of the powders calcined at different temperatures using Scherrer formula [18] with Silicon as internal standard.

$$D = (0.899\lambda/B\cos\theta_B) \quad (1)$$

Where D is the crystallite size, B is the full width at half-maximum XRD peak (112) in radians, λ is the wavelength of the X-ray radiation and θ_B is the Bragg angle in radians.

The surface area and pore size distribution of the samples were determined using BET technique. The theoretical particle sizes were calculated from surface area, assuming spherical particles, from the equation:

$$D_{\text{BET}} = [6 \times 1000/\rho \times S] \quad (2)$$

where D_{BET} is the equivalent particle diameter in nanometers, ρ is the density of the material in g/cm³ and S is the specific surface area in m²/g.

The elemental analysis of the samples (La/Al molar ratio) was done by Energy Dispersive Analysis of X-rays (EDAX, Zeiss DSM 960) integrated into a scanning electron microscope (Leica Stereoscan 440, LEICA, England). The surface composition of the samples was analyzed by Electron Spectroscopy for Chemical Analysis in XPS mode (ESCA, Model No. ESCA-3 MK-2, VG Scientific, England).

The coordination state of aluminum in the samples was analyzed by solid-state ²⁷Al ($I=5/2$) solid-state magic angle spinning Nuclear Magnetic Resonance (MAS-NMR, Avance 500 MHz, Bruker), recorded using Al(NO₃)₃ solution as external reference. The samples were subjected to an operating frequency of 130.32 MHz. The samples were scanned at two MAS spin rates, 8 and 10 kHz, to clearly distinguish between the observed isotropic chemical shift (δ_{iso}) of ²⁷Al and the side bands arising due to second order satellite transitions.

Scanning Electron Microscope (Leica Stereoscan 440, LEICA) in secondary electron mode was used to analyze the amount of agglomeration in the powders. Transmission Electron Microscopy (TEM 1200 EX, JEOL, Japan) was used to study the particle/agglomerate size, morphology and the amount of agglomeration of the particles. The powder samples were dispersed ultrasonically in isopropanol and then deposited on a polymer coated copper grid and TEM was used at an accelerating voltage of 100 KV.

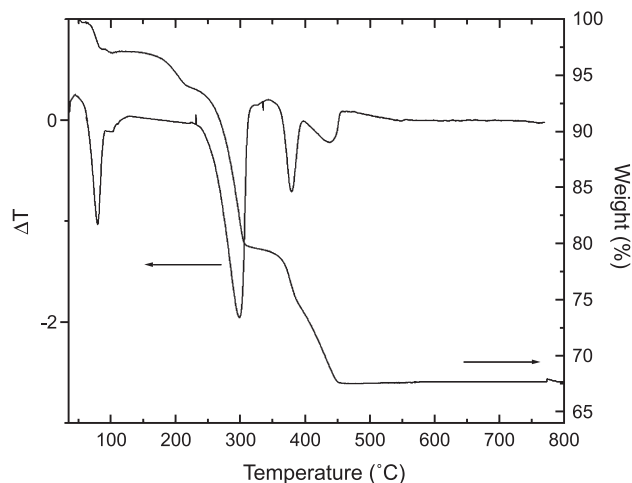
3. Results and discussion

3.1. Thermal behavior

It was found by the DTA runs of individual hydroxide gels of La and Al (not in figure) that while the decomposition of La(OH)₃ is a one step process, the same for Al(OH)₃ takes place in three steps. Previous workers have also reported the three-step decomposition of Al(OH)₃ [16]. The DTA of the washed gel of mixed hydroxides (Fig. 2) showed four distinct endothermic peaks. The first endothermic peak at 80 °C may be due to the loss of moisture from the washed gel powders. The endothermic peak at 300 °C corresponds to the decomposition of La(OH)₃ to La₂O₃. On the other hand, Al(OH)₃ decomposition takes place in three steps corresponding to the endothermic peaks at 300, 375 and 425 °C which finally results in Al₂O₃ formation. It may be inferred that the endothermic peak around 300 °C represents the decomposition of La(OH)₃ as well as the initial stage of Al(OH)₃ decomposition. The endothermic peaks at 375 and 425 °C are indicative of the subsequent stages of Al(OH)₃ decomposition. The TG Analysis of the as-synthesized powders is in agreement with the DTA peaks showing distinct regimes of weight loss corresponding to the temperature regions mentioned in the DTA.

3.2. X-ray diffraction

The as-synthesized washed gel powders were X-ray amorphous and no distinct crystalline phase could be detected (Fig. 3) confirming amorphous nature of the powders. The absence of NH₄Cl peaks (which is an obvious reaction product since the solution is destabilized by ammonia addition) suggests that the centrifugal washing has been effective in removing it. Also, the absence of peaks corresponding to La(OH)₃ or Al(OH)₃ indicates the amorphous nature of the precipitated hydroxides.



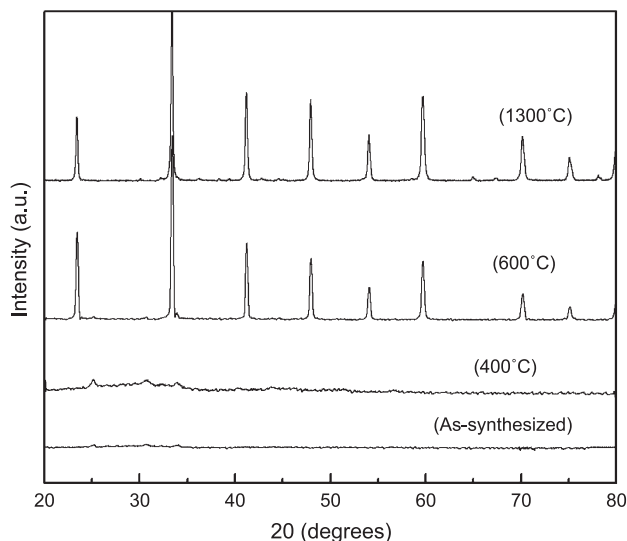


Fig. 3. XRD pattern of LaAlO_3 powders calcined at different temperatures.

In a combined gel synthesis the precipitated particles cross link to form a structure that is capable of arresting remaining solution thus preventing the precipitation of all the solutes [15,16]. In a three-dimensional network of precipitated hydroxides, many of the unprecipitated solutes are immobilized resulting in a perfectly homogeneous distribution of metal ions in the synthesized powder. However, by ultrasonication the mass transfer rate and molecular diffusion might have increased. Ultrasonic causes formation and collapse of microbubbles that can break the gel network and can also disrupt agglomeration, subsequently improving the solvent penetration into particulate matter. This might have resulted in enhanced removal of soluble material that is trapped inside a structure/network. Thus with the addition of excess ammonia and ultrasonication the solutes trapped inside the gel network might have precipitated. Repeated centrifugal washing might have washed off the NH_4Cl produced as a result of destabilization of the mixed metal chloride solution.

However, in powders calcined at 600°C for 4 h complete crystallization of LaAlO_3 was observed which could be indexed on rhombohedral symmetry (ICDD File Card No: 31-0022). The crystallization temperature, thus, is considerably lower than that reported by Adak and Pramanik [14] who have reported it to be 675°C . The measured lattice parameters of both the crystallized powders [$a=5.357 \text{ \AA}$, $\alpha=60.1$, $V=108.951 \text{ \AA}^3$] confirmed with reported values of LaAlO_3 perovskite [18]. In the present work, the crystalline LaAlO_3 phase probably have evolved from a completely homogeneous mixture of the very fine metal hydroxides in the precipitated gel. In addition to this, the ultrasonication of the precipitated gel employed may have contributed to this. Fine particles normally tend to agglomerate in suspensions and this could be controlled by repeated ultrasonication of the gel. This combined effect of gel precipitation and ultrasonication may have resulted a low temperature phase

Table 1

Variation of crystallite size of gel powders calcined at different temperatures

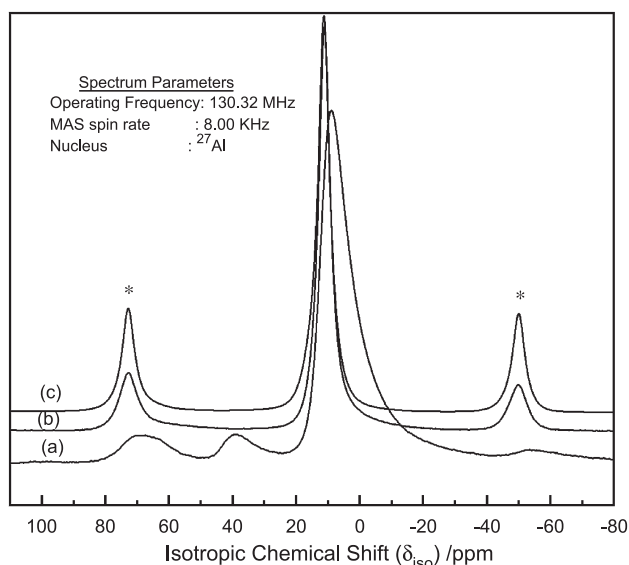
Calcination conditions	Crystallite size (nm)
$600^\circ\text{C}/4 \text{ h}$	15
$1000^\circ\text{C}/4 \text{ h}$	25
$1100^\circ\text{C}/4 \text{ h}$	28
$1300^\circ\text{C}/4 \text{ h}$	32

formation of LaAlO_3 . The diffractograms of powders calcined at higher temperatures showed gradual increase in their sharpness. The crystallite size, calculated from the diffractograms at HRFM, of powders calcined at different temperatures was found to be increasing gradually. The crystallite sizes at various calcinations conditions are reported in Table 1.

3.3. Al MAS NMR spectroscopy

The coordination number of Al, local order and its evolution during the synthesis and calcination steps were studied by ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR). The isotropic chemical shift (δ_{iso}) in ^{27}Al solid-state NMR depends on the local Al coordination. The shift for AlO_6 octahedra is between 20 and -20 ppm, for AlO_4 tetrahedra between 80 and 45 ppm and AlO_5 polyhedra between 45 and 20 ppm. Moreover, depending on the local symmetry the resonances are broadened and shifted (δ_{qis}) by the second-order quadrupolar interactions [19].

The ^{27}Al MAS NMR spectra of the as-synthesized powders (curve a, Fig. 4) show a distinct peak centering between 0 and 20 ppm, which can be assigned to six-coordinated aluminum found in aluminum hydroxide. This coordination is brought about by H_2O and OH^- ions in viscous gels, and OH^- and O^{2-} in the case of xerogels [19].



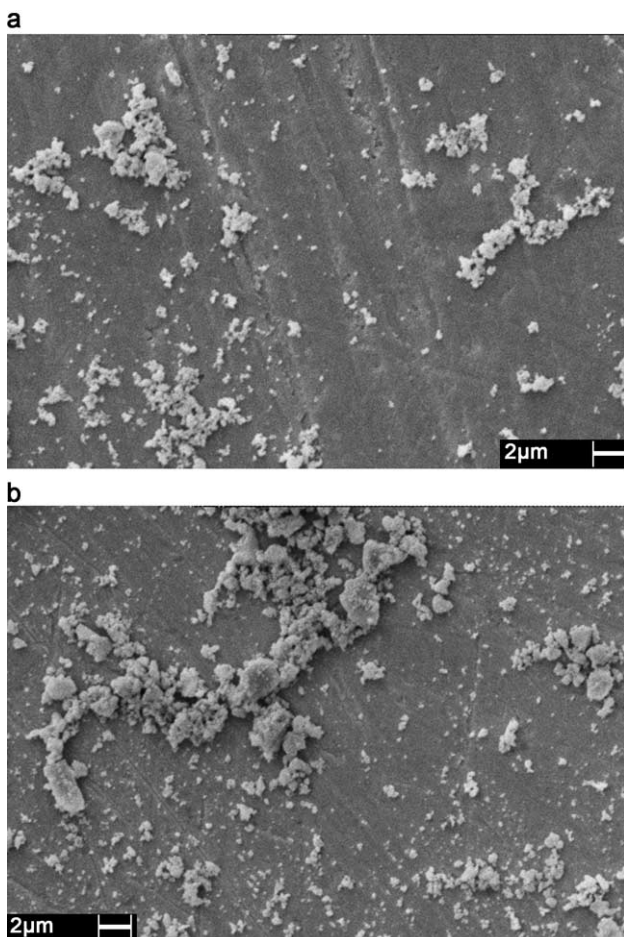


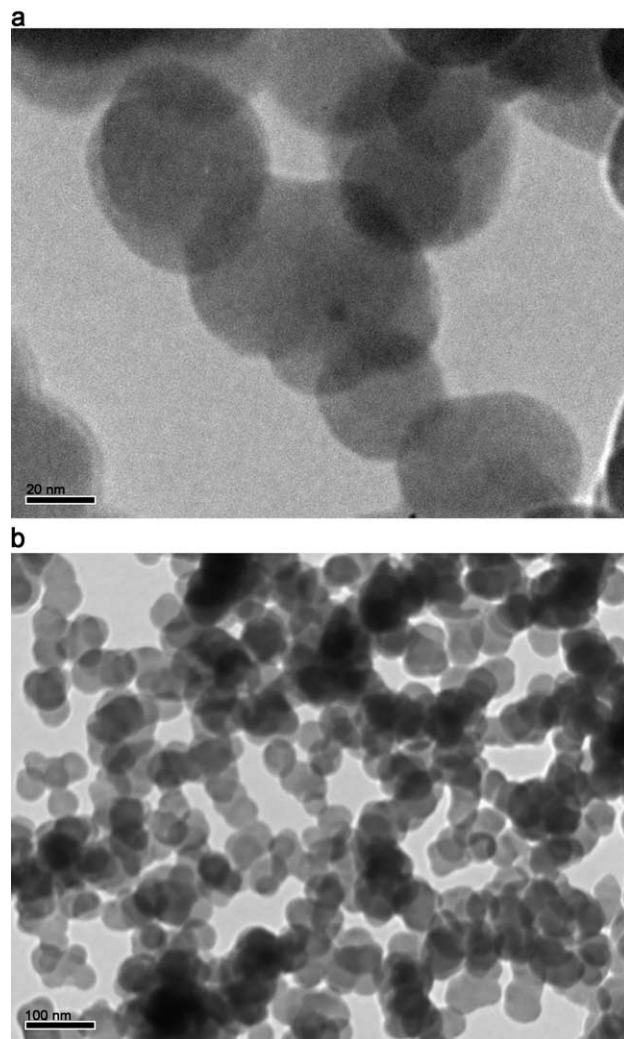
Fig. 5. SEM micrographs of the LaAlO_3 powders (a) calcined at $600\text{ }^\circ\text{C}$ and (b) calcined at $1100\text{ }^\circ\text{C}$.

However, two small asymmetric peaks in the range of 55 to 80 ppm and 20 to 45 ppm also accompany this peak. The peak in the range of 45 to 80 ppm can be assigned to four-coordinated aluminum [20], whereas the resonance in the region of 55 to 80 ppm can be ascribed to the presence of five-coordinated aluminum [21]. However, from the intensity of those peaks it can be inferred from the spectra that the combined-gel precipitated powder is predominantly six-coordinated ($\delta_{\text{iso}}=8.31$ ppm), with small amounts of four- and five-coordinated Al. For powders calcined at $600\text{ }^\circ\text{C}$ the NMR spectra (curve b, Fig. 4) shows that the small peaks corresponding to the AlO_5 and AlO_4 polyhedra (δ_{iso} between 20 and 80 ppm) have disappeared and a distinct symmetric peak with a center of gravity at around 12 ppm appears, having shifted slightly from its position in the as-synthesized powder spectra. This may be ascribed to the resonance of a six-coordinated aluminum, as expected in a LaAlO_3 perovskite structure [22]. In this spectra a set of spinning sidebands (marked *) also appear, originating from the $\langle \pm 1/2 \rangle \leftrightarrow |\pm 3/2 \rangle$ satellite transitions [20]. This is a further indication that the Al surroundings are better ordered and the samples are fully crystalline in agreement with the XRD analysis, which shows fully crystallized LaAlO_3 powders.

The NMR spectra for powders calcined at $1100\text{ }^\circ\text{C}$ (curve c, Fig. 4) is also similar to the one for $600\text{ }^\circ\text{C}$ calcined powders showing resonances corresponding only to AlO_6 polyhedra.

3.4. Surface analyses and surface area

The surface analysis of the as-synthesized amorphous powder shows that there is significantly less amount of Al on the surface than La. However, in samples calcined at 1100 and $1300\text{ }^\circ\text{C}$ the La/Al ratio is very close to 1 and the small variation of La/Al ratio at different points on the surface of the calcined samples show that there is a uniform distribution of the La and Al ions on the surface. From these observations it may be inferred that during the simultaneous gelation and precipitation process $\text{Al}(\text{OH})_3$ precipitates first, around which $\text{La}(\text{OH})_3$ starts precipitating. This process creates active nucleation sites for LaAlO_3 crystals from the La and Al ions, facilitating crystallization at a much lower temperature. The phase composition of the powder surface could



not be determined from the observed values of binding energy of La 3d and Al 2p peaks, but the surface composition found (22.4 at.% La, 22.8 at.% Al, 54.8 at.% O) gives some information in this respect. This is close to the stoichiometric composition for LaAlO₃ and correlates well with the X-ray diffraction data.

The BET specific surface area of the as-synthesized amorphous powder was ~72 m²/g, which reduced to 45 m²/g and after calcination at 600 °C for 4 h. However, even this value of surface area is much higher than reported values for phase pure crystalline LaAlO₃ [14,15]. The particle size calculated from surface area, assuming spherical particles, was found to be 23 nm. This retention of high surface area LaAlO₃ is a combined effect of finer particle size resulting from lower crystallization temperature.

3.5. Powder morphology

The as-synthesized washed gel powders were very fine and agglomerated in nature. The agglomeration may have resulted from the high surface energy of the particles. The SEM micrographs of powders calcined at 600 °C (Fig. 5a) show that the primary agglomerates are well dispersed with sizes ranging between 200 and 300 nm. The micrograph of powders calcined at 1100 °C (Fig. 5b) also shows same nature of dispersion with similar size range. Thus it may be inferred that the powders synthesized through this route can retain high surface area even at higher temperature. The TEM of the washed gel powders calcined at 600 °C (Fig. 6a) show that individual particles are spherical in shape with particle diameters in the range of 20–30 nm. Upon ultrasonic irradiation, the agitation by countless small and intensely collapsing bubbles create a highly effective scrubbing of both the exposed and hidden particle surfaces. This might have produced monodisperse powders with spherical morphology. The particle size strongly agrees with the calculated particle size from specific surface area and with the crystallite sizes calculated from X-ray line broadening. The particles are fairly uniform and are loosely agglomerated as shown (Fig. 6b) in lower magnification.

4. Conclusion

Phase pure LaAlO₃ could be prepared by combined gel synthesis from low cost precursors, like metal chlorides. The ultrasonication and centrifugal washing process adopted in combination with the conventional gel-precipitation process

has not deteriorated the uniformity and homogeneity of the LaAlO₃ powders. Powders synthesized by this method were found to be very fine and fluffy in nature and produced crystalline LA at a much lower temperature of 600 °C, which is considerably lower than that reported previously for this system. NMR studies show that all aluminum ions are six-coordinated, confirming the perovskite structure of LaAlO₃. The powders retained high specific surface area even after calcination at higher temperature. Thus the chemical synthesis route followed here is an easy, inexpensive and effective approach to produce homogeneous monodisperse spherical nanoparticles of LaAlO₃ from low cost precursors.

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