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Synthesis and characterization of lanthanum monoaluminate by co-precipitation method

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Abstract. Our contribution has focused on the synthesis and characterization of lanthanum monoaluminate LaAlO3 by the method of co-precipitation. The powder was successfully synthesized using NaOH, La $(NO_3)_3.6H_2O$ and Al $(NO_3)_3.9H_2O$ as raw materials by this method and calcined at different temperatures. It was characterized by several techniques: Fourier transform infrared spectroscopy (FT-IR), thermogravimetric and differential thermal analysis (TGA/DTA), X-ray diffraction (XRD) and laser diffusion. All the results for physico-chemicals characterizations show that the crystallization temperature of the $LaAlO_3$ precursor gels precipitated is estimated as 790 °C by TG/DTA. The XRD pattern of the $LaAlO_3$ precursor gels calcined at 700 ◦C for 6 h has a perovskite structure of rhombohedral hexagonal phase formed and the presence of crystalline impurities is not found. The crystallite size of $LaAlO_3$ slightly increases from 31to 44.5 nm with calcination temperature increasing from 700to1000 °C for 6 h.
Key words. Lanthanum monoaluminate; method of coprecipitation; thermal analysis; perovskite; rhombohedral hexagonal; LaAlO3.

1 Introduction

Lanthanum aluminate ($LaAlO_3$) has attracted a great attention in recent years because of its variety of applications [1–8]. $LaAlO_3$ with a perovskite-type structure [9] is widely used as substrates and electrically insulating buffers for depositing high-temperature superconducting films due to its high quality factor and excellent lattice and thermal expansion matching ability [2, 6]. Its use as a gate dielectric material has also been explored [10, 11] .In addition, $LaAlO_3$ powder has been studied as a catalyst for oxidative coupling of methane and hydrogenation and hydrogenolysis of hydrocarbons due to its high catalytic activity [12].Polycrystalline $LaAlO_3$ has been commonly prepared by a solid-state reaction method: i.e. direct mixing and firing of pure oxides of La_2O_3 and Al_2O_3 at temperature greater than 1550 ◦C [13-16]. The full development of the LaAlO3 phase has been exercised by only heating the sample to 1600 ◦C and then reheating to 1750 ◦C for 3 h to form a polycrystalline disk. The preparation of a buffer disk of 123 nm thick $LaAlO_3$ by radiofrequency magnetron sputtering has also been reported by Sung et al. [14].

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Although the solid-state reaction is very simple, this process is not entirely satisfactory because of several serious drawbacks such as introduction of impurities during milling, high reaction temperature, limit of complete oxide reaction and chemical homogeneity, large particle sizes and low sintering ability [17, 18]. Therefore, extensive investigations have been performed for preparing finer and more homogeneous powders at lower temperatures using various chemical processes. Vidyasagar et al. [18] have obtained pure $LaAlO_3$ powders by calcining the precursor at 947 ◦C for 12 h in air via urea solution route. Pure $LaAlO_3$ powders have been synthesized at 860 ◦C using polyacrylamide by Douy and Odier [19]. Lux et al. [20] have also attempted to prepare $LaAlO_3$ powders by an aerosol-furnace technique, using water-soluble lanthanum and aluminum salts, and furnace temperature between 1200 and 1500 ◦C, where the formation of $LaAlO_3$ has been reported to be again only partial, and the sample still contains La_2O_3 and Al_2O_3. Moreover, Taspinar and Tas [16] have also reported the synthesized pure LaAlO3 powders by calcining at 750 ◦C for 16 h, using a self propagating combustion method from aqueous solutions containing CH_4N_2O and respective nitrates of lanthanum and aluminum. Furthermore, they have also synthesized pure $LaAlO_3$ powders at 850 ◦C by the homogeneous precipitation from an aqueous solution containing CH_4N_2O in nitrate salts [16]. Kakihana and Okubo [21] have reported that in the polymerization route of citric acid and ethylene glycol, pure perovskite $LaAlO_3$ has been obtained when the precursor is heat-treated in a furnace at 700 ◦C for 8 h or at 750 ◦C for 2 h. Furthermore, al Behera et al. [22] have produced spherical $LaAlO_3$ nanoparticles by a novel ultrasonic assisted combined gel synthesis from $LaCl_3$ and $AlCl_3$ solution with ammonia destabilization. On the other hand, the synthesis and luminescence properties of $LaAlO_3$: 1% Eu^{3+} nanocrystals have been discussed by Hreniak et al. [23]. They have pointed out the increasing luminescence life time with decreasing nanocrystals size. Moreover, the formation mechanism of the $LaAlO_3$ powders from aluminum hydroxide and lanthanum oxide using an evaporation process have been studied by Danchevskaya et al. [24]. They have demonstrated that $LaAlO_3$ has formed through the intermediate crystalline substances of oxyhydroxide LaOOH and hydroxide La (OH) $_3$.

However, all these processes are either complex or expensive, and limit their large scale production. However, an extensive search on the sintering behavior of low-temperature synthesized LaAlO3 nanopowders has been limited [17, 25, 26].

Chemical coprecipitation route is a simple method for synthesizing nanopowders [25].The base precipitant most used in this method is NH_4OH.

Recently, Li et al. [17]; Nair et al. [26]; and *Kuo et al*. [8-27] have used this method to synthesize pure $LaAlO_3$ using the mixed solution of NH_4OH and calcined at 700, 800 and 1000 ◦C, respectively. However, the synthesis of lanthanum monoaluminate has been rarely reported using a mixture of sodium hydroxide such as base precipitant

In the present study, nanocrystalline $LaAlO_3$ powders have been successfully synthesized using the mixed solution of NaOH in low temperature range of 500–1000 ◦C and pH 9. The preparation technique, thermal behavior, crystal structure, crystallite size, volume distribution of particle size, behavior of the low-temperature synthesized $LaAlO_3$ nanopowders have been discussed in detail.

2 Experimental procedure

2.1 Sample preparation

The starting materials were reagent-grade lanthanum nitrate [La $(NO_3)_3.6H_2O$, purity 98%, supplied by BIOCHEM Chemopharma Montreal Quebec], aluminum nitrate [Al $(NO_3)_3.9H_2O$, purity 99%, supplied by BIOCHEM Chemopharma Montreal Quebec] and hydroxide Sodium12N [NaOH, purity98%, supplied by BIOCHEM Chemopharma United Kingdom].The aqueous solution was prepared from reagent-grade La $(NO_3)_3.6H_2O$ and $Al(NO_3)_3$ $9H_2O$ by dropping then slowly into the dilute hydroxide Sodium solution was used as the precipitant (pH 12) with vigorous agitation for 2.5h; the pH value was kept at 9 by adjusting the amount of NaOH to form white precipitates In all cases, after the reaction was completed, the white precipitates were centrifugally washed thoroughly

for 10 min, four times with a distilled water and two times with ethanol, for each washing they were filtered then the resultant gelatinous precipitates were dried overnight at 110°C in oven .
The calcinations of the precursor powder $LaALO_3$ was conducted in an Al_2O_3 boat in a temperature range of 500–1000° C for6 h.at heating rate of 5 ◦C/min.
The flow chart for preparing $LaAlO_3$ nanoparticles by co-precipitation method is shown in Figure 1

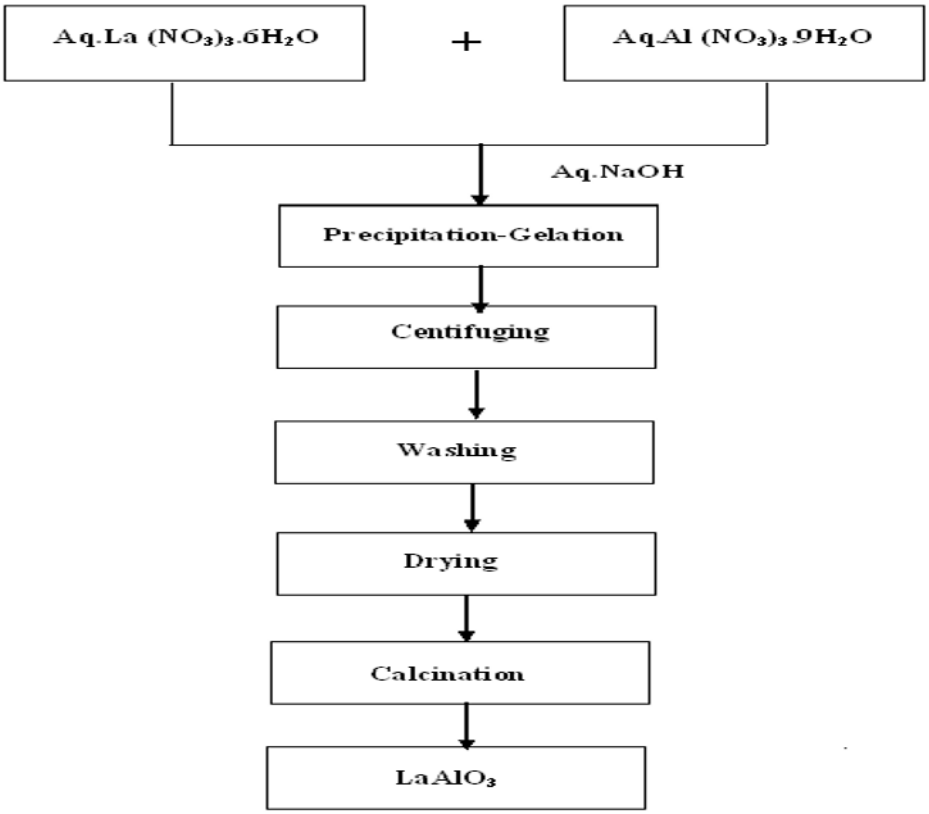

Fig. 1. Flow chart for preparing $LaAlO_3$ nanoparticles by co-precipitation method

2.2 Sample characterization

The thermal decomposition processes of the precursor gels were studied in air atmosphere by thermogravimetric and differential thermal analyses using TG/DTA, STAPT-1600 LINSEIS were conducted on a 50mg powder sample at a heating rate of 5 °C/min in air with Al_2O_3 powders as a reference material. The calcination temperature was determined from DTA.The Fourier transform infrared (FT-IR) absorption spectra were obtained by Processing on an optical bench of the standard PYE UMCAM PHILIPS FTIR spectrometer (4000–400 cm^{-1}).The samples were mixed in a KBr matrix (1:200) and pressed pellets and the spectra were averaged out from 64 scans with a nominal resolution of $2cm^{-1}$. X-ray diffraction (XRD) patterns were recorded using XRD,Model BRUKER – AXE type D8) with Cu K_α radiation ($\lambda_{K\alpha}$=1.54056 Å) and a Ni filter, operated at an accelerating voltage of 40 kV, a current of 40mA and a scanning rate of .25◦/min The powder samples were mounted on a flat XRD plate and scanned at room temperature in the range 10°-90° to identify the crystalline phases present in the calcined powders By comparison with Joint Committee on Powder Diffraction Standards(JCPDS)files. The crystallite sizes of the powders were calculated from full-

width at half-maximum (FWHM) values from the most intense peak of the diffractogram, the (110) reflection in this case, using the Scherer formula [28].

$$D_{XRD} = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

Where D_{XRD} is the crystallite size in nm, λ is the radiation wavelength, θ is the diffraction peak angle and b is the corrected line width at half-peak intensity. The correction for instrumental peak broadening was made using the Warren formula: $\boldsymbol{\beta = (b_{obs}^2 - b^2)^{1/2}}$, where $\mathbf{b_{obs}}$ is the line width at half-peak intensity related to LaAlO3 powder and **b** is the line width of the (1 1 0) diffraction peak.
Particles size distribution in solution was measured with a Malvern Mastersizer Hydro2000G granulometer**.**The equipment can measure grain sizes ranging from 0.02 to 2000 µm.The measurements are performed in an aqueous (water with added sodium hexametaphosphate (dispersant) with agitation and ultrasonic are applied for 15 min

3 Result and discussion

3.1 Thermal behavior and phase formation of the LaAlO3 gel powders

Figure 2 illustrates the TG/DTA curves of the precursor powders heated at a rate of 5 °C/min in the temperature range between 50 and 1000 °C in static air. The TG curve shows the first weight loss at 330 °C (−18.80%) can be ascribed to the decomposition and burnout of most sodium nitrate in the precursor powders. The second weight loss (−8.8 %) between 400 and 520 °C is mostly due to the dehydration of the lanthanum and aluminum hydroxides. The weight loss between 520 and 750 °C with a clear plateau is presumably by the formation of an intermediate decomposition product and a small weight loss between 750 and 790 °C by the decomposition of residual nitrates involved in the intermediate product.
The DTA result in Figure 2 also reveals two main endothermic events at 130 and 490°C, respectively. At the temperature below 130°C is assigned to the loss of moisture from the washed precursor powders [22]. The second endothermic peak at 490°C is attributed to the decomposition of the lanthanum and aluminum hydroxides. The sharp exothermic peak at 790 °C is due to the formation of the $LaAlO_3$.

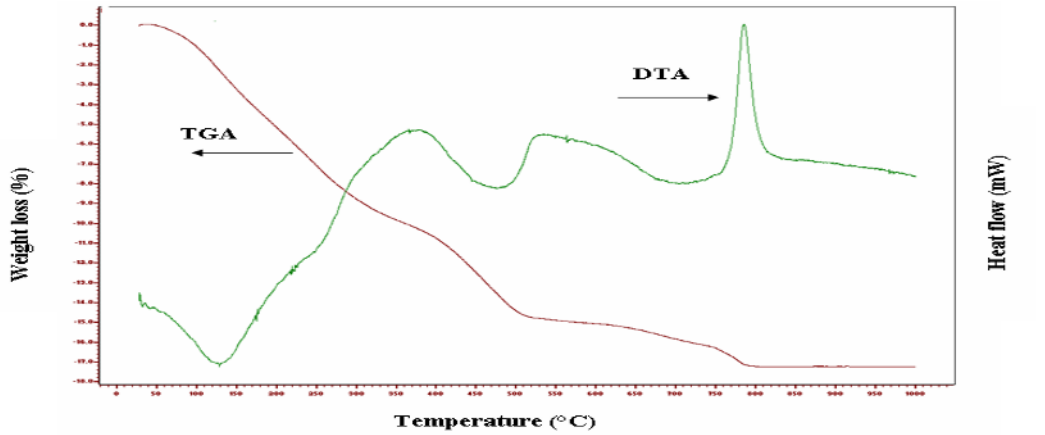

Fig. 2. DTA/TG curves of the LaAlO3 precursor powders with a heating rate of 5°C/min.

Kakihana and Okubo [21] have synthesized the $LaAlO_3$ powders through the in situ polymerization route utilizing citric acid and ethylene glycol and found no clear exothermic peak corresponding to $LaAlO_3$ crystallization. On the other hand, Taspinar and Tas [16] have indicated that the crystallization temperature of $LaAlO_3$ measured by DTA is 992 °C for the precursor powders prepared by the homogeneous precipitation process; so as *Kuo and al* [8,27] have indicated that the crystallization temperature of $LaAlO_3$ measured by DTA is 810 °C for the precursor powders prepared by co-precipitation process. The distinction between the present and other reports [8, 16, 21,27] can be caused by different process routes creating various crystallization temperatures in the DTA curves [8] ; Moreover at various heating rates is found that the exothermic peak shifts to high temperature with increasing heating rate which is demonstrated by *Kuo and al*. This phenomenon suggests that irregular lanthanum and aluminum ions are rearranged into the periodic lattice of the growing crystal. When the heating rate increases the rearrangement is delayed to the high temperature side [27].

3.2 Infrared spectra

IR analysis of synthesized samples is important both for the control of the reaction process and of the properties of materials obtained. The FT-IR absorption spectra of the $LaAlO_3$ precursor powders, calcined at various temperatures for 6h are shown in Figure 3.The spectrums between 3600 and 3200 cm−1 in Figure 3 (a), (b), (c) and (d) are related to the stretching vibration of the free hydroxyl group. Also indicates the presence of adsorbed water [29].The characteristic nitrate stretching frequencies at 1700–1600 cm^{-1}.However, the peaks due to the stretch vibrations in NO_3^- at 1410–1360 cm^{-1} (strong bands) [30, 31] are shown in Figure 3 (a),(b) ,(c) and (d) are evident. In the 700–400 cm^{-1} region of the IR spectrum is shown in Figure 3 (a), (b) ,(c),(d) and (e) ,the observed specific peaks at 681,676,667,596, 458, and 447 cm^{-1}may be attributed to the characteristic M–O (Possibly La–O and Al–O stretching frequencies) vibrations for the perovskite structure compounds [32].

After the $LaAlO_3$ powders calcined at 700°C is shown in Figure 3 (e), the only distinguishable transmittance bands detected in the specimen were those for LaAlO3 (the characteristic bands at 667and 447cm^{-1}) [33, 34]. XRD analysis (refer to Figure 4) confirmed the formation of crystalline$LaAlO_3$ at 700 °C.

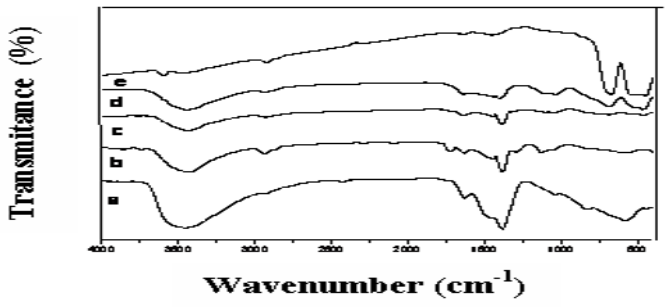

Fig. 3. FT-IR absorption spectra of the LaAlO3 precursor powders, calcined at various temperatures for 6h: (a) room temperature, (b) 200° C, (c) 500°C, (d) 600°C and (e) 700°C.

3.3 Phase characterization of the $LaAlO_3$ precursor powders after calcined

Figure 4 illustrates the XRD patterns of the $LaAlO_3$ powders calcined at different temperatures for 6h. The XRD pattern of the $LaAlO_3$ powders calcined at 500°C for 6h is shown in Figure 4 (a), which reveals that the calcined powders are still amorphous.

The absence of peaks corresponding to La (OH) $_3$ or Al (OH) $_3$ indicates the amorphous nature of the precipitated hydroxides. Figure 4(b) indicates that after calcined at 600 ◦C for 6 h, the crystalline phase is the rhombohedral LaAlO3 with poor crystallinity. When the LaAlO3 precursor powders calcined at 700–1000 ◦C (Figure 4 (C), (d), (e) and (f)), shows good crystallinity. These XRD peaks correspond to reflections from pure rhombohedral LaAlO3 with a perovskite structure. They are in good agreement with JCPDS card 31-0022.Moreover, the result of Figure 4 also reconfirms that the exothermic peak of Figure 2, spanning from 740 to 820 °C, is due to the formation of the rhombohedral of $LaAlO_3$ nanopowders.

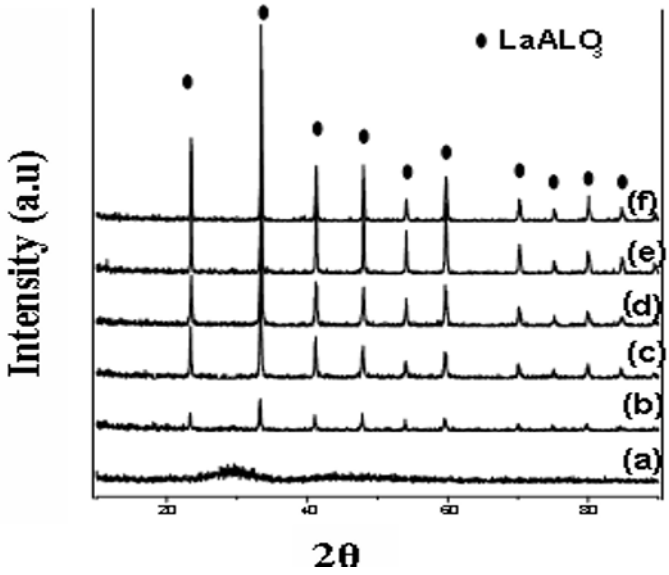

Fig. 4. XRD patterns of the LaAlO3 precursor powders calcined at different temperatures for 6 h: (a) 500 ◦C, (b) 600 ◦C, (c) 700 ◦C, (d) 800 ◦C, (e) 900 ◦C and (f) 1000°C .

Furthermore, Figure 4 indicate that the XRD patterns of the calcined $LaAlO_3$ precursor powders are representative of LaAlO3, and no reflections from La2O3 and Al_2O_3 are observed as distinct intermediate phases period to the formation of LaAlO3 during the thermal decomposition of the precursor powders even at 1000° C [22]. Kakihana and Okubo [21] have pointed out that no detection of La_2O_3 and Al_2O_3 implies almost perfect mixing of the constituent cations in the precursor powders. They have also indicated that $LaAlO_3$ does not form through a solid-state reaction between isolated La_2O_3 and Al_2O_3 fine particles but forms directly from the amorphous precursor powder without significant segregation of individual materials [21]. Moreover, in the present study, the intermediate crystalline substances of LaOOH and La (OH) $_3$ are not observed; this is consistent with the results of *Kuo and al* [8, 27]. On the other hand this result contradicts to that of Danchevskaya et al. [24].

The relation between phase and calcination temperature of the low-temperature synthesized $LaAlO_3$ powders has been examined earlier by XRD [16–18, 20, 21]. Taspinar and Tas [16] have successfully synthesized $LaAlO_3$ powders by two chemical preparation techniques: (i) homogeneous precipitation from aqueous solutions containing urea (CH_4N_2O) in the presence of nitrate salts and (ii) self-propagation combustion synthesis (SPCS) from aqueous solutions containing CH_4N_2O and respective nitrate salts of lanthanum and aluminum. In the homogeneous precipitation process, when calcined up to 700 ◦C, theLa_2O_3 phase is still detected and completely converted to pure$LaAlO_3$ at 850 ◦C. Therefore, 750 ◦C is the lowest temperature necessitated for the formation of $LaAlO_3$ powders by the SPCS route. Li et al. [17] have used La $(NO_3)_3$ and Al $(NO_3)_3$ as raw materials and kept pH about at 9 in the coprecipitation method. Pure $LaAlO_3$ powders have been obtained after

calcined at 700 ◦C for 32 h or 800 ◦C for 2 h using hydroxide, cyanide and nitrate solid solution precursors as the starting materials. The appearance of $LaAlO_3$ is observed when calcined at 947 ◦C for12 h in air, as reported by Vidyasagar et al. [18]. Furthermore, Lux et al. [20] have used reagent-grade lanthanum nitrate and aluminum nitrate as the starting materials. The XRD data on the aerosol-derived particles indicate that the material is amorphous until processing temperatures exceed about 900 ◦C. In this case, the crystalline phases observed by XRD are the major lanthanum oxide and minor $LaAlO_3$ phases when calcined at 1200 ◦C. If calcined up to 1500 ◦C, the major phase is $LaAlO_3$, but lanthanum and aluminum oxide phases are still in evidence [20].Moreover, Kakihana and Okubo [21] have obtained the LaAlO3 precursor by heating a mixed solution of citric acid, ethylene glycol and nitrates of lanthanum and aluminum. The formation of pure perovskite $LaAlO_3$ has occurred when the precursor is calcined at 700 ◦C for 8 h or at 750 ◦C for 2 h. There is no XRD evidence for the presence of crystalline impurities**.**

The present investigation has used the mixed solution of NaOH, lanthanum nitrate and aluminum nitrate, precipitation at pH 9, calcination at 700 ◦C for 6 h and then obtained pure perovskite $LaAlO_3$ this result is in good agreement with *Kuo et al*, but being the lowest temperature chemical coprecipitation so far the lowest among others.

3.4 Crystallite size and distribution by volume particle size of LaAlO3 powder

Table 1 shows the variation of average crystallite size (D_{XRD}) of the $LaAlO_3$ powders calcined at different temperatures for 6 h. The crystallite sizes calculated from the Scherrer formula are slightly increase in the range of 31–44.50 nm respectively with the calcination temperature increasing from 700 to 1000°C. On the other hand this result is lower than calculed by *Kuo and al***.** This distinction can be caused of synthesis parameters such as chemical nature of the base precipitant that affects on the morphological characteristics of the nanoparticles $LaAlO_3$ powders**.**

Table 1. Variation of crystallite size of the $LaAlO_3$ powders calcined at different temperatures for 6h

Calcination temperature(°C)	**Crystallite size (nm)**
700	31
800	34.28
900	41.04
1000	44.50

Figure 5 shows that the particle size distribution in volume of $LaAlO_3$ powder calcined at different temperature 800 to1000°C, the average diameters in volume Dv (0.5) = 0.22; 0.25; 0,25 µm respectivly.This result also indicates that the powders are highly agglomerated . This is could be due to the agglomeration of ultra-fine powders, present in the suspension**.**Since the $LaAlO_3$ gel powders are prepared through the wetchemical route; the agglomeration takes place during processing.

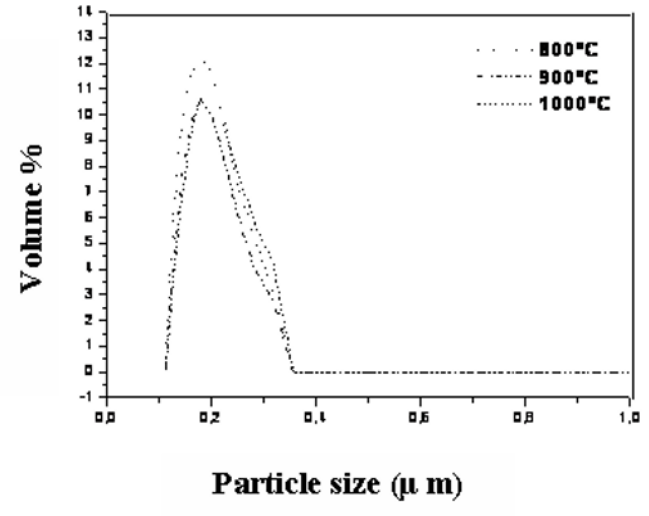

Fig. 5. Particle size distribution in volume of LaAlO3 powder calcined at different temperature 800 to1000°C

4 Conclusions

Nanocrystalline lanthanum monoaluminate powders have been successfully synthesized at low temperature by chemical coprecipitation using a mixture of sodium hydroxide, lanthanum and aluminum nitrate solutions. When the $LaAlO_3$ precursor powders are precipitated at pH 9 and calcined at 700◦C for 6 h, the pure perovskite $LaAlO_3$ is obtained. No reflection peaks of La2O3 and Al2O3 are observed. The calcination temperature of 700 ◦C is so far the lowest process temperature for complete $LaAlO_3$ formation. The nanocrystallite size slightly increase from 31 to 44.5 nm with the calcination temperature increasing from 700 to 1000 °C, for the $LaAlO_3$ precursor powders calcined for 6 h.

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