Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 4
No. 1
pp. 71-74
March 2013

Effect of Fuel to Oxidant Ratio on Structural and Optical Properties of LaAlO3 Nanoparticles

J.T. Anandhi[1], V. Anslin Ferby[1], A. Moses Ezhil Raj[1*], C. Sanjeeviraja[2]

[1] Department of Physics & Research Centre, Scott Christian College (Autonomous), Nagercoil-629 003

[2] Department of Physics, Alagappa University, Karaikudi-630 003.
Corresponding author, e-mail : ezhilmoses@yahoo.co.in, Phone: +91 4652 232888, Fax : +91 4652 298000.

Abstract : Lanthanum Aluminum Oxide nanoparticles have been synthesized by an auto-combustion method for different oxidant to fuel (O/F) ratios (0.5, 1.0 and 1.5). Lanthanum nitrate and Aluminum nitrate were used as oxidants, Citric acid as fuel and Ammonia as buffer to adjust the pH of the solution. Crystallinity and crystalline phases of the prepared samples were analyzed using X-ray diffraction and the reflection planes (100), (110), (111), (200), (210), (211), (220), and (300) revealed the rhombohedral phase as comparable to the JCPDS standards (Card No. 85-0848). FTIR spectra again confirmed the single phase formation of compound by the noticeable metal-oxygen (AlO_6 octahedra) ligand formation band in the lower frequency region at about 665 cm^{-1}. In the higher frequency region, the band appeared at 440 cm^{-1} was assigned to the La-O co-ordination of the samples. Optical measurement revealed absorption in the low wavelength region that corresponds to the optical absorption edge, 4.95eV, 4.77eV, 4.88eV respectively for the $LaAlO_3$ samples prepared for three different F/O ratios.

Key Words : $LaAlO_3$, nanoparticles, X-ray diffraction, Fourier transform infrared spectroscopy, Optical absorption.

(Received January 2013, Accepted March 2013)

1. Introduction

Lanthanum aluminium oxide ($LaAlO_3$) with perovskite structure has gained much attention in the last decade for its dielectric properties and perfect lattice matching to many materials. It can be utilized in dielectric resonators [1], substrate material for thin film high temperature super conductors [2], electrolyte material for the solid oxide fuel cells [3] etc. Such a promising material has been prepared using aerosol furnace technique [4], co-precipitation method [5], sol-gel process [6] and few more.

In the present work we report the synthesis of $LaAlO_3$ nanoparticles prepared through a citrate-nitrate auto-combustion method. The impact of fuel to oxidant ratio on structural evolution, phase formation and optical transitions are reported in this paper.

2. Experimental

$LaAlO_3$ nanoparticles were synthesized using Lanthanum nitrate, aluminum nitrate as oxidizer and citric acid as the fuel. The combustion ratio (O/F) was calculated using the reducing valence of the fuel and the total valence of oxidizer according to the propellant rule. Lanthanum nitrate and aluminium nitrate were dissolved in 25 ml of distilled water and the fuel citric acid was then added for various ratios (O/F=0.5, 1, 1.5) and is stirred for 15 minutes. A small amount of ammonia (NH_3) was added to the solution to adjust the pH value to 7. The solution was heated slowly to evaporate the solvent until a viscous and sticky gel was formed. Then the beaker was transferred to a furnace capable of heating above 200°C. On increasing the temperature, the gel self ignited around 185°C, forming foam, swell and burn with glowing flints with evolution of large amount of gases. Auto ignition was completed within few seconds, giving rise to a black colored powder. The combusted powders were then transferred to a muffle furnace for annealing at 800°C to form single phase $LaAlO_3$ nanopowders. Prepared samples were named as $LaAlO_3$-1, $LaAlO_3$-2, and $LaAlO_3$-3 respectively for different O/F ratios (0.5, 1 and 1.5).

XRD measurements on prepared samples were performed using XPERT-PRO diffractometer over the scanning angles between 10^o and 70^o (2θ). The Fourier Transform Infrared Spectroscopy (FTIR) of the samples was recorded using Thermo Nicolet Avatar 370 spectrometer. The optical properties of the $LaAlO_3$ nanoparticles were investigated from the spectra recorded using Nicolet Avtar spectrophotometer in the wavelength range 200-2500 nm.

3. Results and discussion

Figure 1 shows the XRD spectra of $LaAlO_3$ samples prepared for three different O/F ratios (O/F=0.5, 1 &1.5). Prepared samples are polycrystalline with peak at specific locations confirmed the formation single $LaAlO_3$ perovskite phase without any impurity peaks. The peaks are along the reflection planes (100), (110), (111), (200), (210), (211), (220), (300) which are indexed for its rhombohedral structure with lattice parameter a=3.79Å. Obtained values are comparable to the standard data (JCPDS card no: 85-0848). The widened diffraction peaks indicate that the size of the crystals are very fine or nanometer in size. Absence of La_2O_3 and Al_2O_3 phases indicates the perfect mixing of the constituent cations in the powder. Calculated structural parameters are listed in Table 1.

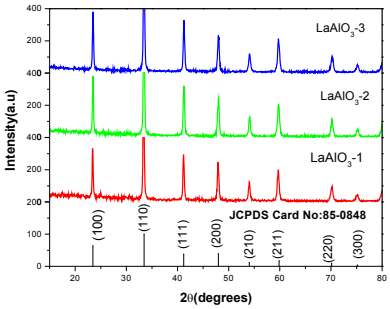

Figure 1. XRD spectra of $LaAlO_3$ samples

Sample Details	Lattice Parameter a(Å)		Unit Cell Volume V (Å^3)		Density ρ (gm/cc)		Crystallite Size (nm)
	Obs.	Std.	Obs.	Std.	Obs.	Std.	
$LaAlO_3$-1	3.7909		54.4787		6.5174		33.064
$LaAlO_3$-2	3.7964	3.789	54.7162	54.396	6.4891	6.529	36.092
$LaAlO_3$-3	3.7890		54.3968		6.5272		34.792

Table 1 : Calculated structural parameters of $LaAlO_3$ samples

As observed, the lattice parameter, unit cell volume and density of the sample prepared with O/F=1.5 reaches the bulk value. The crystallite sizes are also in nanometer size (33-36nm).

Figure 2 shows the FTIR spectra for the prepared $LaAlO_3$ samples. From the spectra, it is noticed that the bandν_1 has the values 665.44, 664.78, 663.17 cm^{-1} respectively for $LaAlO_3$-1, $LaAlO_3$-2, $LaAlO_3$-3 samples. These bands are assigned to the AlO_6 octahedra. In the lower

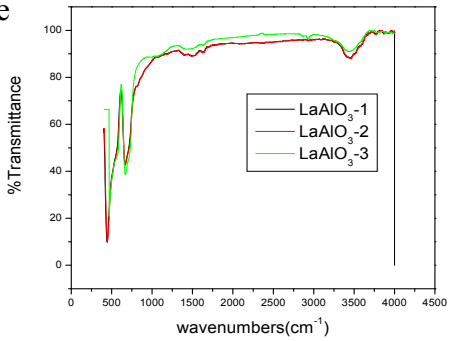

Figure 2. FTIR spectra of $LaAlO_3$ samples

frequency range the band ν_2 appeared at 443.10, 439.1, 439.89 cm^{-1} are assigned respectively to the La-O co-ordination of the $LaAlO_3$-1, $LaAlO_3$-2, $LaAlO_3$-3 samples. Since nanoparticles are prone to absorb moisture when it is exposed to air, the broad band appeared around 3500 cm^{-1} may be assigned to the OH stretching vibration of the surface co-ordinated water.

Figure 3 shows the optical absorption spectra $LaAlO_3$ samples. All the samples have a clear absorption edge around 232nm. This wavelength corresponds to the charge transfer between the bands known as the optical band gap. By constructing Tauc plot between $(\alpha h\upsilon)^2$ versus $h\upsilon$, the optical band gap energy can be evaluated. From the constructed graphs, estimated values are respectively 4.95 eV,4.77eV and 4.88eV.

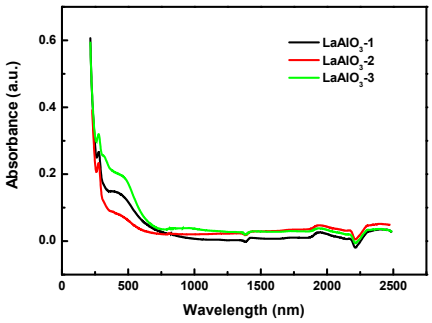

Figure 3. Optical absorption spectra of $LaAlO_3$

4. Conclusions

Phase pure $LaAlO_3$ have been successfully synthesized using an auto-combustion route. The O/F ratio has remarkable effect on the structural evolution of the compound. The lattice structure was confirmed as rhombohedral. The phase formation was confirmed from the FTIR absorption bands at respective wavenumbers. The optical band gap energies were calculated from UV-VIS absorption spectroscopy.

References

[1] S.Y. Cho, I.T. Kim, K.S. Hong, J. Mater. Res. 14 (1999), 114.

[2] R.W. Simon, C.E. Platt, A.E. Lee, K.P. Daly, M.S. Wire, J.A. Luine, M. Urbanic, Appl. Phys. Lett. 53 (1998), 2677.

[3] T. Takahashi, H. Iwahara, Energy Convers. 11 (1971), 105.

[4] B.C. Lux, R.D. Clark, A. Silazar, L.K. Sveum, M.A. Krebs, J. Am. Ceram. Soc. 76 (1993), 2669.

[5] R. Pazk, G.A. Seisenbaeva, R. Wiglusz, L. Kepinski, V.G. Kessler, Inorg. Chem 50 (2011), 2966.

[6] S.N. Koc, F. Oksozomer, E. Yasav, S. Akturk, M.A. Gurkaynak, Mater. Res. Bull. 41 (2006), 2291.