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RESEARCH ARTICLE

LOW TEMPERATURE SYNTHESIS AND CHARACTERIZATION OF LaNiO₃ NANOPARTICLES

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Manuscript Info

Abstract

The synthesis, structure and characterization of LaNiO3 nanoparticles were studied using a simple sol-gel combustion method. The overall process involves three steps – formation of homogenous solution, formation of dried gel and final combustion of the dried gel. On ignition in air, the compound is found to transform into nanosized LaNiO3 nanoparticles. The analysis of X-ray diffraction (XRD) data confirmed the orthorhombic LaNiO3 perovskite of space group R c without any impurity phase. The Scherrer's formula was employed to estimate the crystallite size of the prepared sample. For a further insight into the crystal structure, Scanning electron microscopy (SEM) imaging was done. The estimated values of the crystallite size from Scherrer's formula and SEM were found to be roughly the same. The SEM images confirmed the polycrystalline nature of the prepared sample. Furthermore, UV measurements were performed on the compound to estimate its band gap energy. The values were found to match well with those reported elsewhere in literature.EDX measurements performed on the sample confirmed the existence of La, Ni and O elements.

Introduction:-

Perovskite mixed oxides with the general formula ABO_3 containing both rare earth elements and 3d transition metals have received considerable attention in the past few years on account of their interesting electrical, magnetic, optical and catalytic properties[1]. Among these materials, Lanthanum Nickel Oxide, $LaNiO_3$ herein referred to as LNO with a perovksite structure is considered to be of great interest because of its electronic, optical and catalytic properties which make it a promising material for its use as electrode material for storage and conversion of energy or electrolytic synthesis [1].In this context, it is of relevance to examine the preparation parameters of Lanthanum nickelate for its structural and optical properties that can throw light on some of its applications. The preparation of LNO and other related compounds have been achieved by many methods, including sol-gel [2,3], combustion synthesis [4-6] and hydrothermal synthesis [7]. However, all these wet chemical methods, to some extent, still require calcinations at relatively high temperature and long soaking to produce powders with good crystal structure. This leads to making the crystalline grains grow larger in size and weakens the reactivity, and hence obtaining nanosized particles is difficult. Hence, in LNO, we have followed a novel means to prepare monophasic nanosized LNO powder by the sol-gel process and low temperature combustion processes similar to that reported in [8].

In the present study, nano-synthesized LNO was prepared using a citrate-nitrate auto-combustion technique. In addition, characterization by X-ray diffraction that gives information about the crystal structure, crystal composition, lattice parameter, spacing between two crystal planes, particle size, FTIR(Fourier Transform Infrared Analysis)for

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knowing the molecular bonding between the atoms, UV- Visible spectroscopy that uses absorbance or reflectance in the visible region of the EM spectra to find the band gap energy in the sample, Scanning electron microscopy (SEM) to study the morphological structure and composition analysis of the sample and EDX to confirm composition of the sample elements were performed.

Experimental:

$LaNiO_3$ was prepared using a citrate-nitrate auto-combustion method. Analytical grade $La(NO_3)_2.6H_2O$ and $Ni(NO_3)_2. 6H_2O$ were used as starting materials. The metal nitrates were discretely dissolved in distilled water and then mixed together under constant stirring at 70°C. Citric acid was added to the mixture and the pH of the solution was controlled by drop-wise adding of proper amount of ammonia solution during the stirring process as so maintain the pH = 7. Ethylene glycol was then added to the mixture and heated at about 200°C in open air by decomposing the dried gel and finally a dark brown powder was formed after an intense exothermic combustion reaction. The powder was ground and then calcined at 600°C for three hours followed by pelletization and sintering at 600°C for five hours. Nanocrystalline LNO was obtained.

The sample was deemed to be phase pure, as X-ray diffraction recorded (XRD) data collected on a Rigaku X-ray diffractometer in the range of $10° \leq \Theta \leq 80°$ using CuK_α ($\lambda =1.5418$ A°) radiation showed no impurity reflections. The diffraction pattern was Rietveld refined using FULLPROF suite and structural parameters were obtained. Fourier-transform infrared spectroscopy data was recorded for the sample in the range of 4000 cm^{-1} to 500 cm^{-1} at the Research centre of Dhempe College. UV-visible diffuse reflectance spectra were recorded for the sample in the range of 200 to 800 nm at the Department of Physics, Goa University. Scanning electron microscope (SEM) image and Energy dispersive X-ray spectrometer were recorded on the Zeiss make scanning electron microscope at the Instrumentation Centre, Goa University.

Results and Discussion:-

Fig. 1 shows the room temperature XRD pattern of the gel combustion synthesized LNO powder prepared by the citrate-nitrate auto-combustion technique. The XRD pattern confirms the formation of a pure LNO phase with a well-defined rhombohedral distorted perovskite structure in the space group $R\overline{3}c$., without any impurity phase. All reflections are somewhat broad indicating the nanocrystalline nature of the sample. The XRD pattern is similar to that reported by [9] where the perovsite structure is the only phase observed.
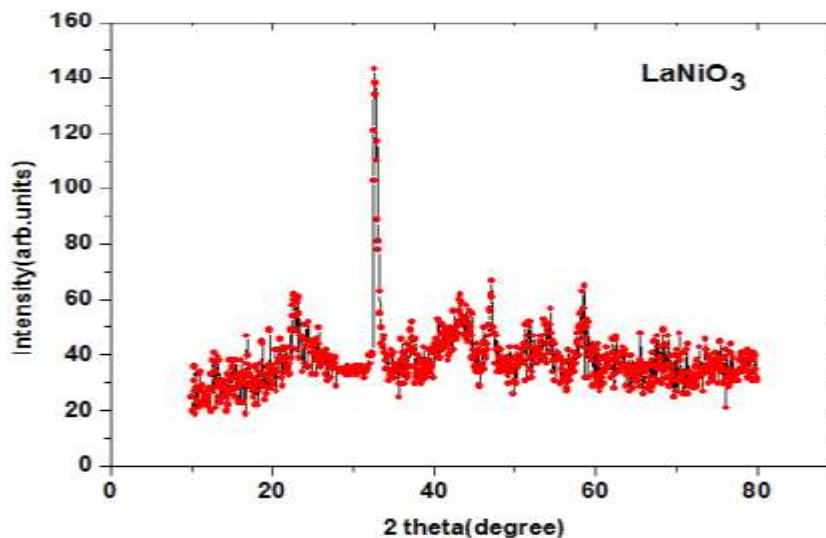

Fig 1:- XRD pattern for LNO in the range $10° \leq \Theta \leq 80°$.

The FULLPROF program was used for Rietveld analysis of the XRD data of LNO as seen in Fig.2. Refinements were performed in the space group $R\overline{3}c$.   In each refinement, a total of more than twenty parameters were refined: zero shift, scale factor, background coefficients, lattice parameters, oxygen parameters for isotropic temperature factor and full width at half maximum. The observed intensity data are plotted in the upper section as points (Black).

The calculated intensities are shown in the same section as curves (Red). The difference between the observed and calculated intensities is shown in the lower section (Blue line). The short vertical bars in the centre of the plot show the Bragg positions (Green). Atomic coordinates for each cation in the A and B sites, the residual errors, and the refined lattice parameters for the rhombohedral LNO perovskite with the space group R $\overline{3}$ c are displayed in Table 1.
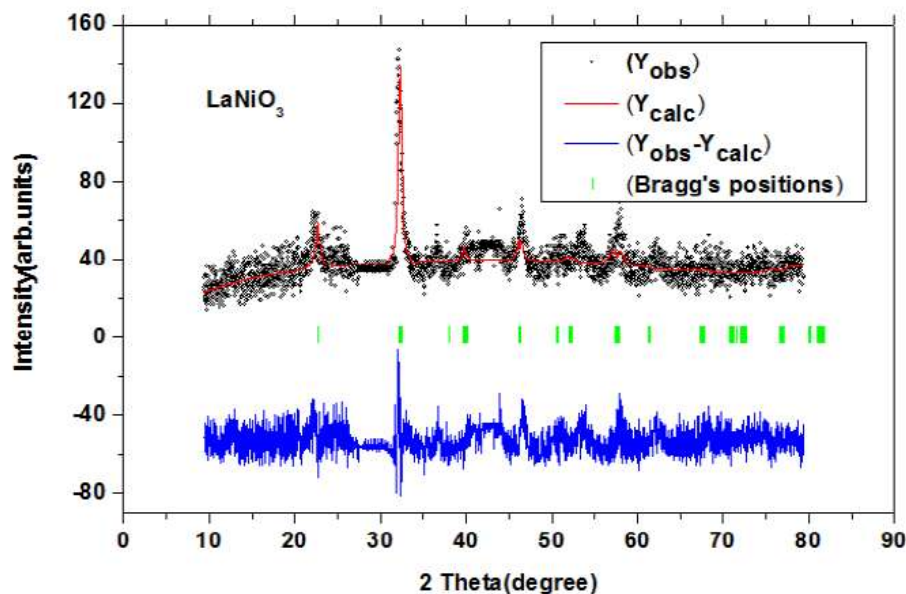

Fig 2:- Rietveld refined XRD pattern for LNO. The open circles (black) show the observed counts, the continuous line (red) passing through these counts is the calculated profile, and the difference between the observed and calculated (blue) is shown as a common line at the bottom of the two profiles. The Bragg positions (green) are shown as vertical bars.

Table 1: Atomic coordinates for each cation in the A and B sites, R factors, equivalent thermal parameters and refined lattice parameters for the orthorhombic LNO perovskite with space group R $\overline{3}$ c.

Label	Type	Atomic coordinates			Biso	Occupancy
		x	y	z		
La	La	0	0	0.25	1.45465	0.5
Ni	Ni	0	0	0	1.04626	0.5
O	O	0.12087	0	0.25	14.16823	1.0

$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$

a/A°	5.56274	R_{exp}	1.71
b/A°	5.56274	R_{wp}	4.76%
c/A°	13.5206	R_P	6.56%
V/A°	241.18	χ^2	1.15
a/b	1	R-factor	1.85%
c/b	2.4305	RF-factor	1.56%

Fig. 3 indicates the crystalline size of the LNO sample calculated by using the X-ray line broadening method and the Scherrer's formula $D = k\lambda/\beta Cos\Theta$ where D is the crystallite size in nanometers, λ is the beam wavelength (λ = 1.5414 A°), k is a constant equal to 0.94, β is the integral breadth and Θ is the peak position. The average crystalline size is calculated to be about 28.6 nm. This is found to be in close agreement with that reported in literature elsewhere.
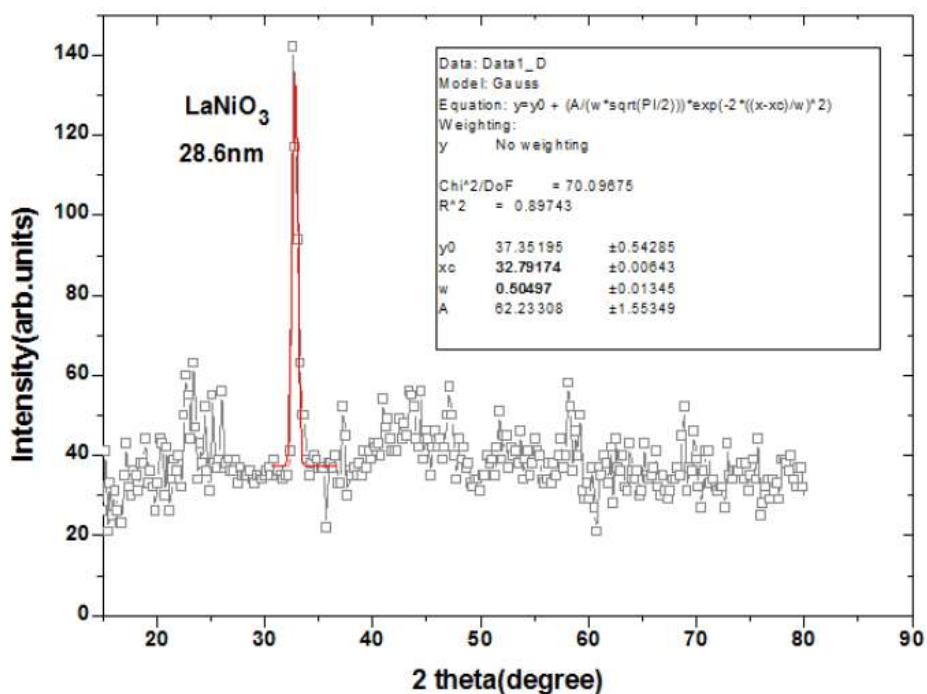

Fig 3:- Gaussian fit to the XRD data for determining particle size of LFO.

To understand the vibrational properties of the LNO nanoparticles, Fourier-transform infrared spectroscopy (FTIR) was performed on the sample in the range of 4000 cm^{-1} to 500 cm^{-1} as shown in Fig. 4. The peak at 1600 cm^{-1} is attributed to the strong O-H stretching vibration originating from condensed maters such as ambient water and incompletely reacted citric acid in our experiment. Two other absorption peaks at 746 and 1024 cm^{-1} were also observed which are assigned to the Ni-O stretching and the bending vibration mode, respectively. These two peaks

are a characteristic of the octahedral NiO_6 groups in the perovskite compound and reveal the existence of the LNO phase.
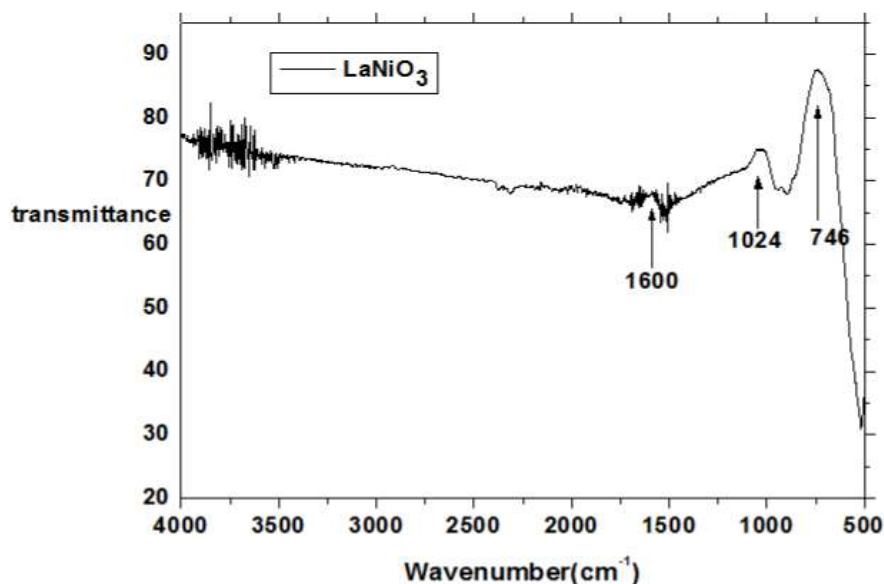

Fig 4:- FTIR for LNO in the range 4000 cm^{-1} to 500 cm^{-1}.

For semiconductor materials, the energy bandgap can be determined by their optical absorption performance. The UV visible diffuse reflectance spectra of the LNO nanoparticles in terms of absorbance as seen in Fig. 5 was collected as a function of the wavelength in nm. The optical bandgap of the LNO nanoparticles can be deduced by determining the cut-off wavelength λ_C from the spectra. The bandgap of the LNO nanoparticles was determined to be 2.12 eV.
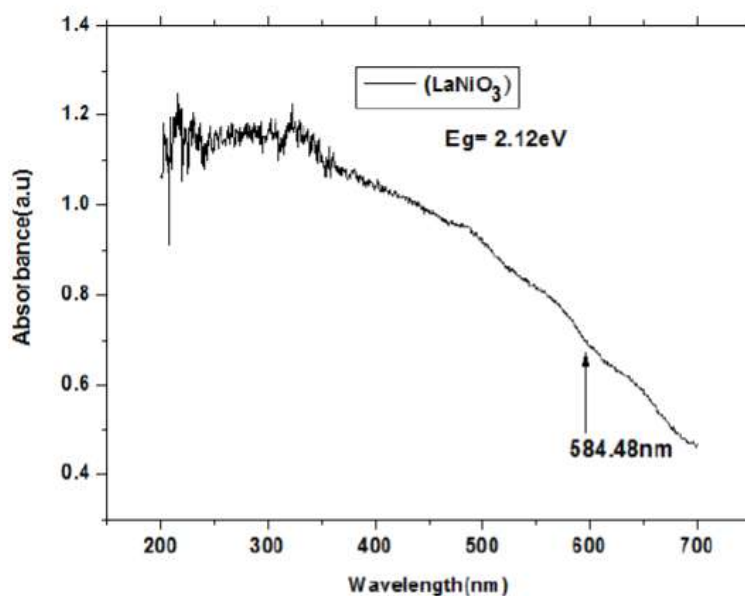

Fig 5:- UV spectra for LNO.

SEM was employed to obtain direct information about the size and structure of the produced LNO nanocrystals. Fig. 6 presents a typical SEM image that shows monodisperse particles with an average size of 36.7 nm, which is consistent with the size obtained from the peak broadening in X-ray diffraction studied of LNO. Such a consistency

implies that the LNO nanoparticles are single crystalline. The results in Fig. 6 show that the structure obtained by the low temperature preparation method is quite heterogeneous.
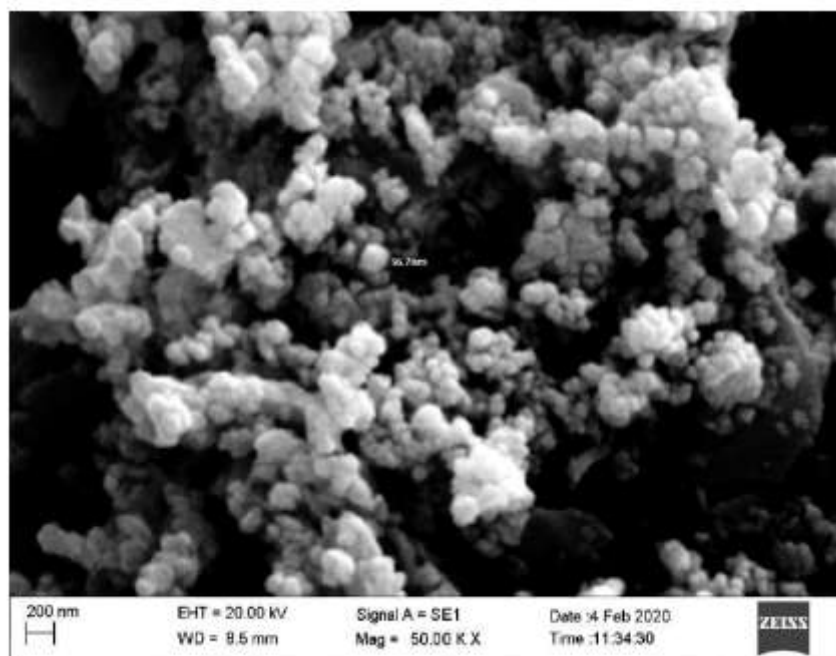

Fig 6:- SEM measurements for LNO with indication of particle size of 36.7 nm at 50K magnification.

Energy dispersive X-ray was performed on the LNO sample to confirm the sample composition. Three different areas of the sample were arbitrarily selected to ascertain the sample composition. The EDX results from the sample as seen in Fig. 7 confirm the existence of La, Ni and O elements. The elements present are La, Ni and O with a mole ratio of 1:1:3 corresponding to the stoichiometric composition of $LaNiO_3$. The results show well-arranged La rich particles and with other regions where the amounts of Ni and La are closer to the ideal ones for the synthesis of perovskite oxides. Table 2 shows the stoichiometric composition of La, Ni and O. The SEM and EDX results are found to match quite well with that cited in [9].
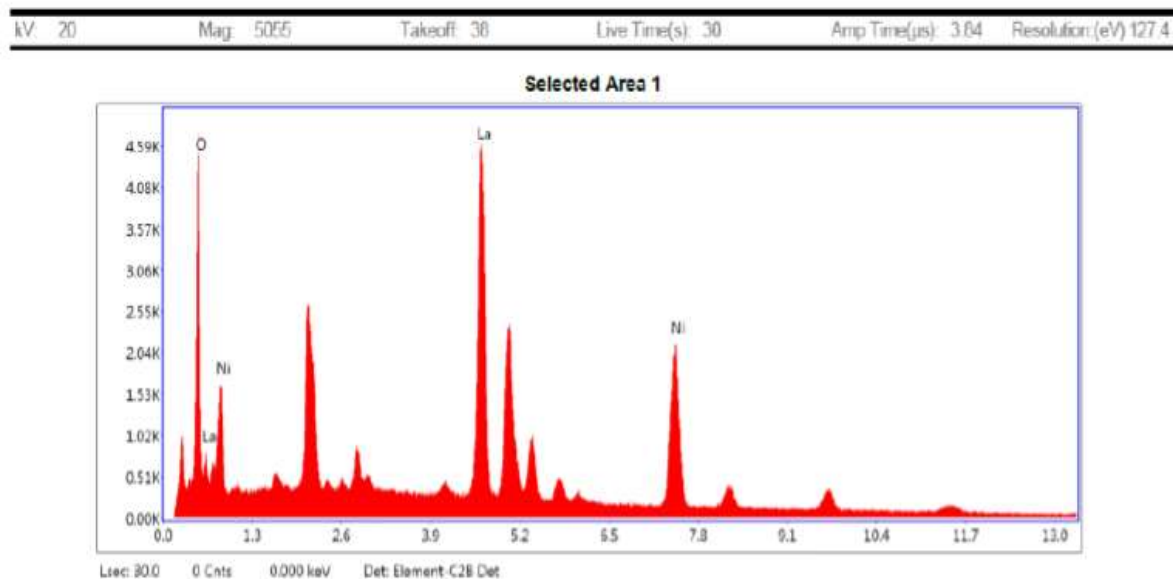

Fig 7:- EDX spectra for LNO nanoparticles.

Table 2:- Stoichiometric ratio of La, Ni and O.

Element	O-K	Ni-K	La-L
Wt%	11.29	29.86	58.86
Atom %	43.09	25.87	31.04

Conclusion:-

In summary, the synthesis, characterization, composition and band gap energy were studied using a simple technique of preparation at a low temperature of 600°C. Nanosized $LaNiO_3$ powders of 36.7 nm particle size were prepared directly through the simple sol-gel auto-combustion technique. The entire process of synthesizing pure nanosized $LaNiO_3$ powders involved three steps: formation of solutions, formation of the dried gel in air followed by auto-combustion that can be considered as a heated-induced exothermic oxidation-reduction reaction between the nitrate and carboxyl groups. The process is easy, simple and cost effective although analytical grade compounds were used as starting materials. The XRD pattern confirmed the formation of a pure LNO phase with a well-defined rhombohedral structure in the space group $R\bar{3}c$, without any impurity phase. The crystalline size of the LNO sample was calculated by the X-ray line broadening method using the Scherrer's formula and average crystalline size is calculated to be about 28.6 nm. FTIR measurements performed on the powders indicate a clear existence of the Ni-O stretching and the bending vibration mode, and the peaks reveal a characteristic of the octahedral NiO_6 groups in the perovskite compound and existence of the LNO phase. UV measurements performed on the powders reveal band gap energy of about 2.12 eV. SEM measurements indicate particles with an average size of 36.7 nm, which is consistent with the size obtained from the peak broadening in X-ray diffraction studied of LNO. Such a consistency implies that the LNO nanoparticles are single crystalline. EDX measurements performed on the powders are a clear confirmation of the existence of La, Ni and O elements.

Acknowledgments:-

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