Studies on Structural, Thermal, Infrared & Morphological Properties of $(La_{1-x}Nd_x)_{0.7}Sr_{0.3}MnO_3$ (x = 0.0, 0.2, 0.4, 0.6, 1.0) prepared by Citrate Precursor Route

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Abstract: *Study of the effect of Nd substitution for polycrystalline perovskites at different concentrations, $(La_{1-x}Nd_x)_{0.7}Sr_{0.3}MnO_3$ (x = 0.0, 0.2, 0.4, 0.6, 1.0) is presented. These nanoparticles were synthesized by citrate-nitrate precursor route. This technique offers better homogeneity, preferred surface morphology, reduced heat-treatment conditions, nano-sized particles and better crystallinity. All the samples were calcined at 1000 °C for 3 h. The samples were characterized by X-ray diffraction (XRD), thermo gravimetric analysis (TG-DTA), fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). The phase contents and lattice parameters were studied by powder XRD. Mass, temperature, crystallinity were measured by TG-DTA. The chemical bonds were identified by the measurements of FTIR spectra. FTIR revealed that stretching and bending modes were influenced by calcination temperature. Morphological and particle size studies were done through TEM.*

Key Words: *CMR manganites, Citrate-nitrate precursor route, XRD, TEM, FTIR.*

1. INTRODUCTION:

The perovskite manganites $A_{1-x}B_xMnO_3$, where A is a trivalent lanthanide cation and B is a divalent cation, have recently attracted much attention because of their technical applications [1]. Among others, Sr-doped LnMnO3 is particularly of interest due to its good magnetic, electrical and physical properties. These materials have novel physical properties and potential applications, such as magnetic-field sensors, hard disk read heads, fuel cells, infrared devices, spintronics, and micro-wave active components, etc. The synthesizing methods are very important to obtain the polycrystalline samples with special microstructure. The structure, electronic, and magnetic properties of $R_{1-x}A_xMnO_3$ perovskite are usually dependent on the preparation routes [2]. A variety of methods have been developed to prepare ABO_3 nanoparticles, including sol–gel route, auto combustion process, hydrothermal synthesis, citric acid-ethylene diamine gel route & amorphous citrate method etc. The citrate gel procedure offers a number of advantages like low cost, is relatively simple, generates less carbon residue and is quite effective in producing highly sinterable ceramic powders [3].

2. METHEDOLOGY :

$(La_{1-x}Nd_x)_{0.7}Sr_{0.3}MnO_3$ (LNSMO) nanoparticles were synthesized by a citrate-nitrate precursor route. In this process high purity lanthanum acetate hydrate, neodymium acetate hydrate, strontium acetate hydrate and manganese (II) acetate tetra hydrate (Sigma-Aldrich, Purity 99.99%) were used as the starting materials, which were dissolved in doubly distilled water. Small amount of nitric acid & aqueous solution of citric acid was also added to convert the corresponding precursors into their respective nitrates. The mixed citrate–nitrate precursor solution was continuously stirred on a hot plate at 85 °C, which resulted in a thickened brown viscous gel. Further heating at 400 °C caused slow ignition of the gel forming a black residue called black ash, which was started to swell and filled the beaker producing a foamy precursor. The foamy precursor was decomposed to give very light homogeneous, black-colored flakes of extremely fine particle size. The powder obtained by pulverizing these flakes was calcined at 1000 °C temperature. XRD data were measured with PANalytical X'pert Pro-Diffrectometer employing CuKα radiation over the range of 20°≤2θ≤80°. Thermal analysis (TG-DTA) of the precursor was recorded on thermal analyzer model LINSEIS STA PT 1600 at the heating rate of 10 °C/min under ambient atmosphere for the purity and structural conformity of the powder. Chemical bonds were identified by fourier transform infrared. Infrared spectra were obtained using KBr pellets, by Nicolet-6700 Thermo Scientific Spectrometer. The homogeneous grain size and a high sinter ability was measured by transmission electron microscopy, Philips, Holland (model: Tecnai 20).

3. RESULTS & DISCUSSION:

The structure of the calcined samples was determined by X-ray diffraction (XRD). The obtained XRD profiles of $La_{0.7}Sr_{0.3}MnO_3$ (x=0.0) and $(La_{0.8}Nd_{0.2})_{0.7}Sr_{0.3}MnO_3$ (x=0.2) could be indexed by monoclinic structure with $P2_1/a$ (14) space group while $(La_{0.6}Nd_{0.4})_{0.7}Sr_{0.3}MnO_3$ (x=0.4), $(La_{0.4}Nd_{0.6})_{0.7}Sr_{0.3}MnO_3$ (x=0.6) and $Nd_{0.7}Sr_{0.3}MnO_3$ (x=1.0) could be best described by orthorhombic structure with Pnma (62) space group, according to the index card JCPDS (86-1531) data base. The XRD patterns show that all of the samples are having perovskite structure and perfect single phase in nature. The average crystallite size for each sample was estimated from respective XRD profile using the Scherrer formula $t=k\lambda/(B\cos\theta)$. The crystallite sizes, cell parameters and cell volume are listed in Table 1. Sudden change in cell volume may be due to the higher doping of Nd.
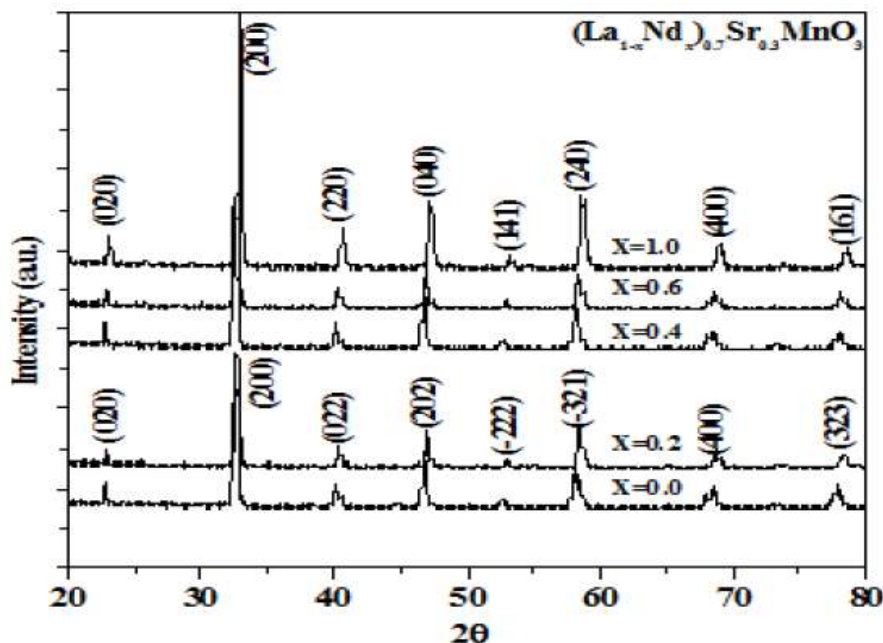

Figure 1. Evolution of the X-ray diffraction patterns of LNSMO at different concentrations.

The TEM micrograph at a calcination temperature of 1000 °C shows the clear coexistence of two types of grains. One is comparatively smaller in size, whereas other is comparatively larger in size. These micrographs show that grains are in the nanometric regime (less than 200 nm) indicating the nanometric particle size distribution. TEM micrograph of the samples reveals that the particles are nearly spherical in shape with a smooth surface morphology and are narrowly distributed in size. The particle size for each concentration is listed in Table 1. The average particle size increases with increasing concentration of Nd at La site.
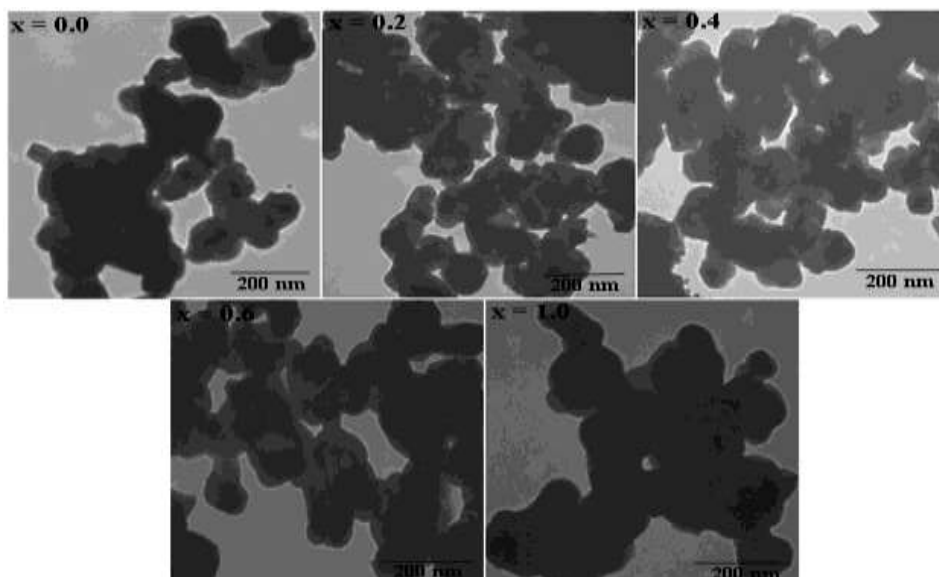

Figure.2: TEM micrographs of LNSMO at different concentrations (x=0.0, 0.2, 0.4, 0.6, 1.0).
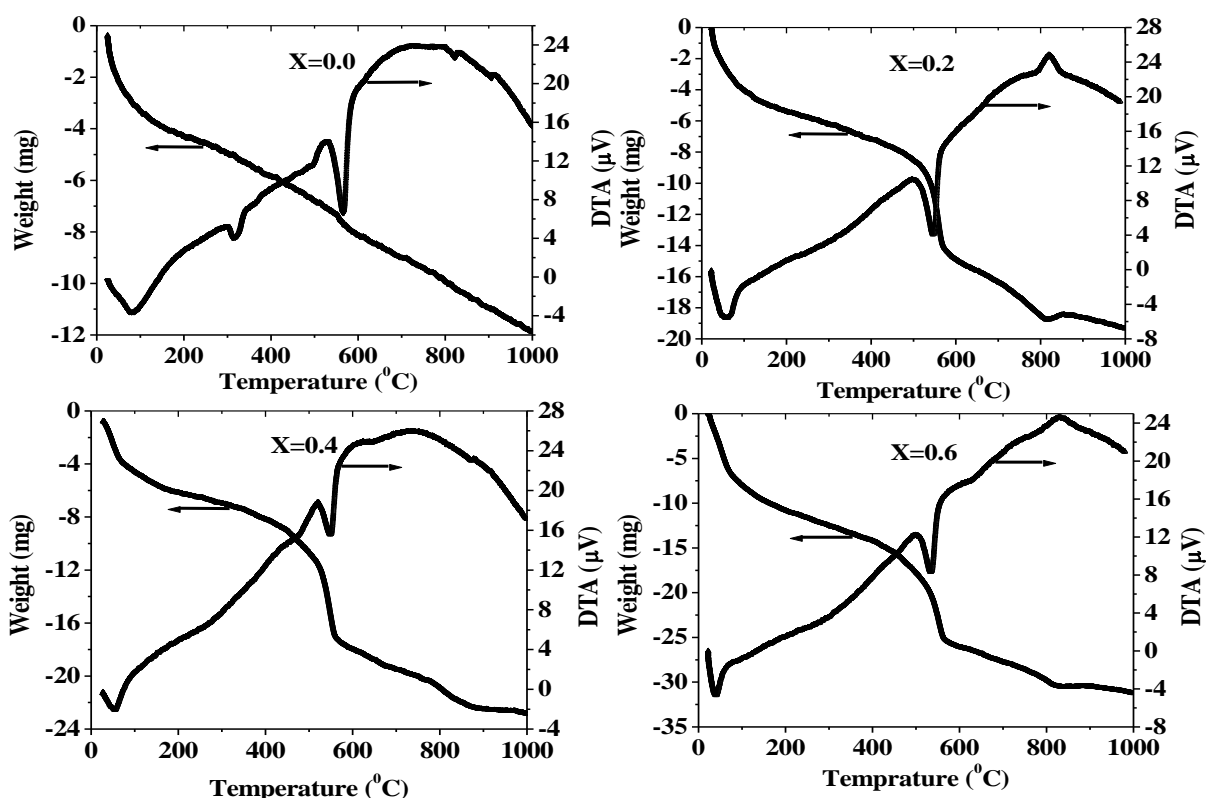
Figure. 3: TG/DTA curves of LNSMO at various concentrations (x=0.0, 0.2, 0.4, 0.6).

The TG-DTA curves of the precursor material heated at 400 °C are shown in Fig. 3. The TG curve indicates three weight loss steps: the first between 20 - 200 °C; which can be due to thermal dehydration of La, Nd, Sr and Mn acetate hydrates, second step between 400 °C - 600 °C; which can be due to the elimination of decomposition of the residual organic compounds of the precursor and the loss in third step between 720 °C - 800 °C; due to the decomposition of metal nitrate-citrate complex. The DTA curves exhibit an endothermic peak around ~70 ℃, ~300 ℃, ~550 ℃ and a large exothermic peak at ~860 °C. Endothermic peaks can be assigned for dehydration of absorbed water from the precursor and decomposition of trapped organic residues or from the ongoing crystallization process and accompanying structural transformations. Exothermic peak can be ascribed to the burning of organic material in the sample and to the gradual crystallizing process of LNSMO.
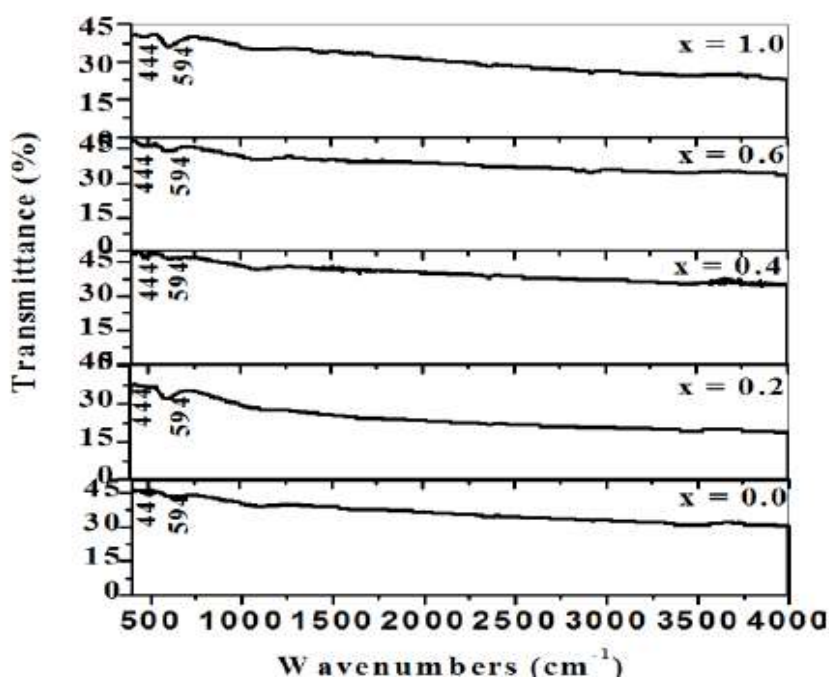
Figure. 4: Infrared spectra of LNSMO at various concentrations (x = 0.0, 0.2, 0.4, 0.6, 1.0).

FTIR spectra were obtained using KBr pellets, from an upper limit of around 4000 cm^{-1} down to 400 cm^{-1}. The IR spectra of the sintered powders at 1000 °C for 3 h are shown in Fig. 4. IR transmittance spectra of the compounds with x = 0.0, x = 0,2, x = 0.4, x = 0.6 & x = 1.0 have been shown. The peaks around 594 cm^{-1} are assigned to the stretching vibration mode of the MnO_6 octahedron in which the Mn–O bond distance is modulated. This represents a crystalline powder containing solely the (LNSMO) perovskites without a trace of any phase impurities. The peaks around 444 cm^{-1} are assigned to the bending vibration in which the Mn–O–Mn bond angle is modulated. The chemistry for the formation of these perovskite materials by this technique may be inferred from the FTIR spectral changes observed during each of the process steps.

Table 1: The structure, cell parameters, cell volume, crystallite size & particle size of LNSMO nanoparticles for

Concentration (x) & Structure	Cell Parameters (Å)			Cell Volume $(Å)^3$	Crystallite Size nm from (XRD)	Particle Size nm from (TEM)
	a (Å)	b (Å)	c (Å)			
x=0.0 (Monoclinic)	5.471	7.771	5.503	233.96	21 nm	28 nm
x=0.2 (Monoclinic)	5.398	7.764	5.512	231.00	28 nm	44 nm
x=0.4 (Orthorhombic)	5.445	7.781	5.545	234.92	36 nm	56 nm
x=0.6 (Orthorhombic)	5.492	7.609	5.415	226.28	40 nm	64 nm
x=1.0 (Orthorhombic)	5.425	7.663	5.490	228.22	43 nm	75 nm

(x=0.0, 0.2, 0.4, 0.6 & 1.0).

4. CONCLUSION:

In summary, LNSMO nanoparticles have been successfully synthesized by citrate precursor route. It exhibits lower calcination time duration, lower processing temperatures, high purity of materials, good control of size and shape of the particles and particle size well below 100 nm at the lower processing temperature.

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