

Studies on Strontium Doped NdGaO₃ Electrolyte

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ABSTRACT: NdGa_{1-x}Sr_xO₃ (0 ≤ x ≤ 0.5) nano crystalline powders were synthesized by Nd(NO₃)₃, Ga(NO₃)₃, Sr(NO₃)₂ and aspartic acid (fuel) in assisted combustion method. This synthesized precursor was heated in a Muffle furnace at 600°C for 6 hours. This process remarkably reduced the synthesis time and less energy consumable to obtain NdGa_{1-x}Sr_xO₃. The structure of NdGa_{1-x}Sr_xO₃ nano powders were confirmed by x-ray diffraction method. The average crystallite size was determined from X-ray line broadening analysis by using the Scherer equation. The surface morphology of the synthesized crystalline powder was characterized by scanning electron microscopy (SEM). Thus, particle size and porosity were determined. The formation of the product NdGa_{1-x}Sr_xO₃ was confirmed by FTIR studies. The synthesis and crystallization were followed by thermochemical techniques (TGA/DTA) studies. The synthesized materials showed reasonable electrical conductivity. These results indicate that assisted combustion method is a promising method to prepare nano crystalline NdGa_{1-x}Sr_xO₃ electrolyte material for solid oxide fuel cell.

Keywords: Electrical conductivity, SEM, Scherer equation, TGA & DTA, XRD and FTIR.

I. INTRODUCTION

Fuel cells are electrochemical device that converts the chemical energy into electrical energy. The electrochemical reactions take place at the electrodes to produce an electric current. Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. Today Combustion synthesis (CS) has become a very popular approach for preparation of nano materials and is practiced in 65 countries. Recently, a number of important breakthroughs in this field have been made, notably for development of new catalysts and nanoparticle carriers with properties were better than those for similar traditional materials. The extensive research carried out in last five years emphasized the capabilities for materials improvement, energy saving and environmental protection. In prior review on CSM of advanced materials published in 2002, the combustion synthesis with special emphasis on the preparation of catalysts by solid state and solution combustion were discussed.

The high oxygen ion conductivity over wide range of temperature and oxygen pressure in developments in the stabilized zirconia has led to its use as a solid oxide electrolyte in a variety of electrochemical applications. These include high temperature solid oxide fuel cells (SOFCs) which offer a clean, pollution-free technology to electrochemically generate electricity at high efficiencies. They have wide range of potential applications ranging from providing power for portable devices (eg. Mobile phones, laptop computers) and transport applications, to small and large scale stationary power applications.

Although the SOFC operates at a high temperature, it has several significant applications because it promises cleaner, more efficient energy conversional power plant or lower temperature polymer-based fuel cells. Targeted applications include the bottoming cycle of an electric power plant, domestic heat, power units and even electric vehicles. Stationary fuel cells are used for commercial, industrial and residential primary and backup power generation. Fuel cells are very useful as power source in remote locations, such as spacecraft remote weather stationary, large parks, communications centers, rural locations including research stations and in certain military

In the present work, synthesis of NdGa_{1-x}Sr_xO₃ nano powders by assisted combustion method. The effect of different ratios on phase evaluation, size and shape of the NdGa_{1-x}Sr_xO₃ particles were studied. Oxide materials with high mobility of oxygen ion receive extensive attention owing to the potential applications in solid oxide fuel cells, oxygen sensors, oxygen pumps, and oxygen-permeable membrane catalysts.

II. EXPERIMENTAL AND CHARACTERIZATION PROCESSES

2.1 Materials

The NdGa_{1-x}Sr_xO₃ solid solution was synthesized through a assisted combustion technique. All starting materials used were highly pure: The Nd(NO₃)₃, Ga(NO₃)₃, Sr(NO₃)₂ were used as reagents and aspartic acid used as fuel (Purity 99.9%, Sigma Aldrich). In this method, stoichiometric amount of Nd(NO₃)₃, Ga(NO₃)₃, Sr(NO₃)₂, and aspartic acid (fuel) in small quantity of distilled water to form a homogeneous solution. This

solution was kept at constant heating at 80°C to obtain the foamy powders of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ is shown. 2.1 For Calcination, the foamy powder was carried out in a muffle furnace at 600°C for 6 hours.

The X-ray data were recorded in terms of the diffracted X-ray intensities (I) vs. 2θ . The crystalline size was calculated with the help of Scherrer's formula, which is given as $D = 0.9\lambda/\beta\cos\theta$, Where D is the crystallite size, β is the full-width at half-maximum (FWHM) of the most intensity λ diffraction peak in radians, θ is the diffraction angle and λ is the wave length of X-ray radiation.

Morphology of the synthesized powder was analysed with scanning electron microscopy (SEM) model (Leo series 1430 VP) equipment with INCA was used to determine the morphology of samples.

TGA is a process which relies on measuring the change in physical and chemical properties of a sample as a function of temperature (with constant heating rate) or as a function of time (with constant temperature). It is predominantly used for determining the features of a material that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles. DTA is a technique which rests on obtaining chemical composition of a substance under heating condition.

The synthesized sample was analysed with FTIR spectrometry. During this process, a small amount of powder was mixed along with IR grade powder and then this powder was transferred in to a sample cup of the diffuse reflectance accessory and scanned in a region of about $400\text{-}4000\text{cm}^{-1}$. The density of the sintered pellets was also determined by the Archimedes method using distilled water at the immersion medium.

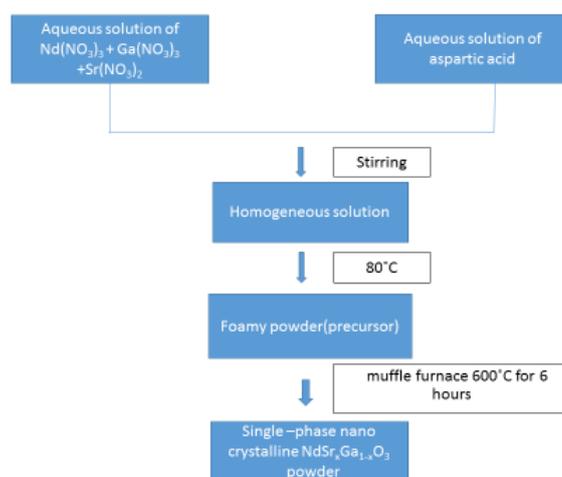
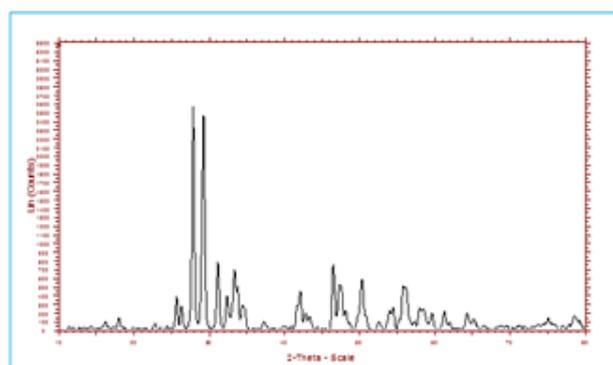


Fig.2.1. Flow chart of assisted combustion synthesis of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$

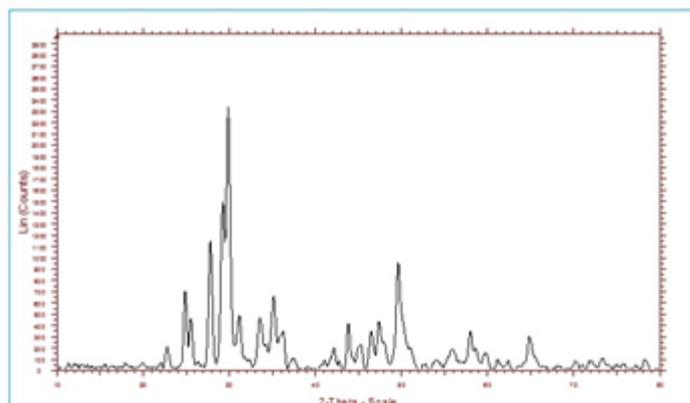
III. RESULT AND DISCUSSION

3.1. Analysis of Crystalline Structure

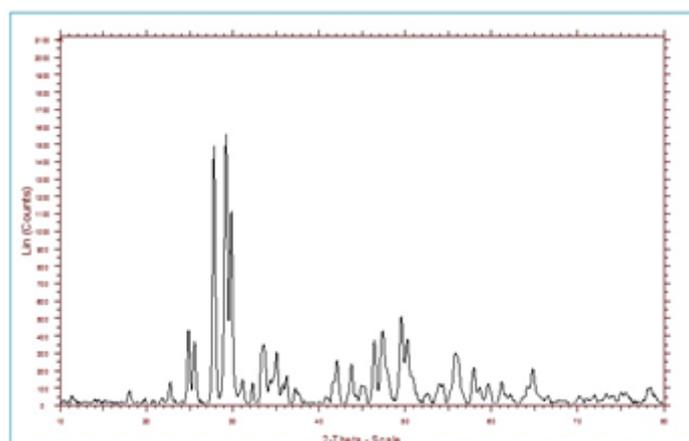
The XRD of synthesized powder and samples sintered at different ratios are shown in Fig.3.1. It can be seen from Fig.3.1, the perovskite phase has existed in the resulting powder, but the impurity phase has exist clearly as well. In general, all the diffracted peaks are broader than usually observed for highly crystalline powder. The lattice parameter calculated for the synthesized $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$, which is good agreement with literature value. The broadening in the diffracted peaks is attributed to the superfine crystalline nature of composites. The size of the particles were calculated by Scherrer equation it was 32 nm.



3.1a XRD pattern of NdGaO_3



3.1b. XRD pattern of $\text{NdGa}_{0.5}\text{Sr}_{0.5}\text{O}_3$



3.1c. XRD pattern of $\text{NdGa}_{0.7}\text{Sr}_{0.3}\text{O}_3$

3.2. SEM analysis:

Fig.3.2 shows the microstructure of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ powder obtained at the 600°C for 6 hours. The surface morphology of material in the form of agglomeration were investigated with scanning electron microscope. The particles are not uniformly distributed. There is agglomeration of the particles. The particles of the synthesized products are in nano range.

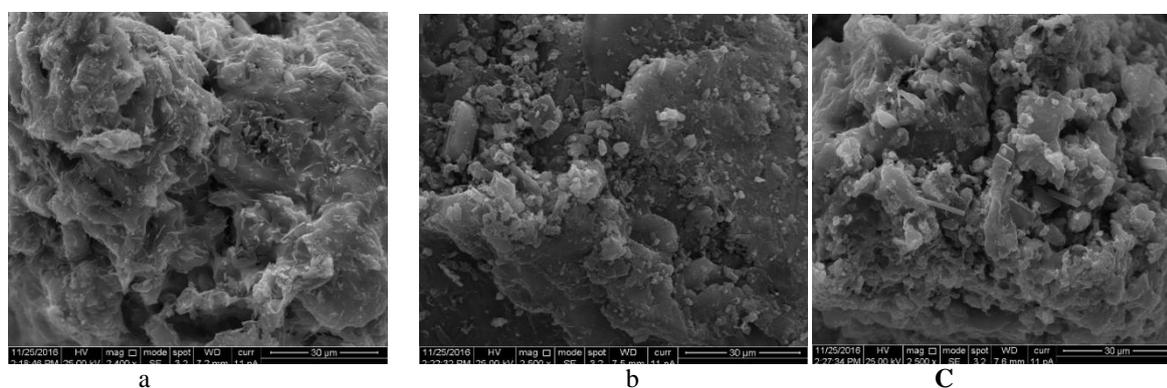


Fig.3.2. SEM photograph of (a) NdGaO_3 , (b) $\text{NdGa}_{0.5}\text{Sr}_{0.5}\text{O}_3$, (c) $\text{NdGa}_{0.7}\text{Sr}_{0.3}\text{O}_3$

3.3. Thermal Analysis TGA/DTA:

Fig 3.1 shows that the TGA/DTA pattern obtained on $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ powder. In the TGA pattern the $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ sample showed a weight loss of about 0.033 mg/min until 65°C . The sample on further heating from 100°C - 800°C , showed a weight increase to 0.068mg/min during 493.51°C - 711.64°C . The weight gain and weight loss indicated that the $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ powder exhibited easy reversible absorption-desorption of oxygen from air. The weight loss is minimum because of the removal of residual H_2O and different gases. The chemical decomposition with an increases of temperature was examined through DTA and it appeared as the endothermic

and exothermic peaks in the DTA curve. From the DTA curve, it is seen that a broad endothermic peak at 586.83°C occurred. From the above TGA/DTA data, the $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ gradually absorbs the oxygen from air with temperature.

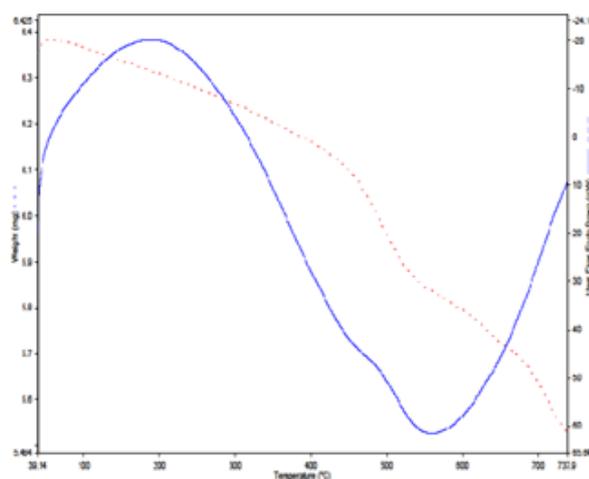


Fig. 3.1 TGA & DTA of $\text{NdGa}_{0.7}\text{Sr}_{0.3}\text{O}_3$

3.4. FTIR analysis:

FTIR spectroscopy was used to verify the functional groups present in the crystal and to investigate their vibrational behavior in solid state. The infrared spectrums of synthesized samples of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ powder are shown in fig 3.1. The powder exhibited a strong bond at $850\text{--}1100\text{ cm}^{-1}$ due to the stretching mode of the Ga-O bond in the structure. The peak appeared at 1444.5 cm^{-1} corresponds to the H-O-H bond mode confirming the presence of moisture in the sample. The peak appeared at 2060.0 cm^{-1} is due to the presence of CO_2 in the sample. The sample $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ exhibited a low intensity peak at 1497.1 cm^{-1} sample exhibited two peaks obtained between the wavelength regions $1400\text{--}2000\text{ cm}^{-1}$ and observed at $1444.5, 2060.0\text{ cm}^{-1}$. The peak appeared at 1444.5 cm^{-1} is related to the O-H stretching vibration of H_2O in the sample. The major peak reported for $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ in literature coincide with the observed FT-IR spectrum for $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ which confirmed the single phase of this material.

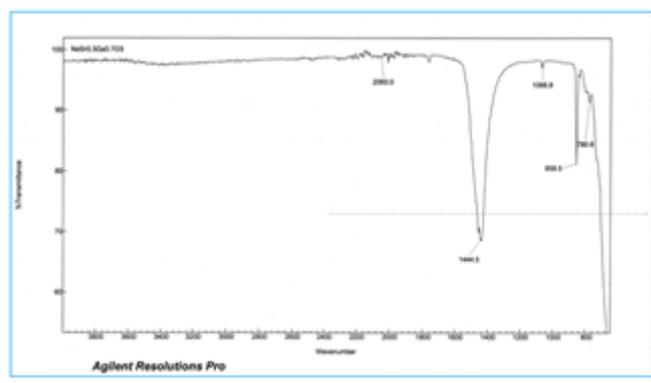


Fig 3.1 FT-IR spectrum of $\text{NdGa}_{0.7}\text{Sr}_{0.3}\text{O}_3$

3.5. Conductivity Studies

Fig.3.5 shows that the Arrhenius plots of conductivity for $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ samples sintered at different ratios. It can be seen from Fig.3.6 that the conductivity of the samples increases gradually with increasing the temperature. In this case, grains grow excessively, and the pores are trapped among the grains or grain boundaries, blocking oxygen ion migration, leading to the decreases in the conductivity of the sample. The volatilization of gaseous Ga_2O and O_2 from $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ at excessively high sintering temperature were detected by mass spectroscopy resulting in the sample volumes bloating and density reduction, so that the conductivity decreases.

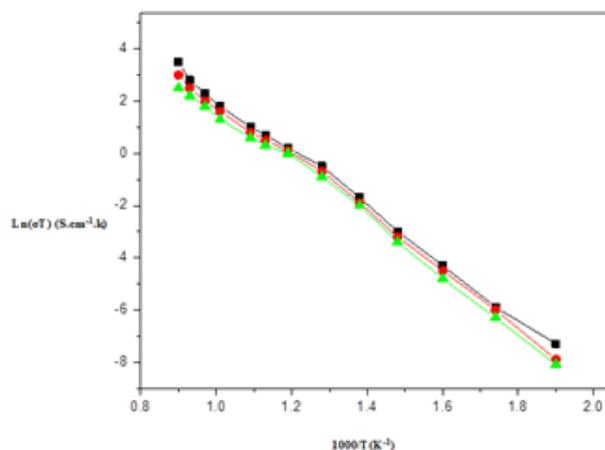


Fig.3.5. Arrhenius plots for the $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ samples sintered at different ratios

IV. CONCLUSION

The present investigation was carried out to improve the performance of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ by the synthesis method. The electrochemical behavior of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$ based materials depends upon the method of synthesis and sintering temperature. Hence, these conditions were adopted for the present work to synthesize the phase-pure, nanocrystallite materials. The present work was mainly focused on synthesis, and ionic conductivity of $\text{NdGa}_{1-x}\text{Sr}_x\text{O}_3$.

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