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Studies On Gdgao$_3$ Electrolyte For Intermediate Temperature Solid Oxide Fuel Cell

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Abstract: *$GdGaO_3$(0 ≤ x ≤ 0.5) nano crystalline powders were synthesized by $Gd(NO_3)_2$, $Ga(NO_3)_2$, and aspartic acid (fuel) in a combustion method with heating at 600^0C for 6 hours. This process remarkably reduced the synthesis time and less energy consumable to obtain $GdGaO_3$. The structure of $GdGaO_3$ nano powders were confirmed by x-ray diffraction method. The average crystallite size was determined from X-ray line broadening analysis by using the scherrer equation. The surface morphology of the synthesized product was observed by SEM studies. The formation of the product $GdGaO_3$ 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 indicates that assisted combustion method is a promising method to prepare nano crystallineGdGaO$_3$electrolyte material for solid oxide fuel cell.*

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

I. Introduction

Solid oxide fuel cells SOFCs, Which convert chemical energy directly into electrical energy, have been viewed as promising newpower-generating systems and true multi-fuel energy devices.(1) Recently significant efforts have been directed towards the development of intermediate temperature solid oxide fuel cell (IT-SOFC) due to its high power density and high working efficiency when operated around 500-800˚C. Mixed ionic-electronic conductivity(MIECs) have attracted attention of researchers due to high thermal and chemical stability along with high oxygen diffusion and electronic conductivity. (2)

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. Today 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 nanocarriers with properties better than those for similar traditional materials. The extensive research carried out in last five years emphasized the (SHS) capabilities for materials improvement, energy saving and environmental protection. In prior review on CS 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. (3)

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 electrically generated 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. (4)

Although the SOFC operates at intermediate temperature,it has several significant applications because it promises cleaner, more efficient energy conversion that either a conventional power plant or lower temperature polymer-based fuel cells. Targeted applications include the bottoming cycle of an electric power plant, domestic heat and power units, and even electric vehicles.(5) In order to extent their range of applications, SOFCs should have a high power density along with a small physical size, in other words a high volumetric power density. This can be achieved by either improving the material properties used for the components.(6)

These fuel cells provide many advantages over traditional energy conversion systems including high efficiency, reliability, modularity, and very low levels of NO_X and SO_X emissions.The major advantage of SOFCs over polymer electrolyte membrane fuel cells (PEMFCs) is their superior tolerance to impurities in the fuel which allows for their operation using lower quality, thus less costly and more widely available, fuel. (7)

II. Experimention And Characterization Processes

2.1 Materials

The $GdGaO_3$ solid solution was synthesized through a assisted combustion technique. All starting materials used were highly pure: The$Gd(NO_3)_2$, $Ga(NO_3)_2$,and aspartic acid (Purity 99.9%, Sigma Aldrich) were used as reagents. All of the reagents, in requisite stoichiometric ratio, were dissolved in the double distilled deionized water, separately. Later, all of the solutions were mixed together and stirred to obtain a homogeneous solution. A gel was appeared after continuous stirring at 80˚C for depending on the element

2.2 preparation

The nano-crystalline $GdGaO_3$was synthesized by assisted combustion method. In this method, stoichiometric amount of $Gd(NO_3)_3$, $Ga(NO_3)_2$, and aspartic acid (fuel) in small quantity of distilled water to form a homogeneous solution.This solution was kept at constant heating at 80^0C to obtain the foamy powders of $GdGaO_3$ is shown in flow chart as.2.1 ForCalcination, the foamy powder was carried out in a muffle furnace at 600˚C for six hours.

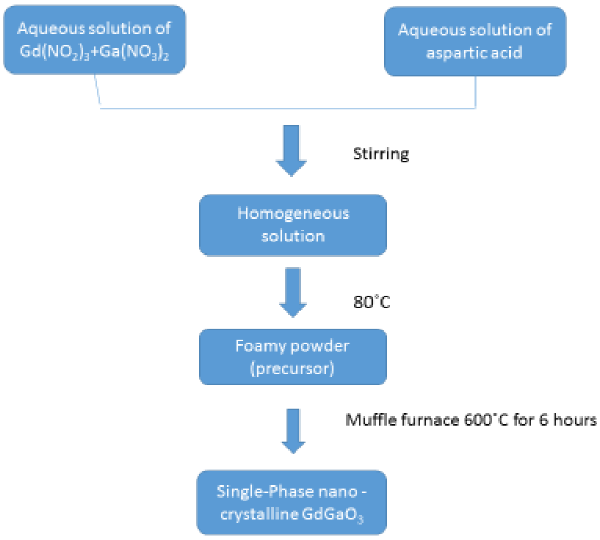

Fig.2.1. Flow chart of assisted combustion synthesis of $GdGaO_3$

2.1 Characterization of produced particles

2.1a. X-ray diffraction (XRD) analysis:

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 \Wdiffraction peak in radians, θ is the diffraction angle and λ is the wave length of X-ray radiation.

2.1b. Morphological studies:

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

2.1c. Thermal gravimetric analysis/differential temperature analysis (TGA/DTA):

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.

2.1d. Fourier transform infrared (FTIR) spectroscopy:

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 400-4000cm^{-1}.The electrical conductivity of the sintered pellets were measured by a dc-four probe method in which temperatures range 200-700^0C in air

III. Result And Discussion

3.1. Analysis Of Crystal Structure

The powder XRD analysis was performed on the prepared$GdGaO_3$nanocrystallinepowders at 600°C for 6 hours. It was used for identifying the crystallite size of $GdGaO_3$ powder. The peaks in the XRD plots were sharp which indicated nanocrystalline structure. The obtained XRD data were profile-fitted with X' pert high score plus software before indexing. All of the diffracted peaks are broader than usually observed for highly crystalline solids. The broadening in the diffracted peak is attributed to the super fine crystalline nature of composites. The obtained lattice constant (a=6.8685Å, b=2.5961Å, and c=3.4343Å) and their lattice volume [61.2381Å], indicates that the $GdGaO_3$ belongs to orthorhombic. Furthermore, the crystalline size increases with an increase in X with in the solid solubility limit.It is identical with sample prepared by conventional solid state method.The crystallite size of the$GdGaO_3$ is 32.

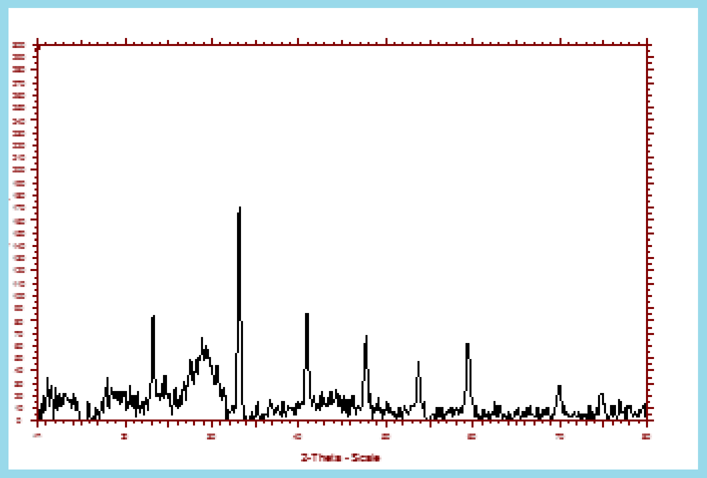

Fig 3.1 X-ray diffraction pattern of $GdGaO_3$

3.2ANALYSIS OF CRYSTAL STRUCTURE

SEM analysis:

Fig.3.2 shows the microstructure of $GdGaO_3$ powder obtained at the 600°C for 6 hours. The surface morphology of material in the form of Ortho rhombic structure and agglomeration were investigated with scanning electron microscope. The particle size was distribution for $GdGaO_3$powders, the average crystallite size was 32 nm. The particles are uniformly distributed. There is agglomeration of the particles. The particles of the synthesized products are in nanorange.

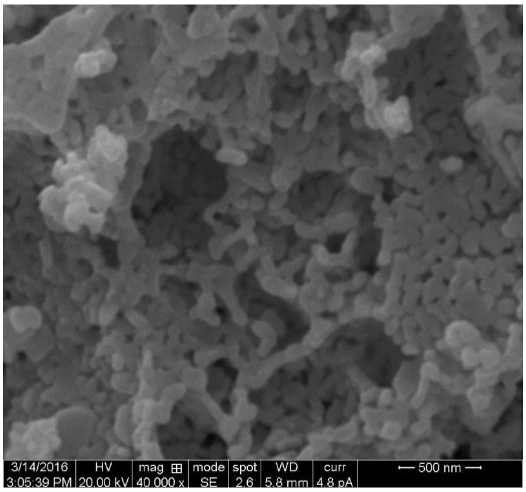

Fig 3. 2 SEM photograph of $GdGaO_3$

3.3. THERMAL ANALYSIS

TGA/DTA:

Fig 3.3 shows that TGA/DTA pattern obtained on $GdGaO_3$ powder. In the TGA pattern the $GdGaO_3$ sample showed a weight loss of about 0.026 mg/min until 65^0C. The sample continuously weight loss at 4.0. The sample on further heating from 100^0C-800^0C, showed slight weight gain and loss of about 0.026mg/min. Again the sample showed a weight increase from 335.97^0C-560.53^0C and loss of 0.580mg/min during further heating upto 584.53^0C. The weight gain and weight loss indicated that the $GdGaO_3$ powder exhibited easy reversible absorbtion-desorbtion 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 exothermic peak at 586.83^{0}C occurred due to the weight losses between 39.95^{0}C-725.7^{0}C in TGA curve. From the above TGA/DTA data, the $GdGaO_3$gradually absorbs the oxygen from air with temperature.

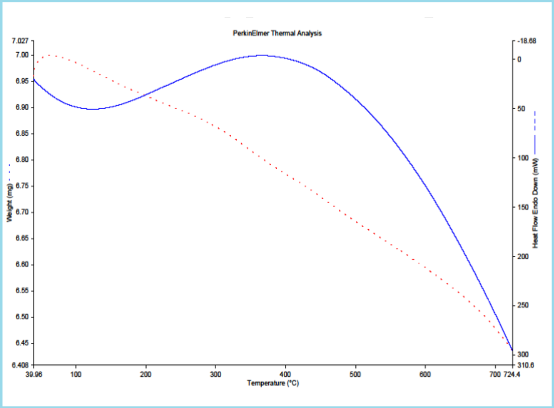

Fig. 3.3 TGA &DTA of $GdGaO_3$

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 $GdGaO_3$ powder are shown in fig.5.4. The powder exhibited a strong bond at 600-900 cm^{-1} due to the stretching mode of the Ba-O bond in the structure. The peak appeared at 1077.0 cm^{-1} corresponds to the H-O-H bond mode confirming the presence of moisture in the sample. The peak appeared at 1406.3 cm $^{-1}$ is due to the presence of CO_2 in the sample. The sample $GdGaO_3$ exhibited a low intensity peak at 1497.1 cm $^{-1}$ sample exhibited two peaks obtained between the wavelength regions 1400-1600 cm^{-1} and observed at 1077.0, 1406.3, and 1497.1 cm $^{-1}$. The peak appeared at 1077.0 cm^{-1} is related to the O-H stretching vibration of H_2O in the sample .The major peak reported for $GdGaO_3$ in literature coincide with the observed FT-IR spectrum for $GdGaO_3$ which confirmed the single phase of this material.

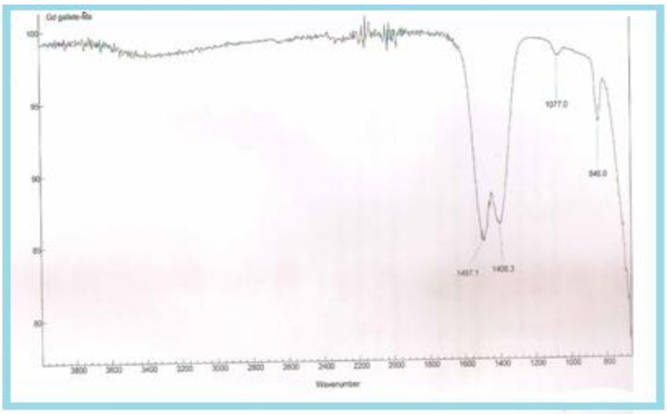

Fig 3.4 FT-IR spectrum of $GdGaO_3$

3.5. CONDUCTIVITY

The Electrical Conductivity of $GdGaO_3$ was measured at temperature 100-700˚C in air is shown in fig 3.5. The $GdGaO_3$ was a mixed conductor. The total conductivity involved both electronic and ionic conductivity terms, due to the presence of holes and oxygen vacancies. The ionic conductivity was about two orders of magnitude lower than electrical conductivity. The charge imbalance caused by a replacement of Ga^{2+} could be accommodated either by an oxidation of Gd^{3+} (electronic compensation) or by the formation of oxide ion vacancies (ionic compensation) in $GdGaO_3$. Electrical conductivity of $GdGaO_3$ increased gradually with temperature.

For the composition with semi conducting behavior, the temperature dependence of the conductivity can be described by the small polar on hopping mechanism as σ=A/T exp (-Ea/KT) the activation energies obtained from the Arrhenius plots of log σ vs1000/T. The changes in the activation energy with temperature for $GdGaO_3$ are attributed to the spin state transition.

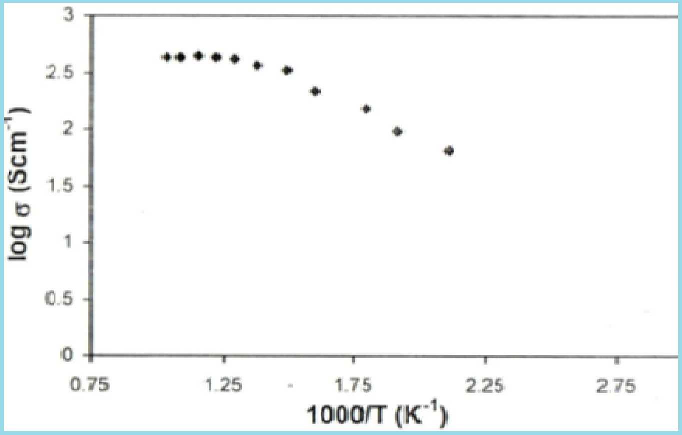

Fig 3.5 Electrical conductivity of $GdGaO_3$

IV. Conclusion

The present investigation was carried out to improve the performance of $GdGaO_3$ by the synthesis method. The electrochemical behavior of $GdGaO_3$ based materials depends upon the method of synthesis and sintering temperature. Hence, these conditions were adopted for the present work to synthesis the phase-pure, nanocrystallite materials. The present work was mainly focused on synthesis, and electronic conductivity of $GdGaO_3$.

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