SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINELAFE0$_3$ DOPED WITH CD FOR GAS SENSOR APPLICATION.

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Abstract :
$Cd_{1-x}La_xFe0_3$ crystallites were prepared by sol-gel citrate method.A stoichiometric mixture of Lanthanum nitrate and Ferric nitrate with citric acid monohydrate and ethylene glycol was used.The solution of Cadmium nitrate was used as dopant in varying wt.% of Cadmium nitrate.Particle size was determined by XRD using Scherrer's equation.XRD analysis confirmed the formation ofnanosizedLaFe0$_3$material.The particle size was found to be ~ 27nm.Conductivity measurements shows the Cadmium doped(15%)LaFeO$_3$shows highest conductivity at 700^{0}C.Gas Sensitivity measurement shows the 10wt% Cd doped $LaFeO_3$ adsorbed maximum H_2S gas at 250^{0}C.

Keywords : Sol- gel, nano composite, Gas sensor, etc.

Introduction :

Over the past 20 years, a great deal of research effort has been directed towards the development of small dimensional gas sensing devices for practical application ranging from toxic gas detection. [1] However, many of these efforts have not yet reach commercial viability because of problem associated with the sensor technologies applied to gas – sensing micro systems.Inaccuracies and inherent characteristics of the sensors themselves have made it difficult to produce fast,reliable and low maintenance sensing systems comparable toother micro sensor technologies that have grown into wide spread use commercially [2] .With the increasing demand for better gas sensors of higher sensitivity and greater selectivity, intense efforts are being made to find more suitable materials with the required surface and bulk properties for use in gas sensors.

The pollutants, which are due to be monitored in the near future, are SO_2, NO_2, PM10 particles, lead, O_3, CO & benzene [3] the key success in developing a single functional gas sensing device is the technology of mastering underside functions such as cross sensitivity with other gas species.The chemical gas sensors generally contain a physical transducers and chemically selective layer[4]. They act as transducers or detecting elements and provides vital information about specific chemical constituents in the environment.Gas sensing generally involves catalytic reactions of the gas or vapor by the surface of the sensor.Different materials such as semiconducting oxides (SnO_2,ZnO,TiO_2),catalytic oxides (V_2O_5,MoO_3,CuO,NiO),metals deposited on oxides supports (Pt/SnO_2,Pt/ZnO,Pd/SnO_2) and mixed oxides exhibit different physical properties on exposer to different gas species. Semiconductor based sensors are being used for many applications due to their low price and simple measurement electronics.

Catalyst such as Pt and Pd increase the rate of oxidation at lower temperatures. The surface conductivity depends on the density of donors and acceptors.The density of these surface species therefore varies due interaction with the intermediates.Silica,alumina and certain specific ceramics substrates are currently being used as basic materials to deposits these gas sensing materials because of their high temperature stability[5].Single crystal silicon wafers,pre-oxidized on both sides for electrical isolation, serve as a better substrate for the gas sensor microsystems.It is also possible to used silicon as a construction material for transducers,exploiting silicon planer processing technology and the excellent mechanical properties[6].

A semiconductor gas sensor possesses an electrical resistance made with a porous assembly of tiny crystals of an n-type metal oxide semiconductor,typically SnO_2,In_2O_3,WO_3.The crystals are often loaded with small amount of foreign substance called a sensitizer.When operated adequate temperature in air,the resistor changes its resistance sharply on contact with small concentration of reducing gas or oxidizing gas, enabling us to know the concentration from the resistance change.With a report by Seiyamaet.al[7] and a patent by Taguchi[8],this groups of sensors has been subjected to a tremendous amount of R & D efforts worldwide aiming at improvements of sensing performances and extensions to new applications.Semiconductor gas sensors are surfacesensitive and bulk sensitive[9].Apart from such remarkable achievements in practical applications, basic understandings of sensors have hardly been satisfactory,despite tremendous efforts of so many researchers as summarized in reviews [10-13].

The Principleobjectives of the work is to establish & define ambient air quality.In this work, the sol gel technique has been employed to synthesized Nano sized $LaFeO_3$ and Cd doped $LaFeO_3$ with different mole percent. The nano sized materials and their electrical and sensing properties have been discussed.

Materials and Methods :- Synthesis of $LaFeO_3$ Nano composite

The Nano crystalline $LaFeO_3$ specimens were prepared by using sol- gel citrate method. A stoichiometry mixture of Lanthanum nitrate (Merck, India) and ferric nitrate (Merck, India) Was magnetically stirred with citric acid monohydrate (Merck, India) and ethylene glycol (Merck, India) at 80^0C for 2 hr to get homogeneous & transparent solution. The Solution was further heated at about 30^0C for 12 hr in a pressure vessel to from the gel precursor. The product was subjected to 3hr heat treatment at 350^0C in amuffle furnace and then milled to a fine powder. The dried powder calcinied in the range of 450 – 650 ^{0}C in order to improve the crystalanity of ceramic. The solution of cadmium nitrate was used as dopant in the precursor of $LaFe0_3$withvarying wt.% of cadmium nitrate.

Results &Discussion:

I] XRDAnalyses

The synthesized materials was characterized by X-ray diffraction technique XRD measurements were performed on Philips Analytic X-ray

B.V. (10 based model). Advanced X-ray diffraction using Cu K 1.54056, as shown in Fig. 1 shows the XRD pattern of a $LaFe0_3$calcinied at 550^0C shows that the product is pervoskite $LaFe0_3$ with an orthorhombic structure. The diffraction data are good agreement with JCPD card of $LaFe0_3$(JCPDS No. 37-1493). The average crystalline size of $LaFe0_3$was estimated with the help of Scherer's equation as given below.

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

The average particle size of Nano-crystalline $LaFe0_3$was found to be 27nm. No additional peaks were observed for CdO.

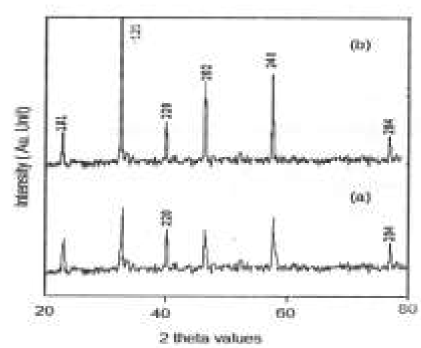
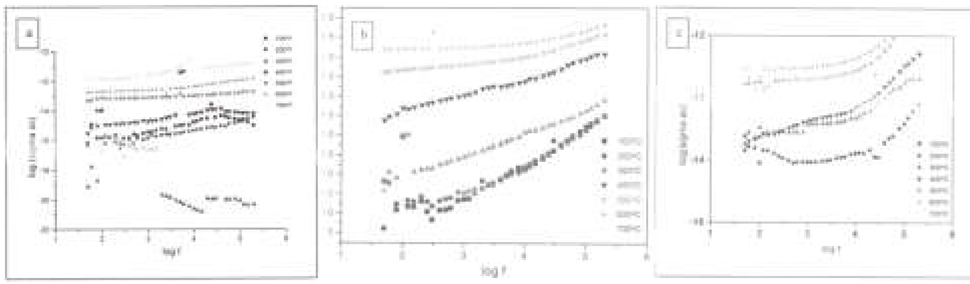


Fig. 1 : XRD pattern of
a) $LaFeO_3$ calcined at 550^0C calcined at 550^0C
b) 10 wt % Cd doped $LaFeO_3$ calcined at 550^0C

Fig. 1 : XRD pattern of a) $LaFeO_3$calcined at 550^0C b) 10wt% Cd doped $LaFeO_3$calcined at 550^0C

Conductivity :

Fig. 2a, 2b& 2cshows the variation of the conductivity with frequency for variable temperature range i.e. from 100-700^0C.From the graph it is clear that the conductivity of the Nano crystalline 10wt % Cd doped $LaFe0_3$sample is increases with increasing frequency as well as with increasing temperature, here at 700^0C particle shows the highest conductivity. When we move from the higher frequency to lower frequency the conductivity of the sample decreases in linear manner, thus it is indicate that the conductivity is the function of the temperature to the frequency.



2(a) 2(b) 2(c)

Fig. 2 :Variation of the conductivity with the frequency for (a) undoped Cd (b) 10wt%, Cd doped $LaFeO_3$ (c) 15wt% Cd doped $LaFeO_3$ Nano-crystalline sample

The electrical conductivity for Nano crystalline 10wt% Cd doped $Lafe0_3$samples show in increases of the conductivity with increasing temperature for all compounds indicating a characteristic activated behaviour over the complete temperature range studies. Rom impedance measurement, the total conductivity activation energies, Ea, were derived, yielding an activation energy 0.00013, 0.000129, 0.000128, 0.000126, 0.000128, 0.000125 eV for the frequencies 10, 50, 100, 120, 150 and 200 kHz respectively.

Gas sensing measurement of $LaFe0_3$:

`In order to calculate the sensitivity electrical resistance of the material measured in the presence & absence of H_2S gas Fig. 3a & 3b shows sensitivity as a function of calcination temperatures in the range of 450 – 850 ^{0}C for $Lafe0_3$based H_2S gas sensor at an operating temperature 250^{0}C. It is observed that the sensitivity increases for the sample ranged from 450-550^{0}C & then decreased above 550^{0}C. This may due to increased in surface area from the sample upgraded in forms of sensitivity, selectivity, reproducibility and stability, Although semiconductor gas sensors have so far been developed mostly be empirical research further development and innovation seems to be impossible without a fundamental understanding of the gas sensing mechanism.

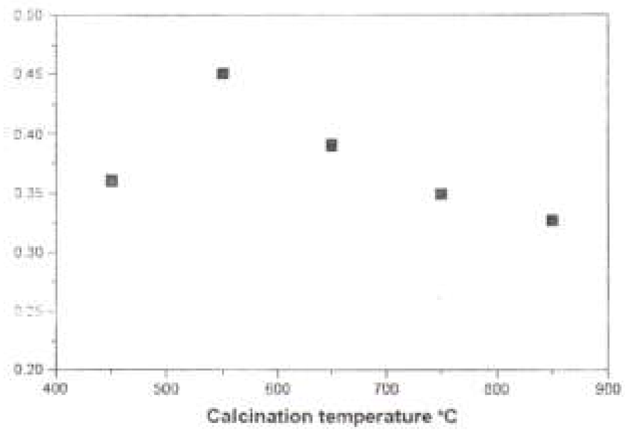


Fig. 3 a : Gas Sensing characteristics of $LaFeO_3$ at different operating temperatures for H_2S gas calcined at temperature ranges from 450-850^{0}C

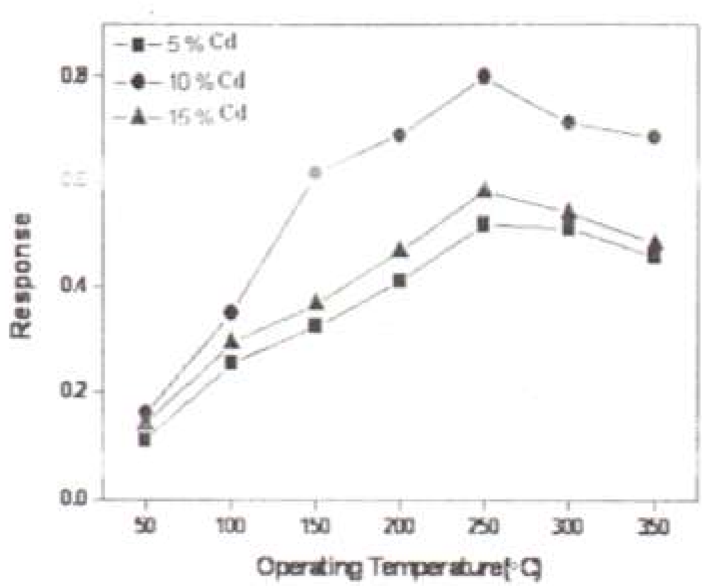


Fig. 3 b : Response of $LaFeO_3$doped with different amount of Cd for H_2S gas sensor (A) 5wt% Cd (B)10 wt% Cd (C) 15 wt% Cd.

Fig. 3(a),3(b) Shows sensitivity as a function of operating temperatures for at wt% cd doped $LaFe0_3$for H_2S gas. The sensitivity values for 10 wt % cd doped $LaFe0_3$ was found to increased as compassed to 5 and 15 wt % cd doped $LaFe0_3$. The highest sensitivity was observed at 250^0C operating temperature.

Conclusions:

We have synthesized $LaFe0_3$dopedwith Cd by using simple, low cost sol gel method having particle size 27nm. $LaFe0_3$showsslightly higher sensitivity towards H_2S at 325^0C., Cd as dopant, increased sensitivity towards H_2S gas with reduced temperature at 250^0C. the material shows good conductivity. The sensitivity for 10wt% Cd doped $LaFe0_3$was found to increase as compared to 5 and 15wt% Cd doped $LaFe0_3$. The highest sensitivity was observed at 250^0C operating temperature. The material synthesized may be useful to remove gases pollutants from atmosphere to establish and define ambient air quality.

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