SYNTHESIS,STRUCTURAL CHARACTERIZATION OF LACRO$_3$ NANOSTRUCTURE AND IT'S GAS SENSING APPLICATION

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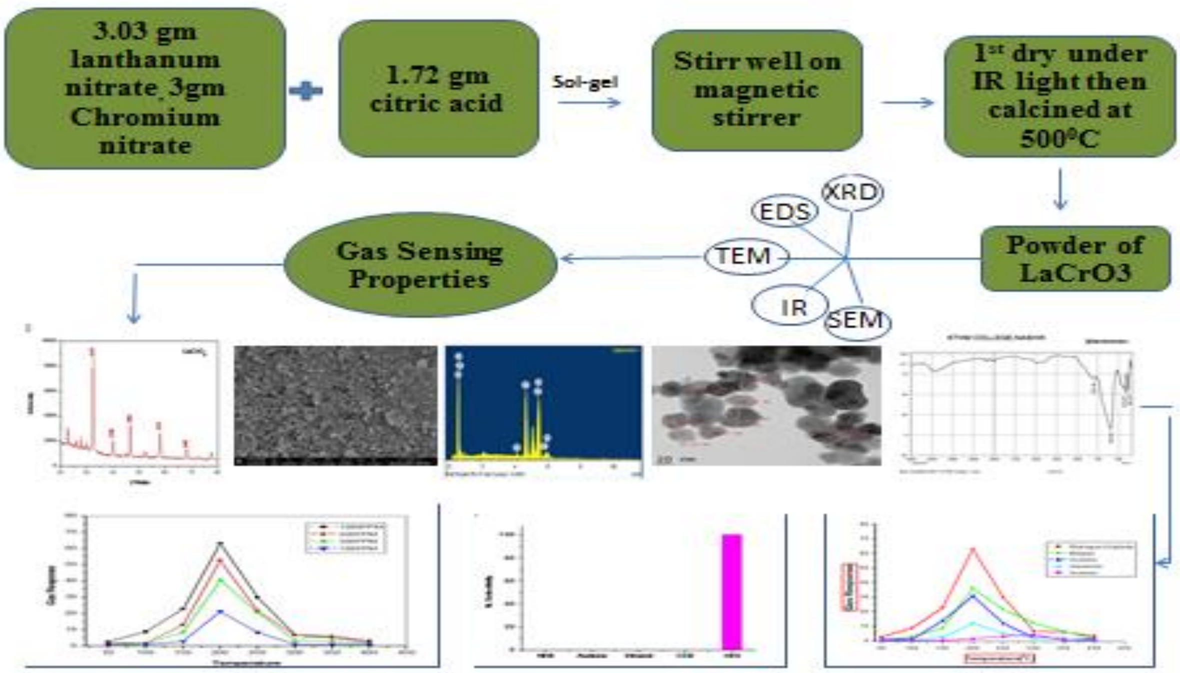
Abstract: In display work we choose Sol-gel route for synthesis of $LaCrO_3$ nanomaterial which found to act as a H_2S gas sensor. Characterization of it was done by XRD, SEM, TEM, EDX etc. From XRD we got a nanomaterial having average crystallite size 13.01nm having JCPDS Card No. 33-0701 from which $LaCrO_3$is having a perovskite type orthorhombic material. The SEM spectrum shows particles which dispersed on surface and the EDX indiates the elemental composition. By TEM we confirmed its particle size is 39.48nm. The bands596 cm^- for La –O stretch and 416.04 cm^- for Cr-O stretch showed by FTIR studies. From this material thick film were prepared by simple screen printing technique. Then the films were calcinated and were exposed to various gases at different temperature. The $LaCrO_3$ sensor shows selectivity for H_2S gas at working temperature range from 150^0C to 250^0C. Its response and recovery time were also studied.

GRAPHICAL ABSTRACT:



Graphical abstract for H_2S Sensing detecting by $LaCrO_3$.

INDEX TERMS:

Sol-gel Method, $LaCrO_3$ nanostructure, XRD, SEM, EDS, TEM, IR, H_2S sensing.

INTRODUCTION:

Day by day the importance of nanomaterials is will increase and we require inexpensive, transportable gas sensors. The gas sensors play the main function in human protection and obviously surroundings safety. Essentially the metal oxides are used as gas sensors for the detection of numerous toxic gases which may be hazardous for human fitness and environment (1, 2, 3,).
Perovskite compounds ABO_3 wherein A is alkali metal, alkaline earth metal or lanthanide elements,where in B is transition metal having vital chemical and physical properties like electric conductivity, stability, magnetic properties and so on. Because of such properties these materials are used as a attractive material,magnetic substances, catalysts and sensors.
$LaCrO_3$ is one of the ABO_3perovskite type materials which are chemically steady for redox environment. It also shows excessive electrical conductivity, stability and magnetic homes (4, 5, 6, 7, 8, 9). Such perovskite have been synthesized through different strategies like hydrothermal (10,11,12), Co-precipitation(13,14), Sol-gel (15,16,17). However from many views Sol-gel strategy is exceptionally imperative, this method having numerous point of interest than the other one. Sol-gel approach offers very high-quality particle size and homogeneous nanomaterials due to proper blending of crude material within the course of product formation. Additionally this approach is price powerful method (18, 19).
In this manner in present work, we have utilized the Sol-gel method to synthesize $LaCrO_3$. H_2S gas harmful for human well-being that is colorless, toxic, combustible fuel.Which ready to found in town sewage,gasoline, common gases and lots of others. Having scent like spoiled eggs. So it's exceptionally basic to screen and recognize its concentration for human wellbeing and ultimately in the surroundings (20-24).

MATERIAL AND METHODS:

Lanthanum nitrate [La $(NO_3)_3$], chromium nitrate [Cr $(NO_3)_3$] and all other chemicals become used in this synthesis are ARgrade purchased from Merck Chemicals India. The prepared compound is characterized in powder form for FTIR by means of the use of Shimadzu IR-affinity 1S. The crystal structure were analyzed by an x-ray diffractometer [Bruker D8, Advance, Germany] using CuKα radiation (λ=1.5409 Å) for the 2θ range from 20 to 80, The Field Emission Scanning Electron Microscopy (SEM) was performed on FEI NOVA SEM 450 and Transmission Electron microscopy (TEM) was performed on sJeol/JSM 2100.

EXPERIMENTAL:

Sol-gel Synthesis of $LaCrO_3$ nanoparticles

$LaCrO_3$ synthesis approach is similar to our prior work (1)**.**The $LaCrO_3$ prepared by sol-gel method. For this synthesis first hydrolyze3.03 g lanthanum nitrate [La$(NO_3)_3$],3 g chromium nitrate [Cr $(NO_3)_3$] in minimum amount of distilled water,and1.72g citric acid in another beaker. Both the solutions then mixed and heated at 80^0C with continuous stirring on magnetic stirrer to evaporate distilled water for minimum 2- 3 hours. During this stirring a homogeneous viscous gel were obtained having dark grayish color. This gel became initially dried under IR lamp for 1-2 hours. Then rough particles were beaten and grinded, and then calcined for 5-6 hours at 550^0 C. We got grayish color fine power of $LaCrO_3$.

Preparation thick films of LaCrO3 nanoparticles

Thick film preparation strategyis just like to our priorwork (1). The powder of nanoparticle of $LaCrO_3$transformed into thixotropic paste which became used to prepare thick films by simple screen printing method. Keeping the inorganic to organic materials ratio at 70:30. The inorganic part consists of nanomaterial ($LaCrO_3$). The organic part consisted of 8% ethyl cellulose and 92% butyl carbitol acetate act as binder. The $LaCrO_3$ with ethyl cellulose (EC) were mixed thoroughly in an acetone medium with mortar and pestle. And solution of BCA was added drop wise until proper thixotropic paste were achieved. Now thick film was prepared on glass substrate by using standard screen -printing technique. The film was dried under IR lamp for 1 hr to remove the organic volatile impurities and then fired at temperature 550^0C for 30 minutes in muffle furnace.

RESULTS AND DISCUSSION:

X-ray diffraction (XRD)

The XRD spectrum for prepared $LaCrO_3$ is as shown in Fig.1.Which were calcined at 550^0C, and then XRD pattern were recorded.The range appears the main diffraction peaks at 32.33^0, 40.050^0,46.56^0,57.99^0,68.020^0, which indicates(121),(220),(202),(321),(242) planes respectively.From which the average crystallite size calculated by Schererformula by Eq.(**1**).is 13.04 nm.
$D = K\lambda/\beta \cos\theta$ ……………. (1)

Where K is constant (0.89 to1.39), λ is Radiation of wavelength (1.54 A0) β is FWHM (Full Width Half wave Maxima), θ is the Bragg angle in degree, D is theParticle Size. The intensities were matched with JCPDS Card No. 33-0701 for this synthesized material. From which we confirmed that our material is orthorhombic.

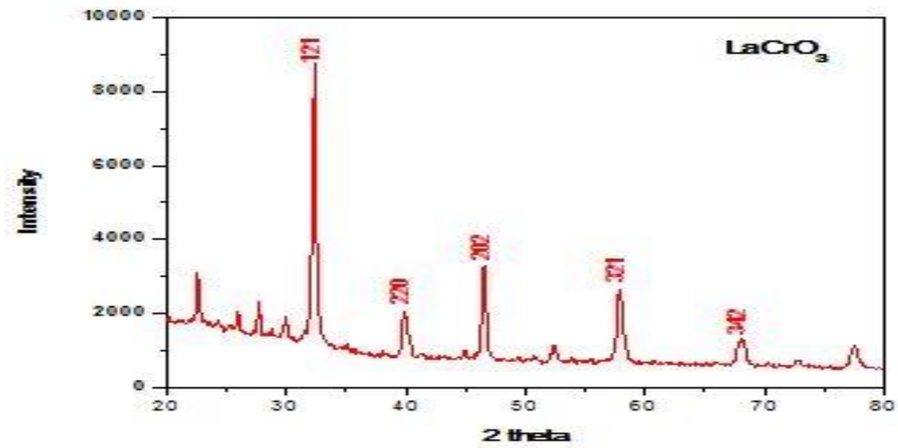


Fig.1 XRD image of prepared $LaCrO_3$Nanoparticles

SEM Analysis:

The scanning electron microscopy(SEM) helps to produce the images of sample by scanning the surface with the help of beam of electron, which helps to give information about surface morphology. Images of prepared $LaCrO_3$Nanoparticles are shown in Fig.2, this image shows the surface texture and its porosity.Images contains different ranges of particles which looks in random distribution.

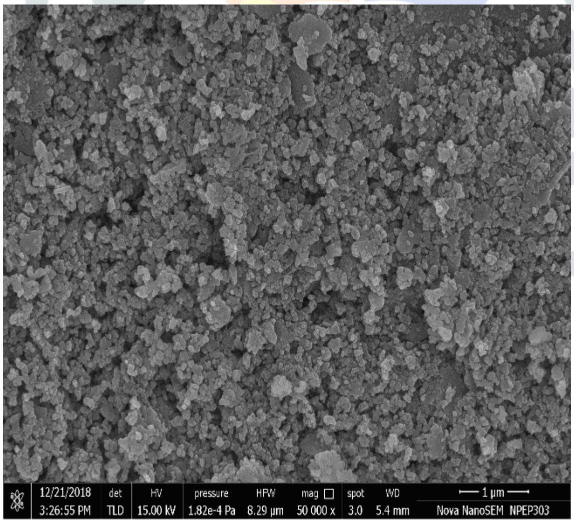


Fig. 2 SEM Images of prepared $LaCrO_3$ nanomaterial.

ELEMENTAL ANALYSIS:

With the assist of energy dispersive spectroscopy (EDS) we able to examine the basic elemental composition in material, which is very beneficial to discoversubtle concentration of elements, present in the prepared material, The EDS spectrum of $LaCrO_3$ shows it's selemental composition, such that La- 11.33%, Cr- 10.46%, O- 78.21% as shown in Table 1, from which the exact elemental ratio of prepared $LaCrO_3$material can be seen from Fig.3.

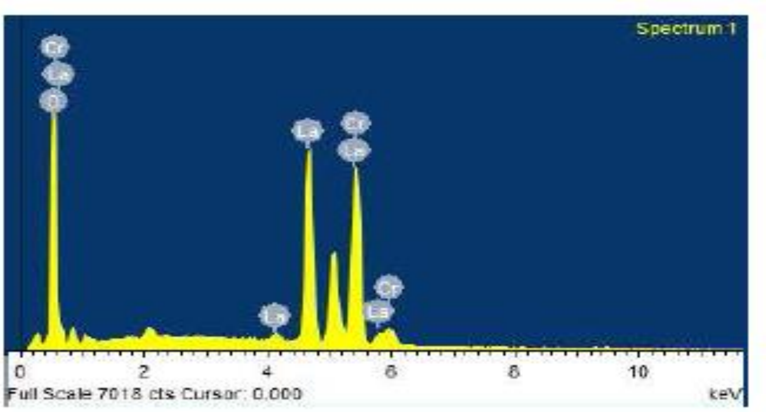


Fig.3EDS image of $LaCrO_3$ nanoparticles showing elemental composition of prepared $LaCrO_3$ material

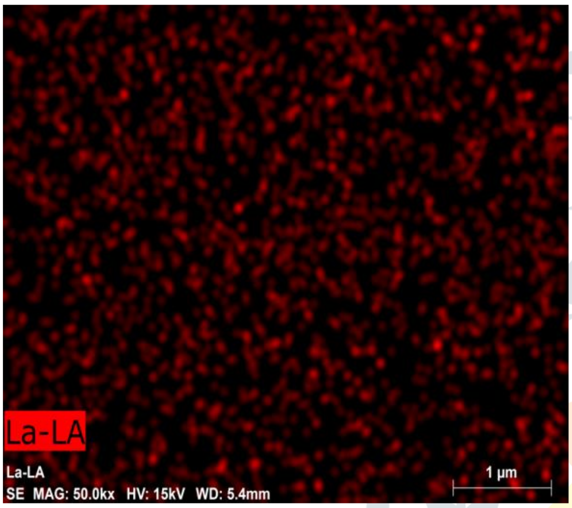


Fig.3 A

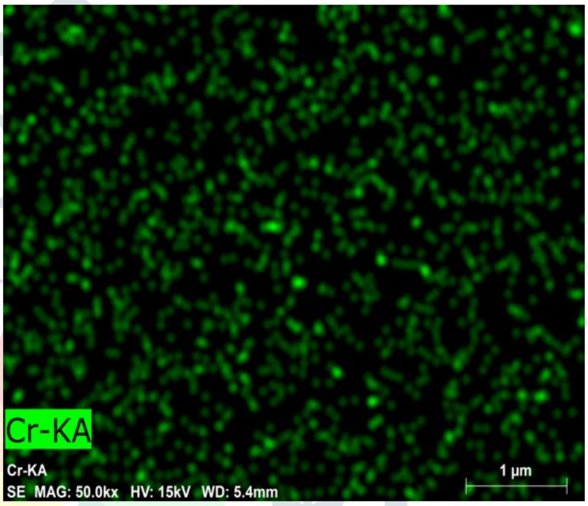


Fig.3B

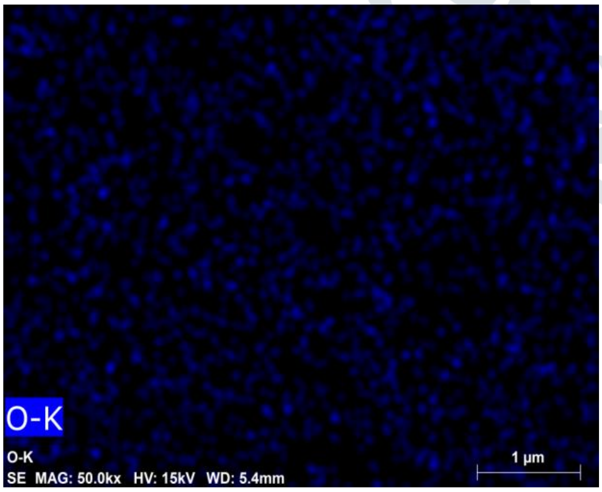


Fig.3 C

The above colourful images of Fig,3 A,B,C shows the mapping of $LaCrO_{3,}$ from which resembles that how much amount of La, Cr and Oxygen present in synthesized material.

Sr No.	Element	Elementary Weight % calculated from EDS
1	Oxygen	78.21%
2	Chromium	10.46%
3	Lanthanum	11.33%
	Total	100%

Table-1
Elemental composition of $LaCrO_3$ nanoparticles

Transmission electron microscopy(TEM)

The images by TEM (Transmission electron microscopy) of organized$LaCrO_3$nanostructure are shown in Fig.4a,4b. The images shows the spherical, rod like and polycrystalline shaped particles which suggests the material size ranges from 29.74nm to 50.82 nm and average particle size is 39.48nm.This particles are well spread on the surface of micrograph.

Selected area diffraction pattern (SAED)

SAED pattern(Selected area electron diffraction) of prepared$LaCrO_3$nanostructureare shown in Fig.5.In SAED the crystallinity of the sample is shown by the bright spots. We can see that the bright spots arranged in ring like pattern. This data which obtained from SAED are contributed with the XRD data.

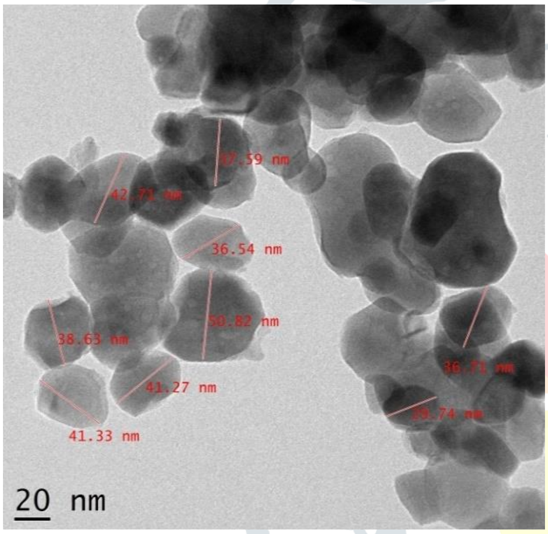


Fig. 4 a

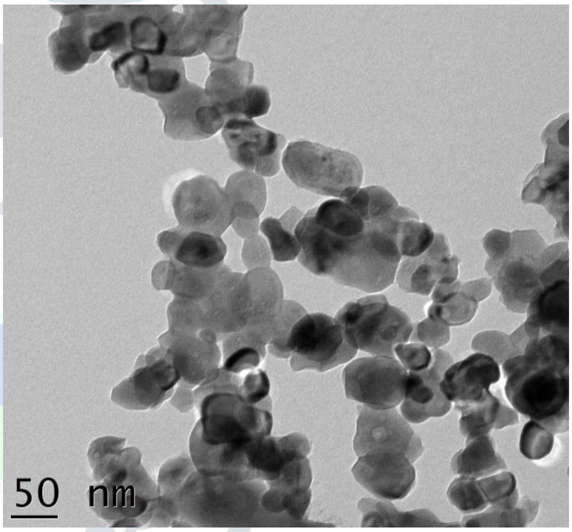


Fig.4 b

Fig. 4a,b TEM Images of prepared $LaCrO_3$ nanomaterial.

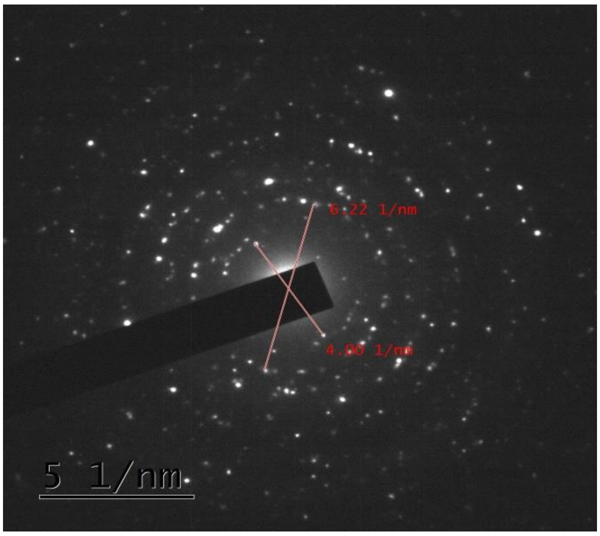


Fig. 5 SAED pattern of prepared $LaCrO_3$ nanomaterial.

FTIR Analysis

Basically FTIR gives the idea about stretching frequencies of functional group of a material. As $LaCrO_3$is ABO_3 type perovskite material in which A and B is any metal from transition elements, inner transition elements and P-block metal element is can be conceivable. The FTIR of prepared $LaCrO_3$material is shown in fig.4 which shows strong absorption bands at 594.08 cm^- for La –O stretch and 420.48 cm^- for Cr-O stretch (13,14,15) can be seen from Fig.6.

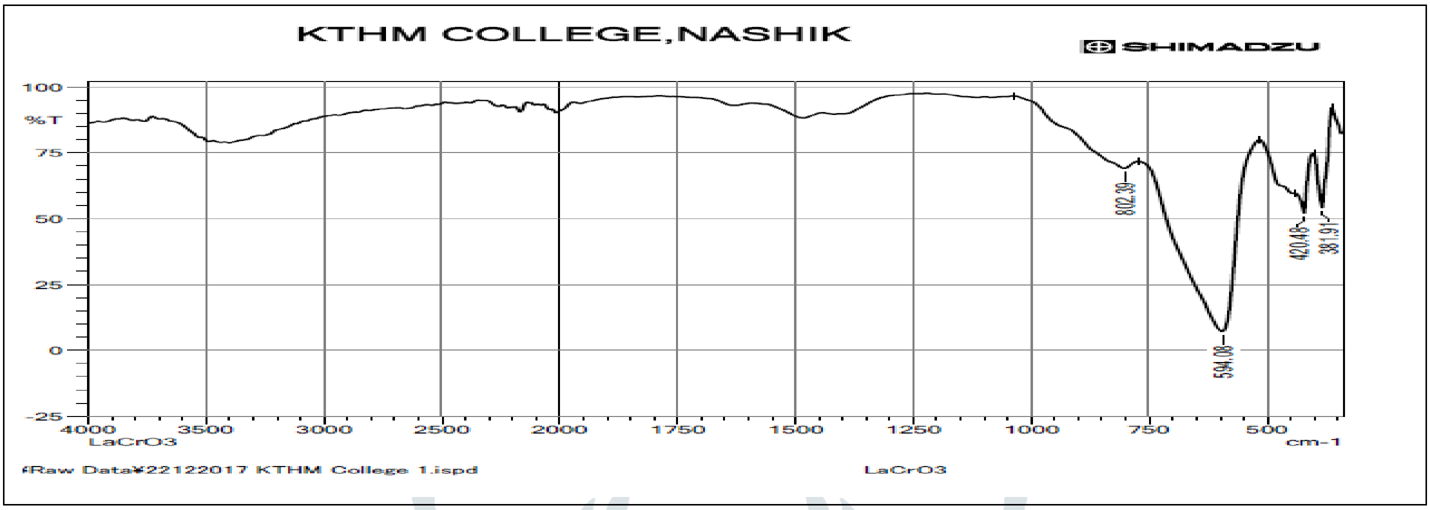


Fig.6FTIR spectrum of synthesized $LaCrO_{3,}$ Nanoparticles.

Gas sensing performance of $LaCrO_3$ nanomaterial thick films

The sensing was performed by using a static gas sensing system shown in fig. 7 by applying 30V bias potential to films. In this system the oxide sensor is fixed in an enclosed test chamber having capacity 15 liter. While measuring the response (resistance) of appropriate sensor, The gas is injected at fixed concentration at temperature s range between 50^0 C to 400^0 C, In this way we have checked the performance of prepared $LaCrO_{3,}$ using this system at different temperature by using different gases with different concentration of gases like H_2S, NH_3, Ethanol, Acetone, $CO_{2,}$ and then from measured resistance gas response were calculated by using following equation 1(3, 20, 26, 27).

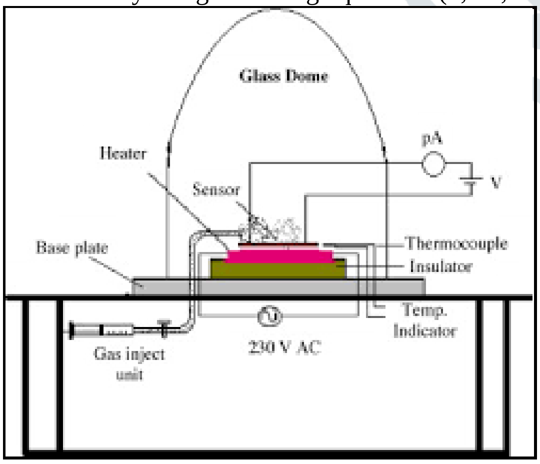


Fig.7Static gas sensing system

S= (Rg - Ra)/Rg
Where,
Rg- Resistance of the thick films in presence of gas
Ra- Resistance of the thick films in air

Selectivity for $LaCrO_3$ thick films

The selectivity means response of a sensor to specific gas at particular temperature. The response for $LaCrO_3$thick films for H_2S, NH_3, Ethanol, Acetone,CO_2 shown at following Fig. 8a. at 1000 ppm. And it is observed that the $LaCrO_3$ sensor selectively sensed to H_2S gas than the other gases at 200^0 C operating temperature shown in Fig. 8b.

Gas	Gas Response	Temperature
Hydrogen Sulphide	63.05	200^0 C
Ethanol	35.95	200^0 C
Acetone	30.60	200^0 C
Ammonia	12.20	200^0 C
Carbon Dioxide	4.31	300^0 C

Response of various gases at 1000PPM

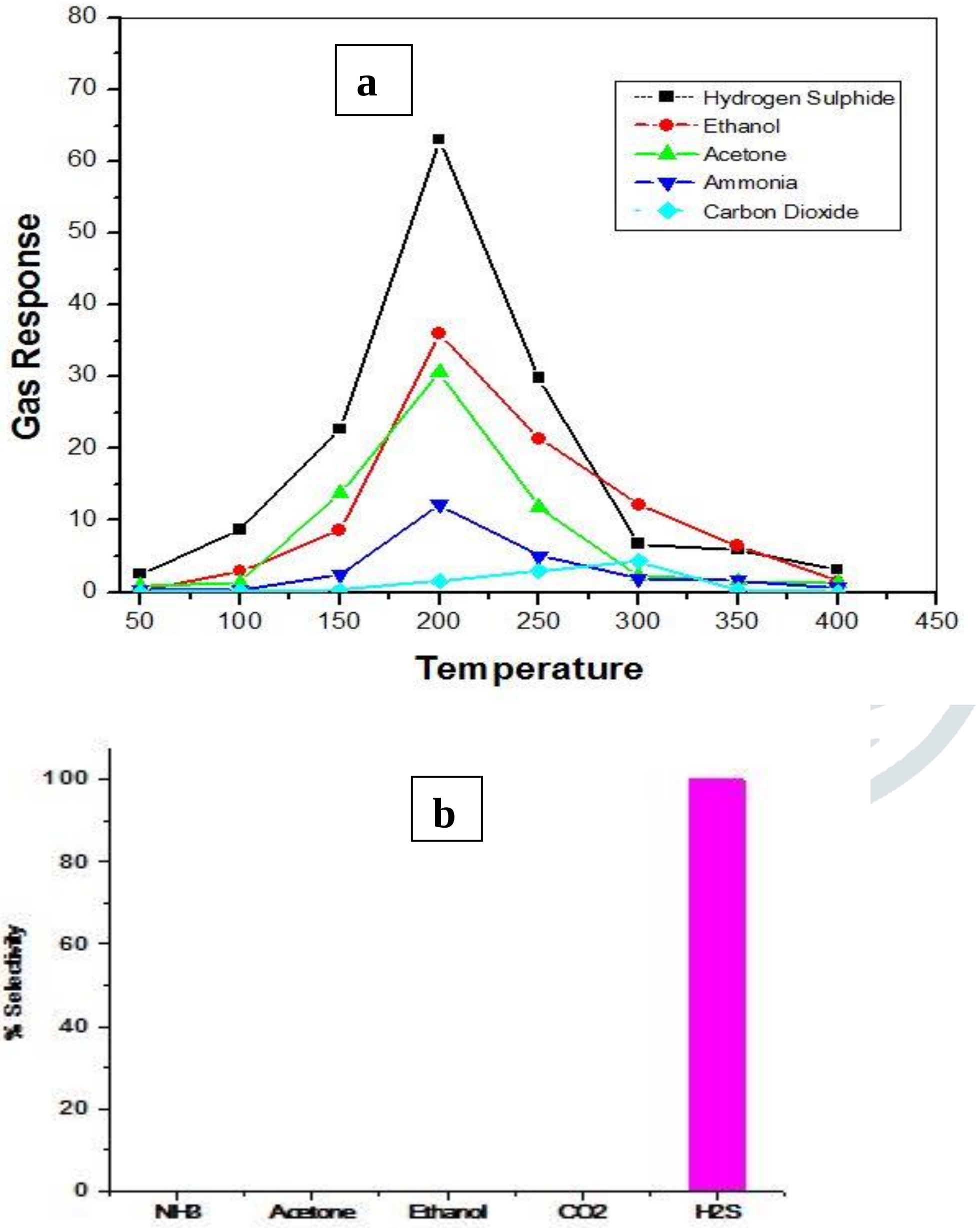
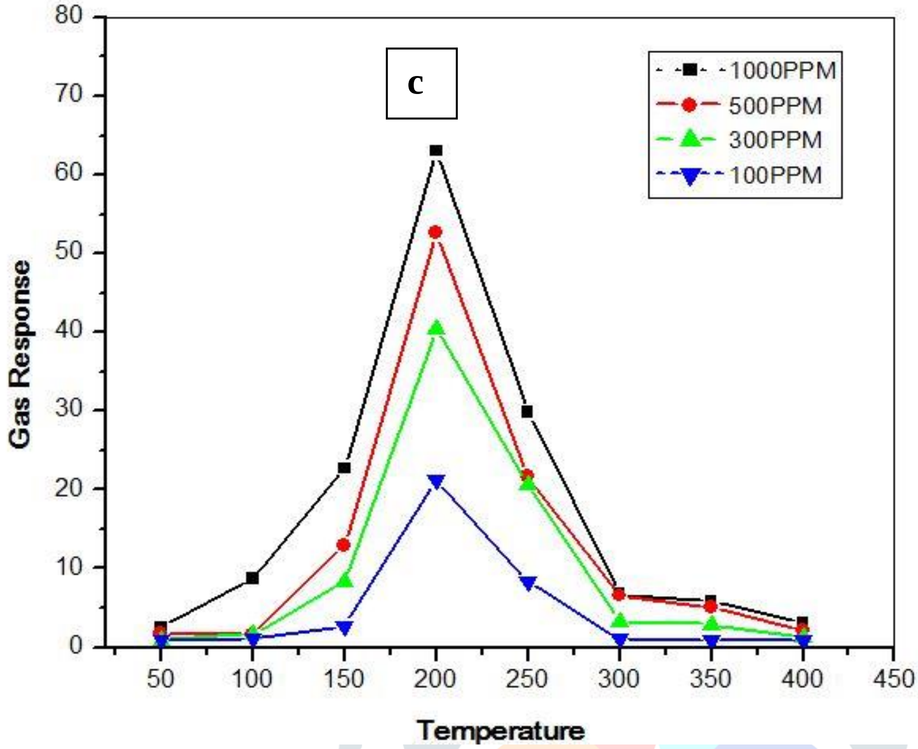


Fig. 8 a. Gas response of LaCrO3 for various gases at different temperature.
b. Selectivity of LaCrO3 for H_2S gas.

Variation of Response with different gas concentration

Variations of H_2S sensitivity with respect to different concentration are shown in Fig. 8c.this figure clearly indicate that as the concentration of gas is increases its sensitivity is also increases. The highest response is shown for 1000ppm at 200^0C.



Gas Concentration	Gas Response	Temperature
1000PPM	63.05	200^0 C
500PPM	55.35	200^0 C
300PPM	40.50	200^0 C
100PPM	21.16	200^0 C

Gas Response Of H_2S gas at various Concentration At 200^0 C

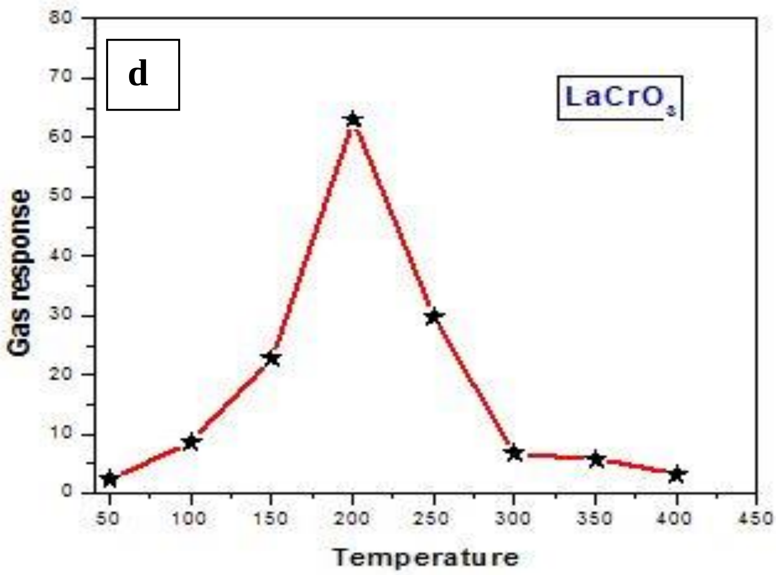


Fig.8 c Gas response of $LaCrO_3$ for various concentrations of H_2S gas at different temperature.
d Gas response of $LaCrO_3$ for H_2S gas (1000ppm) at different temperature.

RESPONSE AND RECOVERY:

Response and recovery is very important parameter while studying the characteristics of sensor, our $LaCrO_3$ sensor shows the quick response in 78 sec and recovery time is 152 sec for 1000ppm at 200^0 C are shown in Fig. 9.

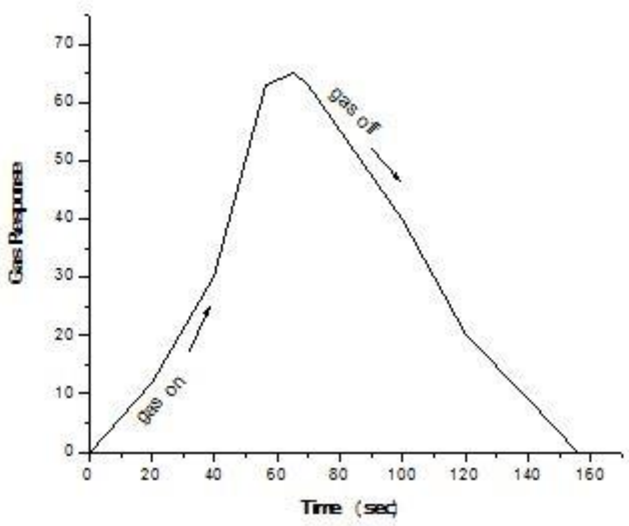


Fig.9 Response and Recovery of $LaCrO_3$ for H_2S gas

DISCUSSION:

As we know that distinctive gases have distinctive energies for adsorption, desorption and response on the surface of metal oxide, and so the reaction of the sensor at distinctive temperature is depends on the concentration of gas (how much amount of gas is adsorb). As the temperature increases the amount of oxygen adsorbed (O^-2, O^-, O^{2-})on the surface of sensor is also increases, then reaches to the maximum and then diminished with a increment in operating temperature. When the reducing gas comes in contact with the surface of sensor, oxidation takes place. As the rate of oxidation is larger, the larger the number of electron is discharged, and bigger would be the gas response. But at the higher temperature the amount of adsorbed oxygen would be small, then smaller the gas response(20).

In case of H_2S reducing gas, when the vapors of H_2S is react with surface of Metal oxide to form elemental Sulphur. When oxygen is adsorbed on the surface of sensor it promotes the response of H_2S vapors (26).

$$2H_2S + 3O_2^- \rightarrow \quad 2H_2O+2SO_2+3e^-$$

Above reaction indicate the formation of H_2O and SO_2 gas.

CONCLUSIONS:

The$LaCrO_3$ nanomaterial was prepared by Sol-gel method. And their thick films also prepared by conventional screen printing method. Characterization is done by XRD from which Crystallite size proved to be 13.01nm. From SEM studies we can observed that the elongated rod shaped particles which dispersed on surface of micrograph.From EDS this is proved that prepared nanoparticles have fixed elemental composition.TEM images shown that the particles are looks like spherical, rod like and polycrystalline shaped which shows the material size ranges from 29.74nm to 50.82 nm and average particle size is 39.48nm. From FTIR the stretching frequencies observed for prepared nanoparticles are the absorption bands at 596 cm^- for La –O stretch and 416.04 cm^- for Cr-O stretch. The $LaCrO_3$ Sensor selectively sensed to H_2S gas at 200^0 C. Response and recovery shown that$LaCrO_3$ sensor shows the quick response in 78 sec and recovery time is 152 sec.

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