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Research Article

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Methanol Gas Sensing Properties of Pervoskite $LaFeO_3$ Nanoparticles Doped by Transition Metals Cr^{3+} and Co^{2+}

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ABSTRACT

Nanomaterials found to be potent catalyst for various applications in today's era. The subtle Nanomaterials are the promising material in the field of catalysis. The nanomaterials are premordeal but their existence came into light with astonishing catalytical properties. The present research explains the synthesis of $LaFeO_3$ doped by transition metals such Cr^{3+} and Co^{2+}. These Nanomaterials are prepared by Sol-gel method followed by preparation of thick films and subsequent gas sensing by methanol. The nanoparticles were characterized by XRD, SEM, EDS and IR. XRD study reveals that the average particle size calculate by Scherer formula is 15.35 nm. The morphological properties and surface of nanomaterials can be imaged by SEM. The SEM investigation shows surface texture, colour and porosity of LaFeO3.It has homogeneous surface, microspores and mesopores as seen from its surface micrographs. EDS shows the elemental composition of every element in doped Pervoskite $LaFeO_3$.The IR characterization shows the typical metal oxygen linkages for prepared nanomaterial. The characterized nanomaterials were subjected for investigation of methanol gas sensing properties by preparing thick films of doped $LaFeO_3$.

Keywords: $LaFeO_3$; Gas sensing; Methanol; XRD; SEM; EDS; IR

INTRODUCTION

The use of nanomaterials in the ceramic fields is at the pre-eminence because of its great use in the field of research .The present study reveals fundamental property of nanomaterials like quick electronic response given by these tiny particles, in the form of catalyst. This special property has a Great vantage in gas sensing properties. The Pervoskite material is the special class of materials studied because of their catalytical propensity. The lanthanum ferrate is an antiferromagnetic oxide with characteristic research properties, because the magnetic domains of LaFeO3 found to be large enough for magnetic and electrical properties. The $LaFeO_3$ is found to be having orthorhombic structure .The typical oxide shows p- type semiconduction, the oxide shows highly non stoichiometric ratio, despite of these oxide are greatly used in most of the technological application such as sensors devices, detection of humidity i.e. Humidity sensors, alcohol detection, oxygen detection, carbon monoxide, and nitric oxide detection etc. There are various methods proposed for constructive synthesis of nanomaterials like mechanical method such as high energy ball milling and melt mixing ,method based on evaporation, such as physical vapour deposition ,laser vaporisation,(ablation) ionised cluster beam deposition ,laser pyrolysis, sputter deposition such as magnetron sputtering, ECR plasma deposition, electric arc deposition, molecular beam epitaxy (MBE),chemical vapour deposition, synthesis of nanoparticles by colloidal route, Langmuir-Blodgett method, hydrothermal synthesis, sonochemical synthesis, microwave synthesis, sol-gel synthesis, even though biological synthesis of nanomaterials is also possible ,such synthesis using microorganism, nanomaterial synthesis using plant extract, synthesis using DNA etc.[1- Sulbha Kulkarni]

In the present research nanoparticles of $LaFeO_3$ prepared by sol-gel method with 3% dopant concentration of transition metals such as Cr^{3+}, Co^{2+} which augments the catalytical properties of lanthanum iron oxide. Ni doped $LaFeO_3$ subjected to ethanol sensitivity at the 773 kelvin shows optimum response towards thin films prepared for $LaFeO_3$ material [1, 2, 3, 4] LaFeO3-type Perovskite is one of the most important materials and has attracted attention because of their wide applications, such as electrodes materials for fuel cells, catalysts, chemical sensors, optoelectronic devices. The non-stoichiometric Pervoskite $LaFeO_3$ has a typical band gap of 2.56 eV [5, 6, 7]

Recently, the inner transition metal oxide as well as doped inner transition metal by transition metal are extensively studied for sensitivity of household gases and industrial gases or gases that are produced in mines and chemical reaction may damage the lives in many ways and therefore their regulation and control is important, which can done by several method such as developing the sensors prepared by using semiconducting and superconducting nanomaterials. Most of the researchers working on this type of methodology where nanomaterial based sensors can be effectively used for detecting even smaller concentration of wide range of gases. The present material $LaFeO_3$ doped by transition metal Cr^{3+} and Co^{2+} has been investigated for electrical response and gas sensitivity for methanol. As methanol being poisonous its detection can reduce the fatal injuries in industries, laboratories and household applications.[8,9,10]The most of the researcher working on sensing devices are trying to develop specific sensors for specific gases using semiconducting nanomaterials. The prepared $LaFeO_3$ doped by transition metals was applied for methanol gas at wide range of temperature found to be sensitive at higher temperature. In some cases the optoelectronic properties also performed for thick and thin films of lanthanum and tungsten selenide oxide. Rare earth Tb^{3+} doped by $LaFeO_3$ used for high frequency devices fabrication.

MATERIALS AND METHODS

All the in chemicals used in synthesis are of AR grade purchased from Loba chemie, Mumbai and used without further purification. Chemicals involves Lanthanum nitrate, Ferric nitrate, Chromium nitrate, Cobalt nitrate, Citric acid, Double distilled water.

Synthesis of nanomaterial $LaFeO_3$ doped by transition metals: Cr^{3+} and Co^{2+} (Sol-gel) method

The synthesis method of doped $LaFeO_3$ involves initial amount of Lanthanum nitrate 3.245gms and 3.03gms of Ferric nitrate (0.0075 moles each) dissolved together in minimum amount of double distilled water .Into a separate beaker take 3% dopant concentration (elemental %) of cobalt nitrate and chromium nitrate mix both the solutions to each other ,take another beaker with minimum amount of water to dissolve citric acid (0.009 moles) add this solution to cumulative metal nitrate solutions, place on magnetic stirrer by adjusting temperature up to 80 ^{0} C. Stirr the total content until the brown colour sol is obtained. The sol was dried into gel firstly then calcined at the different temperature ranging from 400- 700 ^{0} C for 6-7 hours. The dark brown colour doped $LaFeO_3$ nanoparticles are formed which are sonicated for 20 minutes by using ethanol solvent to obtain better size of nanoparticles. Further calcined for 2-3 hours at 400-700 ^{0} C [11, 12, 13, 14]

Preparation thick films of $LaFeO_3$ nanoparticles doped by Cr^{3+} and Co^{2+}

The powder nanoparticle $LaFeo_3$ converted into paste form was used to prepare thick films by screen printing maintaining the inorganic to organic materials ratio at 70:30.The inorganic part consist of Nanomaterial ($LaFeO_3$). The organic part consisted of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA).The lafeo3 with ethyl cellulose (EC) were mixed thoroughly in an acetone medium with mortar and pestle. A solution of BCA which was added drop wise until proper thyrotrophic properties of the paste achieved. Now thick film was prepared on glass substrate by using standard screen -printing technique. The film was dried under IR lamp for 45 minutes to remove the organic volatile impurities and then fired at temperature 400 ^{o} C for 1.5 to 2 hours in muffle furnace. The prepared thick films are now ready for characterization and electrical characterization.

RESULT AND DISCUSSION

XRD analysis

The XRD spectrum for prepared doped $LaFeO_3$ is as shown in fig.1.The spectrum shows the main 2θ peaks at 31.2^0, 38.8^0, 45.2^0 , 56.5^0 66.5^0, 75.8^0 from which the average particle size calculated by Scherer formula Eq. (**1**).is 15.35 nm. As the average nanoparticle size is ranged from 1 to 100 nm, which confirms the prepared nanoparticles of $LaFeO_3$ are highly crystalline and Nano sized. [15, 16, 17, 18,19].

$$D = K\lambda/\beta \cos \theta \ldots\ldots\ldots\ldots\ldots (1)$$

Where K=constant (0.89 to1.39), λ=Radiation of wavelength (1.54 A^0) β=FWHM (Full Width Half wave Maxima), θ=Bragg angle in degree, D=Particle Size.

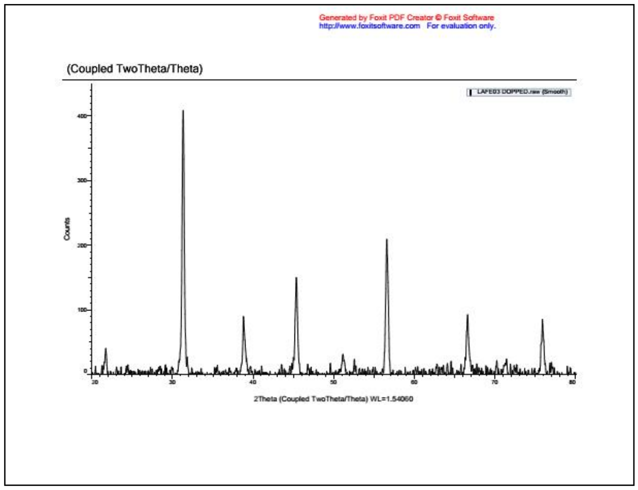

Figure 1: XRD spectrum of $LaFeO_3$ nanoparticles doped by Cr^{3+} and Co^2

SEM analysis

The Scanning electron microscopy (SEM) images of prepared nanomaterial are as shown in figure 2.The images shows surface texture, colour and porosity of doped LaFeO3.It has homogeneous surface, microspores and mesopores as seen from its surface micrographs. [20, 21, 22] It is greyish black in colour, various sized nanoparticles imaged can be seen from SEM images as shown in figure 2

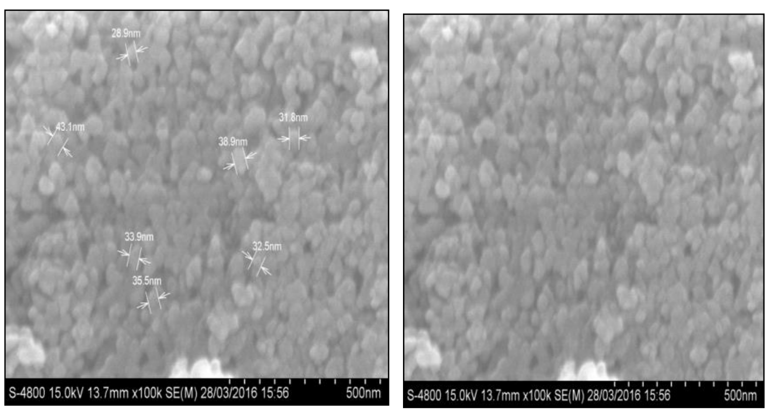

Figure 2: SEM Images of prepared $LaFeO_3$ nanomaterial doped by Cr^{3+} and Co^{2+}

Electron dispersive X-Ray spectroscopy (EDS) analysis

EDS is widely used to detect the elemental composition of metals create element composition maps over a much broader area together, these capabilities provide fundamental compositional information for a wide variety of materials. The spectrum is as shown in fig.3 from which one can find synthesized material contains 67.15% of oxygen, 16.72% of iron, 13.82% of Lanthanum, 1.44% of cobalt and 0.87% of chromium as shown in table 1[23, 24].

Table 1: Percentage of elements and its elementary weight in synthesized $LaFeO_3$ Nanomaterial doped by $Cr^{3+}Co^{2+}$

S.No	Elements	Elementary Weight %
1	O	67.15
2	Fe	16.72
3	La	13.82
4	Co	1.44
5	Cr	0.87

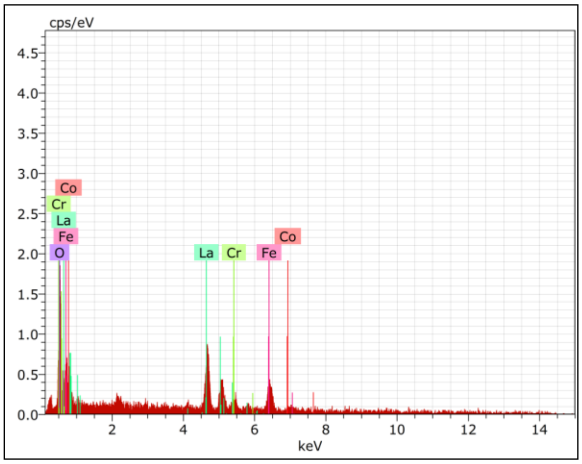

Figure 3: EDS spectrum of synthesized $LaFeO_3$ Nanomaterial doped by $Cr^{3+}Co^{2+}$

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Table 1: 2 Percentage of elements in synthesized $LaFeO_3$ Nanomaterial doped by $Cr^{3+}Co^{2+}$ obtained from EDS spectra

El	AN	Series		unn. C [wt.%]	norm. C [wt.%]	Error(1Sigma) [wt.%]
O	8	K-series	16.7	26.47	67.15	3.38
Cr	24	K-series	0.7	1.12	0.87	0.12
Fe	26	K-series	14.5	23.01	16.72	0.76
Co	27	K-series	1.32	2.09	1.44	0.22
La	57	L-series	29.9	47.31	13.82	1.14
Total:		63.18	100	100		

FTIR analysis

The FTIR spectrum of synthesized material is of $LaFeO_3$ doped by Cr^{3+} and Co^{2+} is as shown in Figure 4 shows characteristic absorption bands at 551.67 for La –O stretch and 418.57 for Fe-O Stretch. Previously, it was reported that the absorption band of Fe–O stretch of Fe_3O_4 solid material was at 599 and 375 cm-1 (Waldron 1995). However, in this case the size of nanoparticles was reduced to nanoscale dimensions, the surface bond force constant increased due to the effect of finite size of nanoparticles.[25].

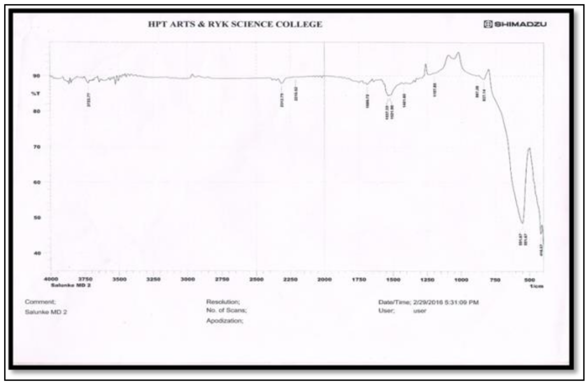

Figure 4: The FTIR spectrum of synthesized material is of $LaFeO_3$ doped by Cr^{3+} and Co^{2}

Electrical characterization

The D.C. resistance of the film samples was measured by using half bridge method as a function of temperature in home built measurement system .The home built characterisation system consists of glass chamber (25 litres) and heater (1000W) of nichrome wire (Resistance-120ohm at room temperature). The heater was used to change the film sample temperature from room temperature (RT) to 400^{0}C By changing its voltage using dimmer stat (maximum current limit upto-8A).The electrical terminals were brought out from the thick film resistor by using insulated feed-through mounted on the stainless steel base plate. The aluminium foil with pressure contacts system use for external contacts. The spring press contacts were used during the measurement. The temperature of the sample was measured by using the temperature indicator with the help of Cr-Al thermocouple. The high resistance of the sample was determined by using the half bridge method.

The gas response of thick films was studied in test assembly. The electrical resistances of thick film in air (*R*a) and in the presence of gas (*Rg*) were measured to evaluate the gas response (*S*) given by the relation

$$S = \frac{Ra - Rg}{Ra}$$

Electrical resistance and effect of temperature

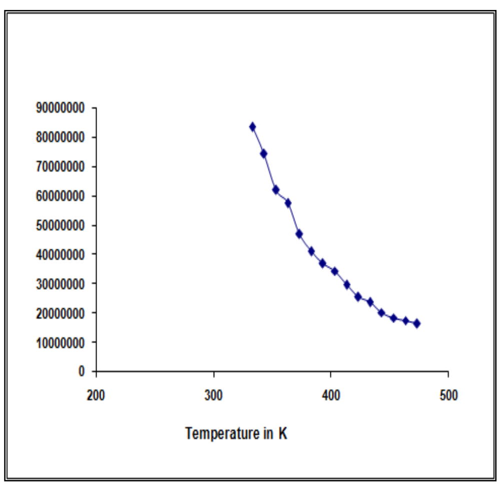

Figure 5: showing graph of Electrical resistance V/s Temperature for $LaFeO_3$ doped thick films.

Figure 5 showing the typical curve of electrical resistance against temperature for prepared thick films of LaFeO3 doped by $Cr3^{+}$ and Co^{2+}.The optimum temperature ranging between 200 to 500 Kelvin The graph shows typical semiconducting behaviour for prepared material of LaFeO3 doped by Cr^{3+} and Co^{2+}, as the electrical resistance is decreasing with increase in temperature, showing a typical NTC semiconducting behaviour. [26]

CH_3OH Gas sensing properties of $LaFeO_3$ doped thick films

The variation of gas response of the $LaFeO_3$ doped thick films sample with CH_3OH (Methanol) gas concentration at 150 ^{o}C temperature is represented in Figure-6 this film was exposed to different gas concentrations of vaporized methanol. The sensitivity values were observed to increase continuously with raising the gas concentration up to 500 ppm.

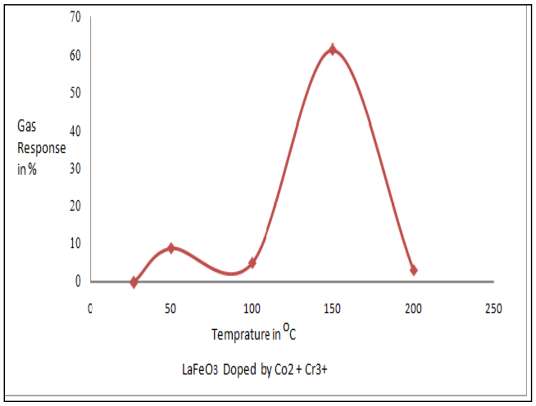

Figure 6: Showing graph variation of gas response with operating temperature for) CH_3OH Gas at 500 ppm for $LaFeO_3$ doped thick films

CONCLUSIONS

The transition metal Co^{2+} and Cr^{3+} doped $LaFeO_3$pervoksite material successfully prepared by sol-gel method and their thick films also prepared by conventional screen printing method. Characterization carried by XRD from which nanoparticles of $LaFeO_3$ up to 15.35 nm are confirmed. From SEM studies it is observed that the homogeneous surface of doped $LaFeO_3$ microspores and mesopores as seen from its surface micrographs. It is greyish black in colour, various sized nanoparticles images ranging from 28 to 43 nm can be seen from SEM images. The prepared nanoparticles have fixed elemental composition confirmed from EDS. The typical IR stretching frequencies observed for prepared nanoparticles the absorption bands at 551.67 for La –O stretch and 418.57 for Fe-O Stretch showed by FTIR studies. [18]The electrical characterization and gas sensing properties examined for doped $LaFeO_3$ thick films for vaporized ethanol gas.

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