Synthesis, characterization, magnetic properties and gas sensing applications of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0.0 \leq x \leq 0.8) nanocomposites

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A B S T R A C T

In the present work Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites were synthesized with a wide composition range (0.0 \leq x \leq 0.8 in the steps of $x = 0.2$) using a sol-gel method and thin films were fabricated using a spin-coating process. The synthesized materials were analyzed using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, differential scanning calorimetry, UV-visible absorption and infrared spectroscopic techniques for their appropriate characterization. The XRD revealed the cubic spinel structure for each composition and the minimum crystallite size was found to be 10.4 nm. In order to study the thermodynamics during the synthesis, pre- and post-annealed materials were analyzed. An influence of the zinc on the magnetic properties was also investigated using a vibrating sample magnetometer. Further, the fabricated thin films were employed as liquefied petroleum gas (LPG) and CO$_2$ gas sensors. Films show better sensing behavior towards LPG in comparison to CO$_2$. Thus this study not only explored the influence of different compositions of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites on their surface morphologies, crystallite sizes, porosities, specific surface areas, UV-visible absorptions and magnetic properties, but also the influence of different in situ compositions on their sensing behaviors.

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1. Introduction

Nanostructured spinel ferrites (MFe$_2$O$_4$, M=Co, Ni, Mn, Mg, Zn, Cu, etc.) are interesting materials due to their potential applications in modern technology because of their electronic, magnetic, electrical and catalytic properties; all of these properties are completely different from those of their bulk materials [1–4]. In addition spinel-type oxides are an alternative for inexpensive and robust detection systems because of their good chemical and thermal stability under operating conditions [5,6]. The structure of the spinel ferrites can be described as a cubic, closely packed arrangement of oxygen atoms, and M$^{2+}$ and Fe$^{3+}$ ions can occupy either tetrahedral (A) or octahedral (B) sites. The sensing, magnetic and electrical properties of spinel ferrites are of academic and technical interest and are dependent on their chemical composition, cation distribution, grain size and the method of preparation [7–12].

The origin of magnetic properties of the spinel oxides is spin magnetic moment of the unpaired 3d electrons of transition element occupied by the super exchange...
interaction via the oxygen ions separation [13–15]. The magnetic properties such as saturation magnetization and Curie temperature are strongly dependent on the distribution of cations and type of the doping atoms [16]. The Curie temperature, magnetic moment, electrical resistivity, and lattice constant are found to be affected by substitution in the spinel lattice and are due to the formation of secondary phase on the grain boundaries [17,18]. The basis for wide range of applications of spinels is related to the variety of transition metal cations, which can be incorporated into the lattice of the parent magnetic structure [19]. Doping in ferrite nano-crystals with various metals, such as chromium, copper, manganese and zinc is usually used to improve their sensing, electrical or magnetic properties [20–22].

Various chemical precipitation techniques have been popularly adapted to synthesize the nanoparticles [23–25]. Among these synthesis methods, it is well conceived that chemical routes are more convenient and less expensive, they have general advantages such as superior uniformity and high yielding of nanoparticles [26–28]. In the present work, mixed ferrites have been synthesized by a sol–gel method to achieve chemically homogeneous and fine particles. This method of synthesis is economical for producing large quantity of small particles. Further it offers good chemical homogeneity, high purity and low sintering temperature and time.

A gas sensor is a device which receives a stimulus and converts it into a measurable electrical/optical signal. In many industrial applications, gas sensors are used to determine gas leaks in order to prevent any harm to human health as well as to protect from any explosions that such leaks may cause. The emphasis is currently being placed on the development of sensor materials for the detection of LPG that offers high sensitivity, short response and recovery times, superior reproducibility and stability. Most of the sensors developed so far were kinetically slow with a limited sensitivity for the detection below the permissible level of LPG and operate above room temperature, although the detection of LPG at room temperature will be very helpful for the chemical industries and research laboratories. Thus, the fabrication of the gas-sensing materials with high performances remains a challenge. Gas sensors with high performances are considered those with high sensitivity and stability, fast response, low working temperature, and tunable parameters, as per requirements. Such performances should be associated not only with the surface properties of the sensing materials but also with their microstructures (such as specific surface area, crystallite size, pores size, porosity, film thickness, etc.). The sensing properties of the spinel ferrites vary greatly with change in their chemical compositions [29–32]. Therefore, in the present investigation a series of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ was synthesized with a wide compositional range of ‘x’ (0.0 ≤ x ≤ 0.8). Further the influence of different compositions on its structural, optical, magnetic and sensing properties has been investigated.

The objective of our work is to fabricate a LPG sensor having high sensitivity, small response and recovery times and good reproducibility and stability. The LPG sensing characteristics of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ thin films were investigated at room temperature which are more reliable, stable and robust in comparison to earlier investigated LPG sensors [33–39]. Surface morphological, compositional and structural investigations were performed in order to understand the advancement in the gas sensing properties.

2. Experimental details

2.1. Synthesis and fabrication of films

Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites were synthesized via the sol–gel method using stoichiometric amounts of the starting materials such as cupric nitrate [Cu(NO$_3$)$_2$· 3H$_2$O], zinc sulfate [ZnSO$_4$· 7H$_2$O] and ferrite nitrate [Fe(NO$_3$)$_3$· 9H$_2$O] taken in (1 – x):x:1 M ratios, respectively. All reagents were purchased from Qualigens, India, were of analytical grades and used without further purification. We have prepared five samples of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ corresponding to x=0.0, 0.2, 0.4, 0.6, and 0.8, and these were labeled as S-1, S-2, S-3, S-4 and S-5, respectively. For the synthesis of S-1, Fe(NO$_3$)$_3$· 9H$_2$O and Cu(NO$_3$)$_2$· 3H$_2$O were used and dissolved in appropriate amount of ethanol to form 0.1 M solution. This solution was magnetically stirred at 80 °C for 2 h to get a homogeneous precursor solution and complete ionization of metal nitrates. Further 20 ml of polyethylene glycol (PEG) was added drop by drop, that works as a capping agent. When iron and copper solution with PEG is continually heated at constant temperature, the solution gradually becomes saturated and super saturated, leading to the nucleation of the crystal. These nuclei are immediately and strongly absorbed and surrounded by the PEG chain. On the other hand, due to very high viscosity of the solution, it decays the transportation of ions and hampers the growth of the crystal. Here, stirring of the solution accelerates the ion diffusion, resulting in continuous movement of ion from the region of high concentration to the surround of crystal nucleation, and the crystal grows. Stirring also results in bridging among long PEG chains that are absorbed simultaneously on different iron and copper salts particles, and increases the chance of collision among the particles. It also causes the growth and aggregation of the particles which may be attributed to the enhanced steric hindrance by the adsorption of PEG on iron and copper particle surfaces. Thus PEG prevents their growth and generates the steric hindrance effect leading to the reduced particle–particle agglomeration.

For the formation of powder, ammonium hydroxide solution was added drop by drop to the as prepared nitrate precursor solution under stirring until the reddish brown colored solution was obtained. Again above solution was magnetically stirred at 80 °C for 6 h. The process of precipitation may be explained by the chemical reactions given as under

$$\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} + 3\text{NH}_4\text{OH} \overset{80 \degree \text{C}}{\rightarrow} \text{Fe(OH)}_3 + 3\text{NH}_4\text{NO}_3 + 9\text{H}_2\text{O}$$

(1)

$$\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O} + 2\text{NH}_4\text{OH} \overset{80 \degree \text{C}}{\rightarrow} \text{Cu(OH)}_2 + 2\text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$$

(2)
The resulting solution was dried at 120 °C for 6 h and then annealed at 500 °C for 3 h to obtain the fine powder of CuFe$_2$O$_4$. The crystalline powder annealed at 500 °C was crushed into fine powder using a pestle and mortar. The resulting powder was pressed uniaxially under a pressure of 616 MPa in stainless steel dies to fabricate the pellet (9 mm in diameter and 4 mm in thickness) of CuFe$_2$O$_4$.

Thin film of the precursor used was fabricated on an alumina substrate (10 × 10 mm$^2$) using a spin coater (Metrex Scientific Instruments, India) at 2000 rpm for 60 s at room temperature (27 °C). The fabricated film was dried at 120 °C for 6 h. This drying process stabilizes the film. The precursor undergoes various forms of hydrolysis and poly-condensation reactions. Further it was annealed at 500 °C for 3 h at a heating and cooling rate of 5 °C/min. This process converts the film as sensing material. Further the film was investigated with the exposition of LPG and CO$_2$. The whole procedure was applied for the synthesis of CuFe$_2$O$_4$. The crystalline powder annealed at 500 °C for 6 h and then annealed at 500 °C for 6 h. This drying process stabilizes the film. The percentage sensor response of CO$_2$ and LPG sensor is defined by Eqs. (5) and (6), respectively given as below

\[
\%S.R. = \frac{R_a - R_g}{R_a} \times 100
\]

(5)

\[
\%S.R. = \frac{R_e - R_g}{R_e} \times 100
\]

(6)

Eqs. (5)–(6) are used for the estimation of the gas sensing characteristics of the fabricated nanocomposite films.

### 3. Results and discussion

#### 3.1. Structural analysis

X-ray diffraction is used to reveal the structure of the synthesized materials because of its qualitative and non-destructive analysis. The structural analysis is essential for optimizing the properties needed for various applications. Fig. 1(a) shows the XRD patterns of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (x=0.0, 0.2, 0.4, 0.6 and 0.8). The data were analyzed using JCPDS standards and confirmed the formation of cubic spinel structure. The obtained XRD patterns show the extent of crystallization. As the zinc content is increased, the diffraction peaks show considerable broadening which illustrates that crystallite size becomes smaller with the increment of zinc content. The wider peak of Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ for x=0.8 proved the smallest crystallite size among all the compositions. The average crystallite sizes of materials S-1, S-2, S-3, S-4 and S-5 were found to be 21.5, 11.2, 10.6, 10.5 and 10.4 nm, respectively. The [h k l] planes are identified and marked at each peak of the diffraction pattern.

The XRD data of CuFe$_2$O$_4$ (S-1) was further analyzed as a function of scattering vector q=(4π/λ)sin(θ), where 2θ is the scattering angle and λ is the wavelength of X-ray, to estimate the crystallite size and size distribution as illustrated in Fig. 1(b). The broad XRD peaks confirm the formation of nano-sized particles. The average crystallite size (D) has been estimated using Debye-Scherrer equation

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

(7)

where K is Scherrer’s constant, λ is wavelength of X-ray, β is FWHM in radians and θ is peak position. Further, crystallite size distribution (SD) of this material has also been estimated by FWHM of peak half method [40]. A detailed description and justification of the FW1/5 and 4/5M method can be found elsewhere [41]. Red line in Fig. 1(b) is the peak fit to get the peak positions, FW1/5 and 4/5M. The crystallite size was found to be 22.79 nm using Scherrer’s method while FW1/5/2M method gave the value 23.75 nm and size distribution (SD) ~ 0.31 which is shown by probability vs. grain size curve.
Further the variation of average crystallite sizes of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ with zinc substitution ($x$) is depicted in Fig. 2(a). It can be seen that for small amount of zinc incorporation there is a sharp and significant decrease in the crystallite size while for higher concentration of zinc, the decrease in size is less pronounced. It is recognized here that an increase in zinc concentration increases the reaction rate which favors the formation of ultrafine particles of mixed ferrites. The difference in average size between the extremes (for $x=0$ and 0.8) was found approximately 11 nm which is quite significant. This accounts for the role of zinc substitution in reducing the size of the series. It demonstrates that the doping of Zn can obviously prevent the growing-up of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ crystallites. Therefore, as the zinc content increases, the size of the nanocomposites decreases.

Further, it is worth to mention that the diffraction peaks shifted towards smaller 2\(\theta\) values with the increase of zinc concentration. The shifting of peaks is shown in Fig. 2(b). Due to the peak shifting towards smaller 2\(\theta\) values the corresponding d-spacing increases which increase the lattice parameters with the composition $x'$. This may also be attributed to the replacement of greater ionic radii of Zn$^{2+}$ (0.074 nm) compared with the radii of Cu$^{2+}$ (0.073 nm). The lattice constant ($a$), unit cell volume ($V$), X-ray density ($d_x$) and porosity ($P$) are calculated by the following formulas [5,26]:

$$a = \frac{d_{hkl}}{\sqrt{h^2+k^2+l^2}}$$

(8)

$$V = a^3$$

(9)
In Eq. (8) \( d_{\text{hkl}} \) is d-spacing, \([hkl]\) are miller indices and in Eq. (10) \( M \), \( N \), and \( a \) represent the molecular weight of the material, the Avogadro’s number, and the lattice constant, respectively. In Eq. (11) \( d \) is the bulk density, measured by usual mass and dimensional consideration, whereas \( d_x \) is the X-ray density calculated using Eq. (10).

Various structural parameters such as lattice constant \( a \), unit cell volume \( V \), X-ray density \( d_x \), porosity \( P \), molecular mass \( M \) and crystallite size \( D \) have been calculated for increasing the concentration of zinc and their values are specified in Table 1. The average crystallite sizes were found in the range of 21.5–10.4 nm and are much smaller as compared to those reported earlier.

Table 1
Different parameters estimated using X-ray diffraction data.

<table>
<thead>
<tr>
<th>Material composition</th>
<th>Lattice constant ((a)) Å</th>
<th>Cell Volume ((V)) Å³</th>
<th>Molar mass ((M))</th>
<th>Crystallite size ((D)) nm</th>
<th>Bulk density ((d)) gm/cm³</th>
<th>X-ray density ((d_x)) gm/cm³</th>
<th>Porosity ((P)) %</th>
<th>Specific surface area ((S)) m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe₂O₄</td>
<td>8.382</td>
<td>588.90</td>
<td>303.23</td>
<td>21.5</td>
<td>4.56</td>
<td>6.839</td>
<td>33.32</td>
<td>40.80</td>
</tr>
<tr>
<td>Zn₀.₈Cu₀.₂Fe₂O₄</td>
<td>8.390</td>
<td>590.59</td>
<td>303.60</td>
<td>11.2</td>
<td>4.41</td>
<td>6.829</td>
<td>35.33</td>
<td>78.44</td>
</tr>
<tr>
<td>Zn₀.₆Cu₀.₄Fe₂O₄</td>
<td>8.396</td>
<td>591.86</td>
<td>303.96</td>
<td>10.6</td>
<td>4.32</td>
<td>6.812</td>
<td>36.66</td>
<td>82.98</td>
</tr>
<tr>
<td>Zn₀.₄Cu₀.₆Fe₂O₄</td>
<td>8.401</td>
<td>592.92</td>
<td>304.33</td>
<td>10.5</td>
<td>4.25</td>
<td>6.817</td>
<td>37.65</td>
<td>83.82</td>
</tr>
<tr>
<td>Zn₀.₂Cu₀.₈Fe₂O₄</td>
<td>8.409</td>
<td>594.61</td>
<td>304.69</td>
<td>10.4</td>
<td>4.19</td>
<td>6.806</td>
<td>38.43</td>
<td>84.77</td>
</tr>
</tbody>
</table>

\[ d_x = \frac{8M}{Na^3} \] \hspace{2cm} (10)

\[ P = 1 - \frac{d}{d_x} \] \hspace{2cm} (11)
as lattice constant increases the X-ray density decreases magnitude in comparisons to bulk densities. This may be X-ray density depends on the lattice constant and mole-
density whereas an increase in porosity is observed. The
increments in the porosities of the materials are again
significantly decrease whereas porosity increases with
the substituted materials. The X-ray and bulk densities
content. The decrease in X-ray density with enhancement
of composition ‘x’. The volume of unit cell has larger increment in comparison to the
large crystallite size and surface area. From table it comes to light
that crystallite size
and surface morphology of the material. SEM images give the information about the intergranular, intra-
granular and pores size among the grains. Fig. 3(a–d) shows representative SEM images of Zn0.8Cu0.2Fe2O4 (x = 0.0, 0.2, 0.6 and 0.8) with increasing Zn content. From Fig. 3(a), it is evident that the particles of CuFe2O4 (S-1) are randomly oriented. However, the packed structure along with a few pores has been observed. These pores are responsible for the adsorption of target gas. As the zinc content increases, more particles became spherical and some are found as elongated. From Fig. 3(a–d) it is visible that the clustering of the particles decreases con-	inuously, due to which the porosity increases and the grain size decreases which was confirmed through XRD analysis. When the content of zinc was increased, porous and agglomeration free microstructure of the nanospheres is predominant. Thus the SEM micrographs exhibit a decrease in grain size with increasing zinc concentration. Zinc doping can prevent the growth of the nanosized crystallites. Considering that the particle growth is dependent on particle boundary motion [44], there are two distinct ways; those can be used to prevent the particle growth, (i) by the reduction of the thermodynamic driving force (surface energy) and (ii) by slowing down of the particle boundary mobility. In the present work for Zn0.8Cu0.2Fe2O4 nanocomposites prepared by the sol–gel method, it is clear that the zinc doping can obviously inhibit the growth of nanosized Zn0.8Cu0.2Fe2O4 crystallites. Among all the SEM images, the SEM image of S-5 shows that the particles of Zn0.8Cu0.2Fe2O4 are less agglomerated, of uniform size and homogeneously distributed with high porosity. This image has particular importance for gas sensing application as gases are always adsorbed and even reactive at the surface of the materials.

3.2. Surface morphological analysis

A scanning electron microscope was employed to obtain the grain size and surface morphology of the material. SEM images give the information about the intergranular, intra-
granular and pores size among the grains. Fig. 3(a–d) shows representative SEM images of Zn0.8Cu0.2Fe2O4 (x = 0.0, 0.2, 0.6 and 0.8) were evaluated assuming cubic symmetry. The variation of lattice parameter with zinc concentration is depicted in Fig. 2(d). The lattice parameter is found to increase with the zinc content. This increase in lattice parameter is due to shifting of diffraction peaks towards lower 2θ values. This variation is also attributed to the substitution of bigger sized ionic radii of Zn2+ compared with the radii of Cu2+.

Table 2
Elemental analysis data of Zn0.8Cu0.2Fe2O4 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic percent (%) of element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>ZnFe2O4</td>
<td>63.96</td>
</tr>
<tr>
<td>Zn0.8Cu0.2Fe2O4</td>
<td>69.08</td>
</tr>
<tr>
<td>Zn0.8Cu0.4Fe2O4</td>
<td>69.19</td>
</tr>
<tr>
<td>Zn0.8Cu0.6Fe2O4</td>
<td>69.52</td>
</tr>
</tbody>
</table>

for sensing point of view. The variations in lattice parameter, with increase in zinc concentration can be attributed to the ionic size differences since the unit cell has to expand when substituted by the ions having larger ionic size. As the ionic radius of the doped cation, i.e. Zn2+ (0.074 nm) [43], is larger than that of Cu2+ (0.073 nm) [44], the substitution is expected to increase the lattice constant with increasing zinc content.

It is also evident from Table 2 that crystallite size, bulk and X-ray densities decrease, whereas lattice parameter, molecular weight, porosity and unit cell volume are found to increase with the increase in Zn2+ content. The volume of the unit cell has larger increment in comparison to the molecular weight, therefore, the lattice parameter decreases with the Zn content. The decrease in X-ray density with enhancement of the Zn content is due to the larger unit cell volumes of the substituted materials. The X-ray and bulk densities significantly decrease whereas porosity increases with increasing zinc concentration which plays a key role in controlling the properties of mixed spinel ferrites. The increments in the porosities of the materials are again good indication for sensing point of view. The pores act as sensing channels (sites) and the target gases always adsorb at these pores and react with pre-adsorbed oxygen molecules. This increases the rate of reaction (surface reaction) and hence the sensitivity of the sensor. The variations of X-ray density and porosity are shown in Fig. 2(c). As the value of composition ‘x’ increases, a decrease in X-ray density whereas an increase in porosity is observed. The X-ray density depends on the lattice constant and molecular weight of the material as given in Eq. (10). Therefore, as lattice constant increases the X-ray density decreases owing to the stoichiometries of the materials. Also from Table 2 it is clear that the X-ray densities are larger in magnitude in comparisons to bulk densities. It may be

attributed to the existence of pores which were formed during the material preparation or annealing process.

The lattice parameters of all compositions in the series of Zn0.8Cu1−xFe2O4 (x = 0.0, 0.2, 0.4, 0.6 and 0.8) are in good agreement with values reported in the literature [42]. An increase in lattice parameter with increase in zinc content is evident from Table 2 that crystallite size, bulk and X-ray densities decrease, whereas lattice parameter, molecular weight, porosity and unit cell volume are found to increase with the increase in Zn2+ content. The volume of the unit cell has larger increment in comparison to the molecular weight, therefore, the lattice parameter decreases with the Zn content. The decrease in X-ray density with enhancement of the Zn content is due to the larger unit cell volumes of the substituted materials. The X-ray and bulk densities significantly decrease whereas porosity increases with increasing zinc concentration which plays a key role in controlling the properties of mixed spinel ferrites. The increments in the porosities of the materials are again good indication for sensing point of view. The pores act as sensing channels (sites) and the target gases always adsorb at these pores and react with pre-adsorbed oxygen molecules. This increases the rate of reaction (surface reaction) and hence the sensitivity of the sensor. The variations of X-ray density and porosity are shown in Fig. 2(c). As the value of composition ‘x’ increases, a decrease in X-ray density whereas an increase in porosity is observed. The X-ray density depends on the lattice constant and molecular weight of the material as given in Eq. (10). Therefore, as lattice constant increases the X-ray density decreases owing to the stoichiometries of the materials. Also from Table 2 it is clear that the X-ray densities are larger in magnitude in comparisons to bulk densities. It may be

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attributed to the existence of pores which were formed during the material preparation or annealing process.
size which suppresses the abnormal grain growth. Thus it is observed that the crystallite size decreases and the surface area increases with an increase in the zinc concentration.

High specific surface area of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (for $x = 0.8$) is of prime importance for sensor applications and catalytic purposes. High surface area of nanomaterials increases the available space for accommodation of the target gas and hence increases the surface sites, which further increases the rate of reaction and response of the sensor. In general, high surface area reflects the smaller particle size, which inspired us to employ the developed system for gas sensing applications.

3.3. Elemental composition analysis

The elements present in Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites with their respective atomic percentages have been studied by energy dispersive X-ray spectroscopy. The spectra shown in Fig. 4(a–d) reveals the presence of Zn, Fe, Cu and O elements, respectively. Elemental analysis data of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (x = 0, 0.2, 0.4, 0.6 and 0.8) is presented in Table 2. It is clear from the spectra and Table 2 that as the value of composition ‘x’ increases, the intensity of zinc peaks increases whereas that of copper peaks decreases, i.e., the intensity ratio of Zn/Cu peak increases for Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites. This is due to the stoichiometry of the synthesized nanocomposites (as the zinc content is increased the copper content decreases owing to their stoichiometries). As a result the intensity ratio of Zn/Cu peak increases. The minimum intensity ratio of Zn/Cu peak is 0.30 as observed in Fig. 4(b) while the maximum intensity ratio of Zn/Cu is 5.77 as found in Fig. 4(d). This analysis proves the stoichiometries of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites.
3.4. Atomic force microscopy analysis

Atomic force microscopy (AFM) is one of the scanning probe microscopies employed for imaging surface profiles. AFM provides three-dimensional real topographical images of material surfaces. In a typical AFM setup, the deflection of a micro-fabricated cantilever with a sharp tip is measured by reflecting a laser beam from the back side of the cantilever as it scans over the surface of the material. In order to carry out AFM observation, a fine powder of the material was dispersed in ethanol and then it was irradiated with ultrasonic waves for 15 min. After this, it was sprayed over the entire area of the polished mica substrate. The morphologies of Zn$_{x}$Cu$_{1-x}$Fe$_2$O$_4$ surfaces were investigated in an extensive series of AFM images. The high resolution AFM images recorded for Zn$_{x}$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites surface and the accumulated effect of different compositions have been shown in Fig. 5(a–d). Fig. 5(a–d) are recorded for compositions $x=0$, 0.2, 0.6 and 0.8, respectively. These images qualitatively depict a compositional effect on Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ series. Larger particle size was observed for $x=0$ whereas smaller particle size was observed for $x=0.8$. As the value of $x$ increases it is found that the particle size becomes smaller. It is evident that the addition of zinc content results in an almost uniform distribution of well-dispersed nanoparticles extending over the entire surface as seen for the compositions $x=0.6$ and 0.8. A typical compositional effect resulted in the reduction of larger nanoclusters, and smaller nanoclusters at a constant coverage were observed. Here, the large nanoclusters are imaged fully bright while those of the small particles appear with a dim contrast.

3.5. Infra-red spectra

The analysis of FT-IR spectra gives the information about the structural transformation and is an important tool to acquire information about position of ions in the material. It also helps to identify the spinel structure as well as chemical substance adsorbed on the surface of the materials. For the recording of FT-IR spectra a few milligrams of synthesized powder was mixed with potassium bromide (KBr) powder in an agate mortar. The mixture was then pressed by means of a hydraulic press. The absorbance was recorded against wave number (cm$^{-1}$). In order to study the effect of annealing on Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites, pre- and post-annealed materials were analyzed. The FT-IR spectra of the

![Fig. 4. (a–d) EDS spectra of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0.0 ≤ x ≤ 0.8) nanocomposites.](image-url)
synthesized nanocomposites, shown in Fig. 6(a–b), confirmed the formation of the mixed spinel structures.

The IR spectra of un-annealed materials are shown in Fig. 6(a). The bands around 3150 cm$^{-1}$ are due to the O–H stretching vibration of the free or absorbed water. This indicates the existence of hydroxyl groups in the as synthesized mixed spinel ferrites. The band at 1380 cm$^{-1}$ is attributed to the N–O stretching mode of nitrates whereas the band around 1100 cm$^{-1}$ is related to the C–O stretching mode of alcohol. Two weak absorption bands also appeared in 400–800 cm$^{-1}$ region. These bands are attributed to the vibration of the tetrahedral and octahedral metal–oxygen (M–O) bonds in the lattices of the synthesized nanocomposites. Assignment of important bands in the IR spectra for Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites (for various Zn and Cu contents) has been listed in Table 3. Small deviations in band positions are found for different Zn and Cu contents.

Fig. 6(b) shows the IR spectra of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites obtained after annealing the powder at 500°C for 3 h. Spectra demonstrate that the common bands exist in all the cases, such as the broad absorption O–H stretching band around 3400 cm$^{-1}$. The high surface area of the annealed materials results in the rapid adsorption of water from the atmosphere. The absorption at 1390 cm$^{-1}$ is attributed to the N–O stretching mode of nitrates and bending mode of absorbed water molecule at 1610 cm$^{-1}$. The very weak absorption band at 2350 cm$^{-1}$ is due to the residual CO$_2$. Broad IR bands around 450 and 610 cm$^{-1}$ which become stronger with the annealing are attributed to the metal–oxide bonding. In the un-annealed materials these absorption bands are weaker. As the temperature increases upto 500°C, the band at 610 cm$^{-1}$ arises, which indicates that after heating the powder at 500°C, it contains Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites. The absorption bands at 1620 and 1400 cm$^{-1}$ correspond to undecomposed nitrate ions.

The addition of Zn$^{2+}$ ions makes the Fe$^{3+}$ ions migrate to the octahedral sites, consequently the vibration frequency of tetrahedral sites decreases. Similarly, migration of the Fe$^{3+}$ ions to the octahedral site increases the octahedral vibration frequency. It is evident from the spectra and Table 3 that there is a minor shift in the IR active modes of different materials which is mainly due to the presence of nano-sized grains. This can be attributed to
the fact that in the case of nanosized grains the arrangement of atoms at the grain boundaries is different from that of the bulk crystals. This leads to disorders in both the coordination number and bond length and this degradation in crystal symmetry is responsible for the shifting in IR active modes. The IR results are in good agreement with those reported earlier in the literature [31].

3.6. UV–visible absorption analysis

Optical characterization of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites was carried out using a UV–visible spectrophotometer (Varian, Carry 50 Bio, 200–800 nm, 1 $\times$ 10$^{-5}$ M ethanol). The prepared materials were dispersed in ethanol and their absorption spectra were observed using the UV–visible spectrophotometer having quartz cell (10 mm path length). Fig. 7(a) shows the plot of absorption spectra of different compositions of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocomposites in 200–800 nm wavelength range. These curves show absorption peak in UV-region and constant absorption in visible region. It is also found that the absorption edge is shifted towards the shorter wavelength with increment in the concentration of zinc content. The quantity of photons reaching to the core of a spherical particle depends on the size of the particle and its optical properties. The smaller particles are generally poorer light scatterer than the larger ones. Also, the penetration of light into the particle is influenced by the surface morphology of the particles. Particles formed from large grains have smoother surface than the particles made from small grains. On the smooth surface, the incident photons are scattered and lost mostly by reflection. The rougher surface formed by the small crystals allows a greater number of scattered photons to penetrate into the particle. It was already observed that the crystallite size decreased with increase in zinc content. This suggests that the photon penetration into nanoparticles is a more likely explanation for the observed dependency of the absorption.

![UV–visible absorption spectra](image)

**Table 3**

IR bands (cm$^{-1}$) of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0.0 $\leq$ x $\leq$ 0.8).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Peaks of as prepared samples (cm$^{-1}$)</th>
<th>Peaks of samples annealed at 500 $^\circ$C (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>665, 831, 1363, 1762, 2409, 3143</td>
<td>450, 608, 1113, 1390, 1612, 3425</td>
</tr>
<tr>
<td>Zn$<em>{0.2}$Cu$</em>{0.8}$Fe$_2$O$_4$</td>
<td>619, 831, 1105, 1386, 1766, 2426, 3145</td>
<td>457, 605, 1118, 1394, 1618, 3431</td>
</tr>
<tr>
<td>Zn$<em>{0.4}$Cu$</em>{0.6}$Fe$_2$O$_4$</td>
<td>619, 830, 1105, 1384, 1761, 2428, 3143</td>
<td>451, 601, 1120, 1388, 1610, 3411</td>
</tr>
<tr>
<td>Zn$<em>{0.6}$Cu$</em>{0.4}$Fe$_2$O$_4$</td>
<td>619, 828, 1099, 1379, 1757, 2420, 3143</td>
<td>439, 603, 1120, 1409, 1610, 3392</td>
</tr>
<tr>
<td>Zn$<em>{0.8}$Cu$</em>{0.2}$Fe$_2$O$_4$</td>
<td>618, 829, 1112, 1379, 1766, 2413, 3136</td>
<td>451, 607, 1145, 1398, 1624, 3346</td>
</tr>
</tbody>
</table>
optical absorption property on the zinc and copper content. The absorption spectra shift to a higher photon energy (lower wavelength) and develop a discrete character, when the size of particles is smaller. In general the quantum effect will become dominant by altering physical properties if the particle size of material reaches 100 nm or below [45].

It is well known that the properties of optical absorption are relevant to the electronic structure and hence are the key factors in determining their band gaps. As semiconductor nanoparticles decrease to the nanosized, the energy band gap is increased. Accordingly, a blue-shift took place which indicates the presence of quantum confinement effect in the UV–visible absorption spectra. The optical band gap energies for different compositions are calculated by Tauc’s relation given as below [46]

\[
\alpha h = A(h\nu - E_g)^{1/2}
\]

(14)

where \( \alpha \) is a constant, \( h\nu \) is the photon energy, \( E_g \) is the energy band gap and \( \alpha \) is the absorption coefficient given as [46]

\[
\alpha = 2.303 \left( \frac{A_0}{t} \right)
\]

(15)

In Eq. (15) \( A_0 \) is the absorbance and \( t \) is the thickness of the cuvette. The plots of \( (\alpha h\nu)^2 \) vs. \( h\nu \) for all compositions are shown by Fig. 7(b). Extrapolation of linear regions of these plots along the X-axis gives the corresponding direct band gaps. Their values were 3.94, 3.97, 3.98, 4.02, and 4.04 eV, respectively, for CuFe2O4, Zn0.2Cu0.8Fe2O4, Zn0.4Cu0.6Fe2O4, Zn0.6Cu0.4Fe2O4, and Zn0.8Cu0.2Fe2O4. It is obvious that the values of direct band gap \( E_g \) increases with increase in zinc content. These band gaps are relatively much higher as compared to their bulk. This increment in the band gap is due to decrease in crystallite size with increase in zinc content, which establishes the quantum confinement effect. The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron. Confinement means to confine the motion of randomly moving electron to restrict its motion in specific energy levels (discreteness) and quantum reflects the atomic realm of particles. So as the size of the particle decreases, the decrease in confining dimension makes the energy levels discrete which increases or widens up the band gap and ultimately the band gap energy also increases, resulting in the emission of blue radiation.

3.7. Differential scanning calorimetry

DSC profiles of the as synthesized powder are shown in Fig. 8. An exothermic peak appears in the DSC curve around 265 °C for material S-1, suggesting a crystallization process; a similar behavior is found to occur for the other compositions as well. The peaks between 210 and 250 °C are mainly ascribed to the elimination of excessive polyethylene glycol.

3.8. Magnetic properties

Fig. 9 shows the magnetic hysteresis loops of ZnxCu1-xFe2O4 (x=0.0, 0.2, 0.4, 0.6 and 0.8) nanocomposites. At x=0, ZnxCu1-xFe2O4 (S-1) under applied magnetic field exhibited the hysteresis loop of ferromagnetic nature. As the zinc content was increased, i.e., x=0.2, 0.4, 0.6 and 0.8, modified magnetic properties were observed. Compositions ‘x’=0.2 and 0.4 show super paramagnetism, whereas ‘x’=0.6 and 0.8 illustrate weak magnetism. From Fig. 9 it is observed that the saturation magnetization and coercivity of the materials vary with the zinc and copper contents. As the zinc content was increased the saturation magnetization found to decrease from 10.5 to 0.9 emu/g. The magnetic parameters such as saturation magnetization \( (M_s) \) and coercivity \( (H_c) \) determined by the hysteric loops are described in Table 4. The data presented in table show that the values of \( M_s \) and \( H_c \) for all materials are smaller than those of pure ferrite particles, and decrease with the increase in zinc content. This is due to the fact that surface effect may lead to the reduced magnetization in nanostructured ferrite particles. As domain walls are transi-
mous amount of energy compared to the larger transi-
tional region. Therefore, as the size of the particle is 
reduced, the available size of the domain wall also reduces. 
Below a certain limiting size, determined by the material, 
domain walls are no longer able to form, as the associated 
energy cost is too large and the entire particle acts as one 
huge moment. In this way, paramagnetism is seen as a 
multi-domain response whereas super paramagnetism is a 
single domain response.

As the zinc content is increased, the demagnetic effect is 
notable in Fig. 9. Therefore, the saturation magnetization 
of composites was lower than that of the pure ferrite particles, 
and decreased with ferrite contents. There are some factors 
that will affect the coercivity such as microstructure, grain 
shape, composition, surface and magnetic anisotropy, magne-
tostriiction, etc. With the increment in zinc content, the 
symmetry of spin-orbit coupling in ferrite surface was 
reduced, and the regular arrangement of magnetic particles 
was destroyed. Therefore, the surface anisotropy constant \(K_s\) and 
magneto crystalline anisotropy constant \(K_u\) reduce. On 
the other hand, charge transfer between ferrites and zinc 
would alter the surface charge density and the electron spin 
mechanism. Moreover, the magnetic particles were dispersed 
by zinc, and the interaction between them reduced along with 
the increase of zinc content. Consequently, the resistance 
of domain wall movement is weakened. Hence, the coercivities 
of composites as shown in Fig. 9 are reduced on increasing the 
value of \(x\) which resembles the quantum theory.

The reduction in the value of \(M_s\) for small size is 
attributed to the existence of a magnetically dead or inter 
surface layer on the particles surface that has low magne-
tization. This surface effect becomes less effective for 
small crystallite size. Another surface-driven effect is the 
enhancement of the magnetic anisotropy with decreasing 
particle size [47]. In addition to the surface effect, the 
order–disorder characteristics of the materials have also a 
strong influence on the decrease of saturation magnetiza-
tion [48]. The absence of hysteresis loop, remanence and 
coercivity for S-2, S-3 and S-4 is indication of the presence 
of super paramagnetic and single domain crystals. This is 
due to an increase in the disorder of the magnetic moments 
orientation in the various sites when the surface/volume 
ratio increases [30]. The observed super paramagnetic 
behavior of the materials at room temperature means that 
the thermal energy can overcome the anisotropy energy 
barrier of a single particle, and the net magnetization of 
the particles in the absence of an external field is zero. Super 
paramagnetism is attractive for the applications where 
using a small field to switch the sense of magnetization 
(taking \(+M_s\) to \(-M_s\)) without dissipative losses is needed, 
e.g., hard drives, transformers, etc.

3.9. LPG sensing properties of \(\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4\) \((0.0 \leq x \leq 0.8)\) nanocomposite thin films

The aim of the present paper is to study the sensing 
behavior of the nanostructured \(\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4\) films. Variations in resistance with time for different concentrations 
of LPG are observed and shown in Fig. 10(a–e) for 
different compositions of the materials. Fig. 10(a) shows 
the variations of CuFe_2O_4, similarly Fig. 10(b), (c), (d) and 
(e) show the variations of \(\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Fe}_2\text{O}_4\), \(\text{Zn}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4\), 
\(\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4\) and \(\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4\), respectively. Each curve of Fig. 10(a–e) shows that the resistance of 
the sensing film increases drastically with time in the begin-
ning and afterwards it increases slowly and finally 
becomes saturated. Further, when the outlet of the cham-
ber is opened, the resistance of the film decreases sharply 
and then slowly until it attains the value of stabilized 
resistance in air \(R_s\). Larger variation in resistance is found in 
Fig. 10(e), which shows that the thin film fabricated 
using \(\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4\) is most sensitive. The values of the 
sensitivity and percentage sensor response were 2.5 and 
153%, respectively. The response and recovery times of 
the sensor were measured from the electrical resistance 
changes upon the LPG injection and purging and found to 
be \(\sim 60\) and \(300\) s, respectively. The investigations of 
sensing characteristics (reproducibility) of the films are 
repeated after two months and plotted in Fig. 10(f) for 
\(\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4\) film. Almost no changes in the sensing 
performances were observed, indicating the stability and 
reliability of the fabricated film. Thus the fabricated films 
have improved gas sensing performance with both high 
humidity and fast response. Sufficient stability and good 
reproducibility of the sensing performance have been 
achieved.

To the best of our knowledge the LPG sensing character-
istics of \(\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4\) thin films at room temperature have 
not been investigated as yet. However, in the present study 
an effort has been made to develop a LPG sensor using 
\(\text{Zn}_{x}\text{Cu}_{1-x}\text{Fe}_2\text{O}_4\) nanocomposites synthesized via the sol–gel 
method which could detect a leakage of small amount of 
LPG at room temperature. The gas sensing characteristics 
showed a linear behaviour with increasing the concentra-
tion of the LPG. Sensitivity of the fabricated sensor was 
found much better in comparison to previously reported 
works on LPG sensor [33–39]. Thus our investigation shows 
significant advancement towards the fabrication of a reliable 
and cost effective LPG sensor operable at room temperature.

The gas sensing mechanism of LPG sensor is a surface 
controlled phenomenon, i.e., it is based on the surface area 
of the film at which the LPG is adsorbed and reacts with 
pre-adsorbed oxygen molecules. The oxygen chemisorp-
tions centers viz., oxygen vacancies, localized donor and 
acceptor states and other defects are formed on the surface 
during the synthesis. These centers are filled by adsorbing 
oxygen from the air. The reaction kinematics can be 
explained by the following reactions:

\[
\text{O}_2\text{(gas)} \rightarrow \text{O}_2\text{(ads)} \quad (16)
\]

\[
\text{O}_2\text{(ads)} + e^- \rightarrow \text{O}_2^- \quad (17)
\]

The electron transfer from the conduction band to the 
chemisorbed oxygen results in the decrease in the electron 
concentration at the film surface. As a consequence, an 
increase in the resistance of the film was observed. When 
the film is exposed to reducing gas like LPG, it reacts with 
the chemisorbed oxygen and a surface charge layer would 
be formed. When the LPG reacts with the surface oxygen 
ions then the combustion products such as water depart 
and a potential barrier to charge transport would be 
developed, i.e., this mechanism involves the displacement.
of adsorbed oxygen species by formation of water. The overall reaction of LPG with the chemisorbed oxygen may be taken place as shown below

$$C_nH_{2n+2} + O_2 \rightarrow C_nH_{2n}O + H_2O + e^-$$

(18)

where $C_nH_{2n+2}$ represents the various hydrocarbons. When the flow of LPG is stopped for recovery, the oxygen molecules in air will adsorb on the surface of film, and the capture of electrons through the processes indicated in equations will reduce the sensor’s resistance towards the
initial stable surface state of the film. Since the sensing mechanism is based on the chemisorptions reaction that take place at the surface of the metal oxide, so increasing specific surface area of the sensitive materials leads to more sites for adsorption of surrounding gases. Here in the present case, it may be seen from the SEM images that Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ offers more gas adsorption sites for interaction of the gas molecules in comparison to other compositions. As a result, this film shows enhanced sensitivity and percentage sensor response among the others. The enhanced
sensing performance may be attributed to its small crystallite size, higher porosity and active surface area. The pores can act as channels for diffusion of LPG, and thus provide more active sites. This improves the reaction of LPG with surface adsorbed oxygen. These features make Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ film better for gas sensing applications.

3.10. CO$_2$ sensing performance of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0.0 \leq x \leq 0.8) nanocomposites

The variations in resistance with time for different concentrations of CO$_2$ are shown in Fig. 11 (a-e). Fig. 11(a) shows the variations of CuFe$_2$O$_4$, similarly Fig. 11(b-e) shows the variations of Zn$_{0.2}$Cu$_{0.8}$Fe$_2$O$_4$, Zn$_{0.4}$Cu$_{0.6}$Fe$_2$O$_4$, Zn$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$, respectively. Each curve of Fig. 11(a-e) shows that as time increases the resistance of the sensing film decreases sharply in the beginning and afterwards it decreases slowly and finally becomes saturated. On opening the outlet of the chamber, the resistance of the film increases sharply and then slowly until it attains the stabilized value of resistance in air ($R_a$) for further range of time. More variations in resistance are found in Fig. 11(e), which exhibits that Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ film is most sensitive among all. The values of the sensitivity and percentage sensor response of this film were 2 and 114%, respectively. The response and recovery times of the sensor were found to be $\sim$200 and 350 s, respectively. Reproducibility curve of Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ film is shown in Fig. 11(f), which shows that the sensing characteristics are 94% reproducible after two months of the fabrication of the sensor. The adsorption kinematics can be explained by the following chemical equations:

$$\text{CO}_2 (\text{gas}) + e^{-} \rightarrow \text{CO}_2 (\text{ads}) \quad (19)$$

$$\text{CO}_2 (\text{ads}) + O^-(\text{ads}) + 2e^{-} \rightarrow \text{CO}(\text{gas}) + 2O^- (\text{ads}) \quad (20)$$

Fig. 12(a) shows the sensitivity of LPG sensor for different compositions of Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$. Best LPG sensitivity was observed for Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ in comparison to other compositions. Similarly, Fig. 12(b) shows the sensitivity of CO$_2$ sensor for different compositions of the materials through a column diagram. In this case, the better sensitivity was also observed for Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ film sensor. The sensitivity of LPG sensor was found large in comparison to CO$_2$ sensor; hence Zn$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ film is selective for the LPG detection with fast response and recovery times.

4. Conclusion

Nanostructured Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0.0 \leq x \leq 0.8) was successfully synthesized by a sol–gel method. The process used here is convenient, environment friendly, inexpensive and efficient for the preparation. It is evident from XRD that the diffraction peaks become broader gradually with the increase of the Zn concentration in ferrite matrix. The crystallites were found in the range of 21.5–10.4 nm size. The increment in the band gap (blue-shifting) for different compositions in the present study is due to the decrease in crystallite size with increase in zinc content which establishes the quantum confinement effect. The dependence of magnetic properties on crystallite size is another significant inference of this work. These magnetic nanoparticles can be used in many other applications, so their detailed characterization would be of considerable interest. Further the variations in resistance were systematically observed with the time for different concentrations of LPG and CO$_2$. The maximum sensitivities for LPG and CO$_2$ sensors were found to be $\sim$2.5 and 2, respectively. The response and recovery times of LPG sensor were $\sim$60 and 300 s, respectively. Better sensitivity, sensor response, small response and recovery times, and good stability present the opportunity to develop it as commercial sensor for the detection of LPG.

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