Effects of Al Doping with Zinc Ferrite Nanoparticles on Structural, Magnetic and Dielectric Properties

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Abstract
Zinc ferrite nanoparticles have wide range of the applications in the field of Electronics, Optoelectronics, Magnetics, Solar cell, Photocatalysts. With Al doping we modify their structural, magnetic and electrical properties of zinc ferrite (ZnFe$_2$O$_4$). In the present studies, zinc ferrite nanoparticles were prepared by sol gel method using glycine as combustion agent. The effects of Al doping concentration on the structural, morphological, optical, magnetic and electrical properties of zinc ferrites were studied. In x-ray diffraction patterns analysis confirmed the formation of the cubic spinel structure. We characterise scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) in the current work to examine the morphology of the nanomaterials. The UV-Vis optical investigation showed that Al$^+$3 doping increased absorbance and significantly decreased energy band gap value (1.90 eV-2.01 eV). The magnetic properties of zinc ferrite NPs were studied by using vibrating samples magnetometer which showed samples of pure zinc ferrites and Al-doped zinc ferrite with paramagnetism. Dielectric properties were studied from impedance analyser. When aluminium concentration increases in the zinc ferrites, dielectric characteristic results were obtained in which dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and tangent loss decreased. Also when frequency increases above all three dielectric parameters remains stable at high frequency. The obtained results of pure and Al doped Zn ferrite are useful for high frequency applications.

Keywords
Al Doping; Dielectric Constant; Sol-Gel Autocombustion; Xrd; Zinc Ferrite.

Introduction
In nanoscience field cubic spinel ferrite have (MFe$_2$O$_4$, M = Zn, Mg, Co, Fe, Mn, Cu, and Ni) excellent magnetic properties due to their particle size and shape. Spinel ferrites nanoparticles are prepared with different method like Microemulsion, Ultrasonic (Sonochemical), non-hydrolytic, Solgel, Microwave-Assisted, Mechanical Milling, solvothermal, electro-

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chemical synthesis, Coprecipitation and Hydro-thermal methods. Spinel ferrite nanoparticles have different shapes like cubic, spherical octahedral, or symmetric. All the prepared samples are annealed which results in improving their structural, magnetic and electrical properties. Spinel ferrite nanoparticles having larger specific surface area that is why used as acatalyst. They are classified into heterogeneous and homogeneous. In catalyst itscost, recovery and reuse are the important factors in photodegradation and wastewater treatments. Proper choice of synthesis method and chemical composition defined its lattice structure with enhanced physical and chemical properties. Spinel ferrite behaves supermagnetic if crystalline size is below 20nm. In supermagnetism magnetic field appears random direction. Super paramagnetic iron oxide nanoparticles are classified into two categories i.e. small synthetic γ-Fe₂O₃ (magnetite) or Fe₂O₃ (magnetite) particles with its core range in between 10 nm and 100 nm in diameter. Transition metal ions such as copper, cobalt, nickel, and manganese are mixed with iron oxides behaviour superparamagnetic and included into superparamagnetic iron oxide nanoparticles. These are used in biomedical applications. Smaller crystalline size and larger surface area to enhanced their structural, magnetic, electronic, and optical properties of spinel ferrite nanoparticles. Crystalline size and shape are changed to vary their physical, magnetic and chemical properties. The cubic spinel ferrite nanoparticles are most important aspects of about magnetism with the parameters of crystal and magnetic structure. Magnetic performance of the spinel ferrite is classified into three level like atomic level, single particle level and mesoscopic level. All these levels are depending on preparation method of the nanoparticles. Sol gel method is very easy and its annealing temperature used for converting gel to ash is important aspect for the particle size. In spinel ferrite nanoparticles diameter of particles is determined with the help of transmission electron microscopy (TEM) which gives true particle size. With reference to information of nanoparticle dimension in spinel ferrite are the types of shapes like spherical, cubic, octahedral, and symmetric star. Transmission electron microscopy gives the knowledge of on aggregation, chaining of particles, morphological specificities, thickness of disordered surface layer and defects. In spinel ferrite nanoparticles structural, electrical and magnetic properties varied with their material composition, synthesis methods and nanoparticles sizes. Fuel like citric acid, urea and glycine varies chemical reaction with their chemical compositions.

In this paper we focused on sol–gel auto-combustion method due to their simple process nanoparticles with its high purity, composition homogeneity and well crystalline size of the spinel ferrite nanoparticles.

**Experimental Details**

**Synthesis of ZnFe₂ₙ₋ₓAlₓO₄ Nanoparticles**

In order to synthesize Al modified ZnFe₂O₄ analytical graded Zinc (II) nitrate hexahydrate (Zn(NO₃)₂.6H₂O), Iron (III) nitrate nonahydrate (Fe(NO₃)₃.9H₂O) and aluminium nitrate nanohydrate (Al(NO₃)₃.9H₂O) with purity of 99.9% were used raw materials in this synthesis, as such without further purification. ZnFe₂₋ₓAlₓO₄ with x=0, 0.1, 0.2, 0.3, 0.4 were prepared by sol–gel auto-combustion method using glycine as the fuel. Initially all the chemicals are used with their stoichiometric ratio 1:3 was dissolved in 200 ml distilled water. Drop wise addammonia for maintaining pH 7(i.e.netural). Final solution was continuously stirred on a magnetic hot plate for upto 3-4 hrs under the temperature 70–90°C obtained sol. Gradually sol was convert brown colour organic gel. After forming gel we given to heat treatment at 120°C-130°C to remove water content, decompose hydroxyl groups, and organic matter. Autocombustion start in certain period brown ZnFe₂₋ₓAlₓO₄ powder was formed. The brown powder was grind in an agate mortar to make a fine and homogenous powder. Fine powder was annealed at 600°C for 5 hrs in air for better crystallization. Fig.1 shows a flow chart representation of the zinc ferrite nanopowder synthesis.

**Characterization Techniques**

Crystal structure and phase composition of the prepared nanoparticle of the zinc ferrite was characterized by X-ray diffraction (XRD) analysis with CuKα radiation (λ= 0.154 nm) within the angular range 20°-80°. With the help of vibrating sample magnetometer (VSM) magnetic behaviour of the samples was studied. The dielectric properties of the nanoparticles including dielectric constant, real and complex permittivity, dielectric loss, and also AC conductivity with the help of LCR meter at broad frequency range were studied.
Result and Discussion

Structural Analysis

With X-ray diffraction (XRD) in the range of 2θ between 20º and 80º we investigated their structural analysis of the zinc ferrite nanoparticles. From the XRD patterns Fig.2 (a, b), it can be detected that all the reflection peaks of zinc ferrite and Al-doped zinc ferrite. The diffraction peaks at 2θ values of 29.85, 35.2, 36.83, 42.8, 53.11, 56.61, 62.16, 70.51, 73.52 and 74.57 correspond to major hkl
planes (220), (311), (222), (400), (422), (511), (440), (620), (533) and (444) confirmed. All the diffraction peaks are corresponding that FCC structure with Fd3m space group. We observed that there is no additional peak for both the samples. Higher diffraction peak at the (311) plane was considered as a measure of its better crystalline structure and phase purity. With the help of X-ray diffraction it can be observed that the width and the peaks changed due to deposition of aluminium(x=0 to 0.4) in ZnFe$_{2-x}$Al$_x$O$_4$. The crystallite size (D) of the spinel ferrite nanoparticles was calculated with the help of Debye-Scherer’s equation Eq. (1)

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

$(1)$

Where D is crystallite size, $\lambda$ is the wavelength, $\theta$ is the Bragg’s diffraction angle, $\beta$ is the full width at half maximum (FWHM) and K is constant (K=0.94). The crystallite size was observed in the range 33-24 nm (Table 1). The crystallite size and lattice constant ‘a’ decreased linearly with substitution of Al$^{3+}$ in ZnFe$_2$O$_4$. Lattice constant varies with the basis of difference in ionic radii, Al$^{3+}$ ionic radius (0.051nm) and Fe$^{3+}$ (0.064nm) of substituted ions. Bond energy, synthesis method and chemical composition plays significant role to form crystalline size.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystal structure</th>
<th>Lattice angle (°)</th>
<th>Lattice parameter (a = b = c)(°)</th>
<th>D (nm)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>Cubic</td>
<td>$\alpha = \beta = \gamma = 90^{\circ}$</td>
<td>8.437</td>
<td>32.58</td>
<td>600.57</td>
</tr>
<tr>
<td>ZnFe$<em>{1.6}$Al$</em>{0.4}$O$_4$</td>
<td>Cubic</td>
<td>$\alpha = \beta = \gamma = 90^{\circ}$</td>
<td>8.359</td>
<td>24.15</td>
<td>584.07</td>
</tr>
</tbody>
</table>

**Scanning Electron Microscopic (SEM) Analysis**

Scanning electron microscopy (SEM) was used to examine the appearance and structure of the produced material. Fig. 3 shows SEM images of unsubstituted and Al-substituted ZnFe$_{2-x}$Al$_x$O$_4$ spinel ferrite nanoparticles. The representative SEM profile images of ZnFe$_{2-x}$Al$_x$O$_4$ shown in Fig. 3 (a & b) illustrates nanostructural behaviour of ferrite and doped ferrite samples. The ferrite samples of ZnFe$_{2-x}$Al$_x$O$_4$ where x =0.0, 0.3 etc.

![Fig. 3 (a): SEM micrographs and EDX analysis of ZnFe$_2$O$_4$](image-url)
The incorporation of ions is said to change the particle size of the ferrite sample. As added Al$^{3+}$ the crystalline grain size decreased. Al$^{3+}$ substitution also had an impact on the sample's density, porosity, density, and lattice parameter.

Optical Properties
UV-Visible absorption, reflectance, and transmittance analysis was used to evaluate the optical band gap and electrical architectures of the metal oxide semiconductor materials. In order to determine the band gap energy (Eg) of metal oxide semiconductors, UV-Visible diffuse reflectance spectroscopy (DRS) experiments are essential. The spinel ZnFe$_2$O$_4$ optical absorption characteristic, which is related to its electronic structural feature, is found to be a crucial determinant of the photocatalytic activity. The optical properties of the ZnFe$_2-x$Al$_x$O$_4$ (x= 0.0, 0.3) nanoparticles were investigated by UV-Vis spectroscopy. The absorbance of sample was measured in the wavelength range 200 nm –700 nm. The spinel ZnFe$_2$O$_4$ showed prolonged photoabsorption in this spectrum, extending from UV to visible area shorter than 750 nm, suggesting the prospect of strong photocatalytic activity of this material under visible light. The direct band gap energy of the specimen is determined from the Tauc plot by using Kubelka-Munk function. Fig.4 (a and b) shows the Tauc plot derived from absorbance spectra of the typical sample (ZnFe$_2$O$_4$). The band gap value determined from the Tauc plot was found to be 1.90 to 2.01 eV. ZnFe$_2-x$Al$_x$O$_4$ photo absorption from the UV to visible area may be attributed to increased band gap energy levels brought on by the abundance of surface and interface defects in the aggregated nanoparticles.

Table 2 (a): Elemental analysis of ZnFe$_2$O$_4$

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>38.77</td>
<td>65.67</td>
</tr>
<tr>
<td>Fe K</td>
<td>42.32</td>
<td>25.61</td>
</tr>
<tr>
<td>Zn K</td>
<td>18.68</td>
<td>8.72</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 2 (b): Elemental analysis of ZnFe$_{1.7}$Al$_{0.3}$O$_4$

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>42.67</td>
<td>64.26</td>
</tr>
<tr>
<td>Al K</td>
<td>8.55</td>
<td>5.77</td>
</tr>
<tr>
<td>Fe K</td>
<td>29.40</td>
<td>20.53</td>
</tr>
<tr>
<td>Zn K</td>
<td>19.38</td>
<td>9.44</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

The incorporation of ions is said to change the particle size of the ferrite sample. As added Al$^{3+}$ the crystalline grain size decreased. Al$^{3+}$ substitution also had an impact on the sample's density, porosity, density, and lattice parameter. The spinel ZnFe$_2$O$_4$ optical absorption characteristic, which is related to its electronic structural feature, is found to be a crucial determinant of the photocatalytic activity. The optical properties of the ZnFe$_2-x$Al$_x$O$_4$ (x= 0.0, 0.3) nanoparticles were investigated by UV-Vis spectroscopy. The absorbance of sample was measured in the wavelength range 200 nm –700 nm. The spinel ZnFe$_2$O$_4$ showed prolonged photoabsorption in this spectrum, extending from UV to visible area shorter than 750 nm, suggesting the prospect of strong photocatalytic activity of this material under visible light. The direct band gap energy of the specimen is determined from the Tauc plot by using Kubelka-Munk function. Fig.4 (a and b) shows the Tauc plot derived from absorbance spectra of the typical sample (ZnFe$_2$O$_4$). The band gap value determined from the Tauc plot was found to be 1.90 to 2.01 eV. ZnFe$_2-x$Al$_x$O$_4$ photo absorption from the UV to visible area may be attributed to increased band gap energy levels brought on by the abundance of surface and interface defects in the aggregated nanoparticles.
By analyzing UV-Visible absorption, reflectance, and transmittance data, the optical band gap and electrical structures of metal oxide semiconductor materials were identified. The following equation has been used to determine the band-gap energy with the use of Tauc plots.

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hspace{1cm} (3.20)

Where “A” is constant, “h\nu” is the photon energy \((\nu = c/\lambda)\) “Eg” is the band gap energy of the material, and the exponent ‘n’ depends on the type of transition (\(n = 1/2\) for direct allowed transition, \(n = 2\) for indirect).^{12}

**Vibrating Sample Magnetometry**

With the help of vibrating-sample magnetometer (VSM) a magnetic property which is based on Faraday’s Law of Induction was studied.^{13} With the help of magnetic properties M-H curves of ZnFe\(_{2-x}\)Al\(_x\)O\(_4\) nanoparticles was obtained. By analysis of M-H curves, we get the value of magnetic moment (\(\mu\)), saturation magnetization (MS), remanence (Mr), coercivity (Hc) and the anisotropy constant (K).^{14} Magnetization totally depends on crystalline particle size, we observed magnetization decreases when particle size increases. Zinc ferrite nanoparticles behave ferromagnetic when particles size is 19-21 nm and also paramagnetic behaviour when particle size 29 to 35nm.^{15}

**Table 3: Band-gap energy of ZnFe\(_{2-x}\)Al\(_x\)O\(_4\) (x=0.0, 0.3)**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Composition</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnFe(_2)O(_4)</td>
<td>1.90</td>
</tr>
<tr>
<td>2</td>
<td>ZnFe(<em>{1.7})Al(</em>{0.3})O(_4)</td>
<td>2.01</td>
</tr>
</tbody>
</table>

![Fig. 4. (a, b): UV-Vis plot of plot of nanoparticles ZnFe\(_{2-x}\)Al\(_x\)O\(_4\) (x=0.0, 0.3)](image)

![Fig. 4: Hysteresis loops of ZnFe\(_{2-x}\)Al\(_x\)O\(_4\) nanoparticles](image)
The M-H curves of the magnetization in Fig.4 confirmed the paramagnetic behaviour of the nanoparticles. In plot magnetic field at x-axis and magnetization at y-axis data showed. In table 2 shows that values of magnetic parameters ZnFe$_{2-x}$Al$_x$O$_4$. In this case saturation magnetization decreases and aluminium composition increases and also due to smaller particle size as well as replacement of ions (Fe$^{3+}$ to Al$^{3+}$). Mr (remanence) and Hc(coercivity) values were small due to their different bond energy of Al$^{3+}$-O$^{2-}$, Fe$^{3+}$-O$^{2-}$ and Zn$^{2+}$-O$^{2-}$.16,17

<table>
<thead>
<tr>
<th>Composition</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
<th>Magnetic moment ($\mu$)</th>
<th>Anisotropy constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>1.832</td>
<td>0.0095</td>
<td>2.439</td>
<td>0.079</td>
<td>2.234</td>
</tr>
<tr>
<td>ZnFe$<em>{1.6}$Al$</em>{0.4}$O$_4$</td>
<td>1.601</td>
<td>0.0125</td>
<td>2.538</td>
<td>0.066</td>
<td>2.032</td>
</tr>
</tbody>
</table>

The magnetic moment of the ZnFe$_{2-x}$Al$_x$O$_4$ nanoparticles were calculated by the given formula.

$\mu=(MXMs)/5585$ ...(2)

From Eq. (2) $M$ = molecular mass of the material, $M_s$ = saturation magnetization and also anisotropy constant of the synthesized ZnFe$_{2-x}$Al$_x$O$_4$ nanoparticles was calculated by the formula.

$K=(H_c XMs)/2$ ...(3)

We observed small value of the coercivity for benefits to use as a soft magnetic materials and low resistive for magnetization. Substitution of aluminium in spinel ferrite (Ni–Zn ferrite) is not found in literature in bulk due to their saturation magnetization ($M_s$), and magnetic moment ($\mu$) decrease. Finally we got the result increased substitution of aluminium decreased its magnetic moment ($\mu$), this effect is known to spin canting.18

**Frequency Dependent Dielectric Property**

Dielectric properties totally depend upon the type of ferrite, doping concentration, annealing temperature and it's time, synthesis method, structural parameters, crystalline size, porosity, density and polymer which are used in composite sample.19 Complex permittivity in dielectric study can be expressed by the relations in Eq (4).

$\varepsilon=\varepsilon'+i\varepsilon''$ ...(4)

Where, $\varepsilon'$ is the real part and $\varepsilon''$ imaginary parts of dielectric constant. Electric permittivity high values are occurs from thin grain boundary.20 Dielectric properties were analysed using Maxwell-Wagner model, Koop's phenomenological theory. We use Koop's theory to establish frequency and AC conductivity relations in different ferrites. In the dielectric properties of ZnFe$_{2-x}$Al$_x$O$_4$ dielectric constant, complex permittivity, dielectric loss, and AC conductivity with the help of LCR meter can be calculated.21,22 This mentioned parameters are very important for the application of high frequency. Zinc ferrite is referred as soft magnetic material due to their low coercivity, magnetization which can be easily reversible.23 The dielectric constant ($\varepsilon'$) of the pellet can be calculated by using the formula

$\varepsilon^\omega=(CP Xt)/(\varepsilon_0 XA)$ ...(5)

Where, $\varepsilon_0$ is permittivity of the free space, $C_p$ is capacitance of pellet, $t$ is thickness of the pellet, and $A$ is area of the pellet. Dielectric loss tangent or dissipation of the dielectric (tan$\delta$) can be calculated by using the formula

$\tan \delta=1/Q$ ...(6)

Dielectric loss tangent is simply reciprocal of quality factor Q and the dielectric loss ($\varepsilon''$) of the material is,

$\varepsilon''=\varepsilon'\tan \delta$ ...(7)
Fig. 4a: Real dielectric constant of ZnFe$_{2-x}$Al$_x$O$_4$($x=0.0 & 0.4$) with frequency

Fig. 4b: Complex dielectric constant of ZnFe$_{2-x}$Al$_x$O$_4$($x=0.0 & 0.4$) with frequency

Fig. 4c: Loss tangent of ZnFe$_{2-x}$Al$_x$O$_4$($x=0.0 & 0.4$) with frequency
Table 4

<table>
<thead>
<tr>
<th>Composition</th>
<th>At 50Hz</th>
<th>At 5KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon'$</td>
<td>$\varepsilon''$</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>306.03</td>
<td>197.49</td>
</tr>
<tr>
<td>ZnFe$<em>{1.6}$Al$</em>{0.4}$O$_4$</td>
<td>342.07</td>
<td>414.06</td>
</tr>
</tbody>
</table>

Fig. 4 (a to c) depicts the relationship between frequency and real dielectric constant($\varepsilon'$), complex dielectric constant($\varepsilon''$) and Loss tangent($\tan\delta$) for ZnFe$_{2-x}$Al$_x$O$_4$ nanoparticles produced using the sol-gel auto-combustion technique with glycine as a fuel agent and 600ºC. The value of $\varepsilon'$ and $\varepsilon''$ is high at low frequencies, as can be shown in mentioned fig of 4a and 4b eventually falls off as the when frequency rises. The free charge mobility within the material is what causes the high value of $\varepsilon'$ at low frequency. The contributions of electronic, ionic, orientation, and interfacial polarisation determine the characteristics of $\varepsilon'$ and $\varepsilon''$ at low frequencies. All the parameters like dielectric constant (real and complex) and dielectric loss for all the samples were studied in the frequency range 50Hz-5MHz. All the parameters are frequency dependent. It values mostly depends on the chemical composition, fabrication route, crystallite size and cation distribution. In all the compositions of sample of ZnFe$_{2-x}$Al$_x$O$_4$ if frequency is increases dielectric parameters are decreases. According to Koop’s model $\tan\delta$ values varied with their frequency range due to their energy loss of Fe$^{2+}$ and Fe$^{3+}$. Basically at high very frequency resistivity and grains plays vital role and for hopping of electrons in between Fe$^{2+}$ and Fe$^{3+}$ need energy and $\tan\delta$ is very small.

Conclusions

Nanocrystalline ZnFe$_{2-x}$Al$_x$O$_4$(x=0.0, 0.1, 0.2, 0.3, 0.4) nanoparticles were successfully prepared with sol gel auto-combustion method with glycine as a fuel. Sol gel method was preferred because of low cost, good crystallinity and reproducibility. Crystalline size was found to vary within range of 32 to 24nm. XRD showed that the formations of cubic face centred structure are confirmed. Al content was added lattice parameters 8.437 to 8.359 reduced. VSM show paramagnetic behaviour due to their particle size 29 to 35nm. The dielectric constant and dielectric loss both are decreased at high frequency.

Acknowledgments

The authors are grateful to Dr.K.M.Jadhav, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Funding

No

Conflict of Interest

There is no conflict of interest.

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