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The Presented Study of Zn-Cu Ferrites for Their Application in “Photocatalytic Activities”

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Abstract

The present chapter summarizes the synthesis and characterization of Zinc Copper (ZnCu) ferrites due to their wide range of applications in many areas. ZnCu ferrites are soft magnetic materials that have exceptional electrical, magnetic, and optical properties. ZnCu ferrites possess high resistivity, permeability, permittivity, saturation magnetization and low power losses, and coercivity. The above features of ZnCu ferrites find application in designing transformers, transducers, and inductors. Ferrites are also used in magnetic fluids, sensors, and biosensors. Apart from these advantages, they play a vital role in practical appliances like mobile, laptops, mobile chargers, refrigerators, washing machines, microwave ovens, printers, and so on. Therefore, the present focus is on the literature of techniques of the synthesis, their characterization, the effect of doping on the behavior of ZnCu ferrite, and, finally, their potential application in technology.

Keywords: spinel, ferrites, magnetic, surface morphology, synthesis techniques

1. Introduction

A ferrite is a ceramic material that is made up of iron oxide (Fe_2O_4) in massive proportion mixed with a metallic element such as barium (Ba), manganese (Mn), nickel (Ni), zinc (Zn) in small proportions [1–9]. The nature of iron oxide and the metal is electrically non-conducting and ferrimagnetic. Ferrimagnetic materials possess unequal opposing magnetic moments which help to retain spontaneous magnetization. Ferrites are generally classified into two types: hard ferrites [10, 11] and soft ferrites [12–15]. Hard ferrites have a high coercivity to magnetize. These materials are used in making permanent magnets which find application in the loudspeaker, washing machine, communication systems, switch-mode power supplies, dc-dc converters, microwave absorbing systems, and high-frequency applications [16–23]. On contrary, soft ferrites have low coercivity as a result of which their magnetization can easily be altered. Soft ferrites are good conductors of the magnetic field which paved the way in developing transformer cores, high-frequency inductors, and microwave components [24–38]. Further, soft ferrites include high resistivity, low cost, temperature stability, low loss, and high permeability [39–42]. The most significant soft ferrites are ZnCu ferrites with high permeability and saturation magnetization [43–49]. Properties of these nanomaterials can be modified by substitution of diamagnetic or

paramagnetic cations and their distribution in the spinel structure which alters the grain sizes, distribution, and surface morphology. The attribution of ZnCu ferrites is dependent on the synthesis methods and concentration of doping [50]. Cu-Zn spinel ferrites possess excellent magnetic behavior that depends on the concentration of Zn^{2+} ions in CuFe_2O_4 . The large saturation magnetization (M_s), high initial permeability, and high resistivity of Cu-Zn ferrites make them a prominent material in electrical switches, memory devices, inductors, and antenna cores [51, 52]. Cu^{2+} has one unpaired electron, and Zn^{2+} has no unpaired electron. So, the replacement of Cu^{2+} ion by Zn^{2+} ion enhances the strength of magnetic ions participating in the exchange interaction. Moreover, the substitution of Zn^{2+} in place of Cu^{2+} changes the cation distribution and arrangement in the spinel structure. So, it is interesting to study the effect of Zn^{2+} substitution on the magnetic properties of Cu-ferrite nanoparticles. Moreover, Zn^{2+} substitution with higher concentration stabilizes the cubic phase of Cu-ferrite. The importance of Zn-Cu ferrites based on a comprehensive review is summarized.

2. Purpose of the review

The prime motive of the review is to focus on the synthesis and characterization methods of ZnCu ferrites. The subject of magnetic nanostructures is wide, and several articles are published. The ZnCu ferrites, constitute a special niche of nanoparticles because of the attraction of the scientific community towards soft ferrites. In addition, the study discusses the choice of techniques for synthesizing ZnCu ferrites by demand. The synthesis techniques such as the sol-gel [53], co-precipitation [54], a conventional ceramic technique [55–57], a hydrothermal method [58], citrate precursor [59], and microemulsion [60] for the synthesis of ZnCu ferrites are discussed.

3. Morphology of ZnCu ferrites

The spinel structure [61]. of ZnCu ferrite consists one major unit cell composed of 8 sub-unit cells having face-centered cubic (FCC) structure with two types of sites in each unit cell i.e. tetrahedral (A) site and octahedral (B) site. There are 64 tetrahedral interstitial sites and 32 octahedral interstitial sites. Spinel structure has closed packed oxygen atoms arrangement in which 32 oxygen atoms form a unit cell. Tetrahedral (A) sites are surrounded by four nearest oxygen atoms and octahedral (B) sites have six neighboring oxygen atoms. In ZnCu spinel ferrite lattice, Zn ions are on the tetrahedral sites while Fe and Cu ions occupy both tetrahedral and octahedral sites. Due to this spinel structure, different metallic ions can be added which brings out a change in the electric and magnetic properties of ferrites. The metal ions introduced may enter the spinel crystal lattice by replacing Fe^{3+} ions and leading to aggregation of these ions on the grain boundary. These morphological features of ZnCu ferrite nanoparticles can be tuned to a larger extent to fulfill the application and to select the appropriate synthesis and characterization techniques. To learn the merits of ZnCu ferrites for various applications, the knowledge of different synthesis and characterization techniques is a must.

3.1 Synthesis methods to prepare ZnCu ferrites

There are two approaches to synthesize nanoparticles: top-down and bottom-up. In top-down, the bulk materials are broken down to get nanosized particles. This

method has many shortcomings which include the presence of impurities, crystal defects, usage of metal oxides, the requirement of high temperature, products are inhomogeneous, broad size distribution, and flaws in surface structure. In the bottom-up approach, small atomic building blocks fuse to produce nanoparticles. This is the most conducive method for synthesis as the products are homogeneous, highly pure, and reveals narrow size distribution.

Various synthesis techniques are used to prepare ZnCu ferrite nanoparticles such as the sol-gel method [62], spray pyrolysis process [63], co-precipitation method [64], citrate precursor method [65]. By doping other elements or oxides the structural, electrical, and magnetic properties of ZnCu ferrite can be improved, leading to an increase in saturation magnetization and a decrease in coercivity in the soft ferrites.

3.1.1 Co-precipitation method

Co-precipitation [66, 67] is an easy and conventional method to synthesize nanomaterials. The ferrites prepared using this method are of controlled size, highly pure, and have a homogeneous structure. Normally inorganic salts (nitrate, chloride, sulfate, etc.) are used in this method as promoting substance that is dissolved in water or another medium that is suitable to form a homogeneous solution. The pH of the solution is adjusted to 7–9 and the solvent is evaporated to get nanoparticle precipitates. It should be observed that the concentration of salt, temperature, rate of change in pH are the parameters that determine the crystal growth and aggregation of the particles. After precipitation, the solid mass is collected and washed. By heating the residue the resultant product is dried to form hydroxides. The hydroxides are then transformed into crystalline oxides by calcination. Gautam et al. [68] used co-precipitation method to synthesize ZnCu ferrite. In this method, Copper chloride, zinc chloride, iron(III) chloride, and sodium hydroxide are used as raw materials. 3 M solution was prepared in 60 ml of distilled water which is mixed with boiling NaOH and stirred for 60 min between temperature 353–358 K using a magnetic stirrer, maintaining the pH between 11 and 12. The precipitates are allowed to settle down and then the sample was washed many times with distilled water. After washing, the sample was dried in hot air followed by crushing, and finally powdered with a mortar pestle. A. C. Prabakar et.al [69] also synthesized ZnCu ferrites by the chemical co-precipitation method by taking a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and $\text{Fe}_2(\text{NO}_3)_9 \cdot 9\text{H}_2\text{O}$ as the initial materials. These were mixed to form a homogeneous solution at 358 K. Then, ammonia solution was added dropwise with constant stirring maintaining the pH between 10 and 11. The mixture was heated at 353 K for 1 hr. After washing and drying the ferrite powder was heated at 673 K, 773 K, and 923 K separately and pressed in the form of circular pellets. Precipitates were washed many times and then dried in an oven at 100°C for 8 hr. The co-precipitation method has a unique advantage as it uses the aqueous medium for synthesis. There is an effective grain size control and morphology of the nanoparticles obtained.

3.1.2 Sol-gel method

The sol-gel method [70, 71] is a promising approach used for the preparation of ferrite nanomaterials. Sol is a colloidal suspension of solid particles of ions in a solvent and gel is a semi-rigid mass that forms when the solvent from the sol starts evaporating and the particles left behind join together. The resultant is in the form of colloidal powder or films. This method is appreciable due to the controlled microstructure. The final particles formed are of uniform and small size. Also, this

technique of synthesis is economical and it is achievable at low temperature. The temperature conductivity was observed to be higher than pure ZnCu ferrite. There was a declination in the dielectric constant with an increase in nickel concentration. This method is advantageous because it is less time-consuming. The prepared ferrite consists of a pure cubic spinel structure.

3.1.3 Combustion method

The combustion process is an effective and low-cost method to synthesize nanomaterials. This process is simple, versatile, and fast for nanomaterial preparation. The salient feature of this method is, it requires less time and energy during the synthesis. The nanoparticles produced are pure and homogeneous. Researchers synthesized ZnCu ferrites by using this method [72, 73]. Copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 2.6\text{H}_2\text{O}]$, zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, iron nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ were taken in appropriate proportions and urea $[\text{CO}(\text{NH}_2)_2]$ was used as a reducing agent in this process. A solution is formed by adding these materials in deionized water and heated at 480°C in air. Then, it is ignited within 5 s with a flame temperature of $\sim 1600^\circ\text{C}$. The combustion technique is doping with other elements to decrease the lattice parameter, which reflects the fact that the ions of dopants get trapped at the grain limits. They hinder the development of grain and may cause an increase in strain on the grains that leads to a decrease in lattice parameters. The fuel chosen has a very vital impact on the ZnCu ferrites prepared. The fuels that are preferred in this method are urea and glycine, by which uniform nano ferrites with controlled stoichiometry are obtained.

3.2 Spectroscopic characterization

The characterizations of ZnCu ferrites are studied with an X-ray diffractometer, scanning electron microscopy [74–76]. The magnetic properties of the ferrites are studied by vibrating sample magnetometer (VSM), magnetization hysteresis ($M - H$) loops [77], and electron spin resonance (ESR) hysteresis loop measurements. The X-ray investigation is carried with an X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Many techniques are used to determine the shape, size, and morphology of magnetic nanoparticles such as XRD, SEM, TEM, HRTEM (High-resolution transmission electron microscopy), and FESEM (Field emission scanning electron microscopy). By using HRTEM we can get information about shape, size, crystallinity, and lattice spacing. XRD is used to determine the size by using the Scherrer equation. However, SEM is effective because the size of very small magnetic nanoparticles is determined.

3.3 XRD analysis

The crystalline structure of the Zinc copper ferrite as prepared and annealed at 500°C and 600°C are shown in **Figure 1**. All the diffraction peaks can be registered to the standard Zinc copper ferrite with the cubic spinel structure and the reflection peaks match adequately with standard data (JCPDS 82–1042). This indicates the synthesized nanoparticles have an $\text{Fd}3\text{m}$ space group and indicating a high degree of purity. The average crystallite sizes, D , are calculated from the (311) peaks through Scherrer's formula around 32 nm. It is observed that the sample $\text{Zn}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ crystallized in cubic structure and the lattice parameter is found to be $8.355 \text{ \AA}$, which is less than the values reported for bulk compounds [78]. The crystallite size of ferrite nanoparticles is in the range of 2.3–11.8 nm and the average crystallite size and lattice constant were found to be 6.52 nm and $8.443 \text{ \AA}$

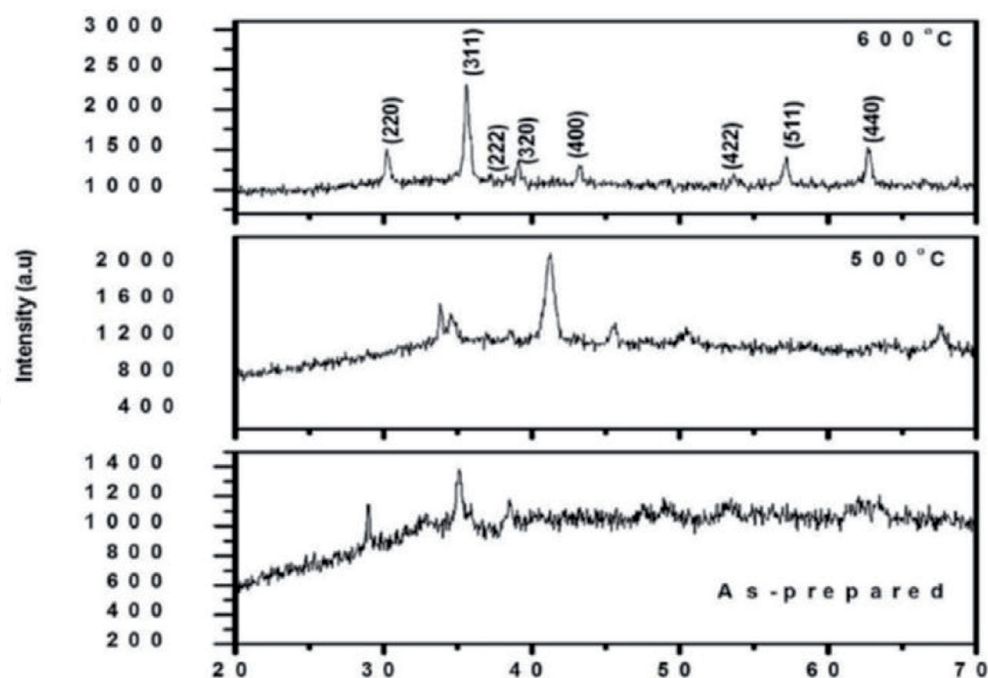


Figure 1.
XRD patterns of zinc copper ferrite nanostructures as prepared, annealed at 500°C, and 600°C.

respectively. Thomas Abo Atia et al. [79] studied the effect of sintering temperature and observed that the average crystallite size was found to increase with an increase in sintering temperature i.e. from 35 nm to 45 nm. Shwetambaram et al. [80]. Crystallite size was calculated and found to be of 7.74, 10.80, 11.58, 12 nm for $x = 0.00, 0.25, 0.50, 0.75$ respectively. Anuj Jain et al. [81] observed that the crystallite size of the composite ferrites increases on increasing the Cu concentration. This is due to the decrement in the densities of nucleation centers in the doped samples which result in the formation of larger crystallite size. S B Kale et al. [82]. The value of crystallite size was 24.17 nm indicates the nanocrystalline nature of the prepared samples. A. Subha et al. [83] observed from grain size calculated using Scherrer's formula applied to the most intense peak shows similar grain size was 30 nm. A. Tony Dhiwahara et al. [84] have indicated in the XRD patterns, the linear change in peak width was reflected in a linear decrease in crystallite size from 19.37 to 15.21 nm with an increase in Zn content in the host sublattice of CuFe_2O_4 . This is mainly because of the replacement of smaller Cu^{2+} ions ($0.72 \text{ \AA}$) by larger Zn^{2+} ions ($0.74 \text{ \AA}$) [85, 86]. In addition, as the ionic radius of Zn^{2+} is larger than the ionic radius of Cu^{2+} , the Zn^{2+} substitution leads to a larger expansion of the lattice. Consequently, the lattice parameter increases more when compared to the Cu^{2+} substitution in the synthesized particles. Since ionic radius of Fe^{2+} ($0.74 \text{ \AA}$) ion is larger than Fe^{3+} ion ($0.64 \text{ \AA}$), the lattice constant increases [87]. Nonmagnetic transition metal ions Zn^{2+} and Cu^{2+} ion prefer octahedral sites whereas Fe^{3+} ions prefer both tetrahedral and octahedral sites. The characteristics peaks correlate with the ferrite particles and show the phase group $\text{Fd}3\text{m}$ and spinel structure having a single phase. Hence, it is concluded that the ZnCu ferrites have a single-phase spinel cubic structure with an $\text{Fd}3\text{m}$ phase group. However, some deviation in the structure can be observed because of doping.

3.4 Morphological structure

Various techniques such as TEM, and SEM, etc. are used to investigate the morphological structure of the ferrite nanoparticles. TEM is preferred because

of its resolution. From the typical SEM analysis, morphological characteristics of Zinc copper ferrite nanoparticles annealed at 600°C are shown in **Figure 2(a)**. They show the formation of multigrain agglomerations consisting of fine crystallites with irregular shapes and sizes. Ferrite powders possessed a coarse structure with crystalline microstructure with an average grain size homogeneous is about 50 μm obtained from SEM images. This is larger than the size of nanocrystals calculated using the XRD measurements, which helps to understand that the grains are formed by aggregation of several nanocrystals. The samples are irregular shapes and sizes, and the cohesion of grains is due to the magnetic attraction. A drastic difference in microstructure of the annealed at 600°C products indicated that the substitution of metal ions like Zn, and Cu on the surface of this microstructure.

EDX analysis confirms the stoichiometric proportion of Zinc copper ferrite nanoparticles annealed at 600°C and also the percentage proportion of the constituent elements is shown in **Figure 2(b)**. The elemental weight proportion percentage is presented in the tables of weight and atomic percentage proportions, the constituent elemental proportion, and the ratios are in agreement with the expected elemental proportion and the oxygen (O) and iron (Fe) being with the highest peaks in all of the samples [88]. Typical EDX analysis reveals the existence of elements of Zn, Cu, Fe, and O. As portrayed in **Figure 3(a)**, HRTEM micrographs also confirm the particle size of ZnCu ferrite nanoparticles annealed at 600°C. The average crystallite size is around 8.38 nm. HRTEM analysis reveals that the particles are nearly spherical. The average crystallite size estimated from the HRTEM image falls in line with the observed values from powder XRD results. From **Figure 3(b)**, the HRTEM image of individual Zinc copper ferrite nanocrystal indicates that the interplanar distance is 0.26. In the SAED (**Figure 3(c)**) image of annealed at 600°C Zinc copper ferrite nanoparticles, the diffraction rings coincide with standards powder XRD diffraction data that confirms good crystallinity. The observed crystallographic d values of 2.52 Å correspond to the lattice space of the (311) plane of the Zinc copper ferrite system. The observed crystallographic d values agree well with those obtained from powder XRD analysis.

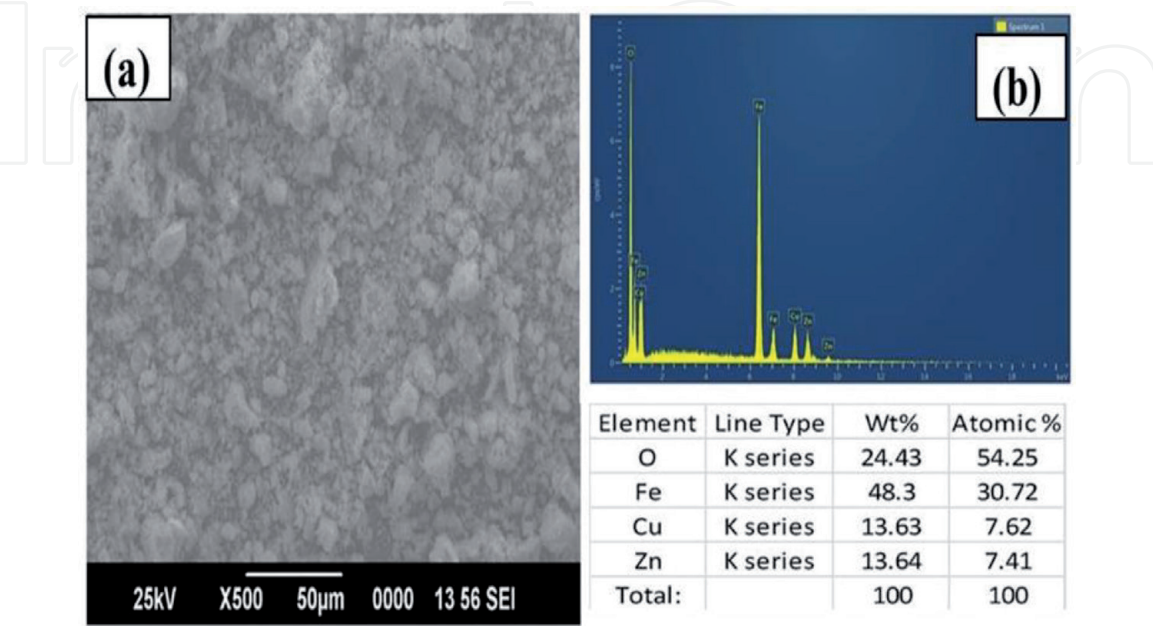


Figure 2. Images of zinc copper ferrite nanostructures annealed at 600°C (a) SEM (b) EDX analysis.

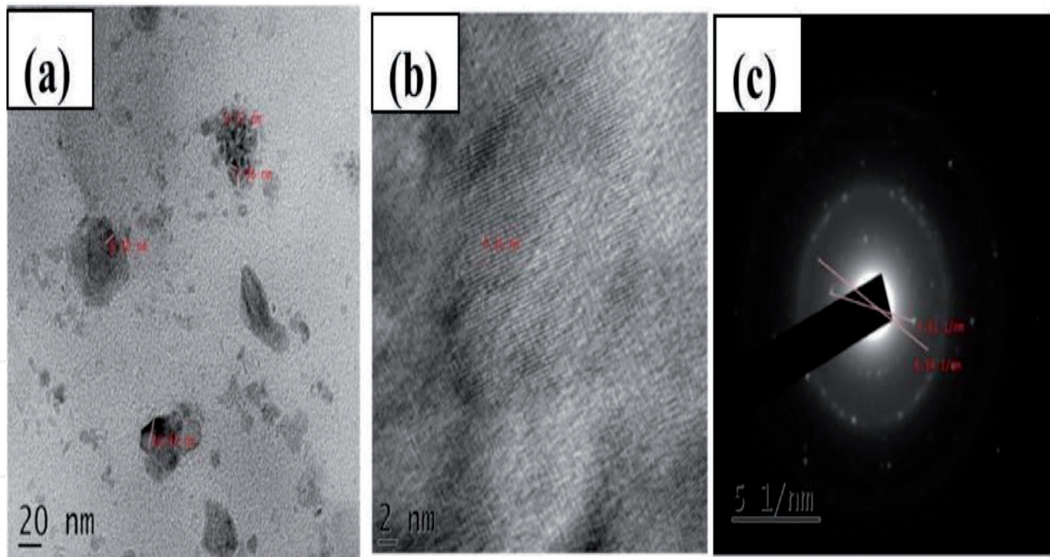


Figure 3.
Image of zinc copper ferrites nanostructures annealed at 600°C, (a) HRTEM (b) inter.

3.5 FT-IR analysis

FT-IR stands for Fourier transform Infrared, the method that is used for infrared spectroscopy. Some of the IR radiation is passed through a sample is absorbed by the sample and few are transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a fingerprint of the sample. **Figure 4** shows the typical FT-IR spectra of Zinc copper ferrite nanostructures recorded between 4000 and 400 cm^{-1} . In the range of 1000–400 cm^{-1} , two main absorption bands of ferrite are appearing. The absorption band $\nu_1 = 580 \text{ cm}^{-1}$ is assigned to the stretching vibration of tetrahedral complexes ($\text{Fe}^{3+}\text{-O}^{2-}$), and the absorption band $\nu_2 = 400 \text{ cm}^{-1}$ is attributed to the octahedral complexes ($\text{Fe}^{3+}\text{-O}^{2-}$). The peak intensity of ν_1 decreases with increasing Cu^{2+} contents, while the position band is shifted to lower frequencies. Synchronously, the intensity and position of ν_2 changed

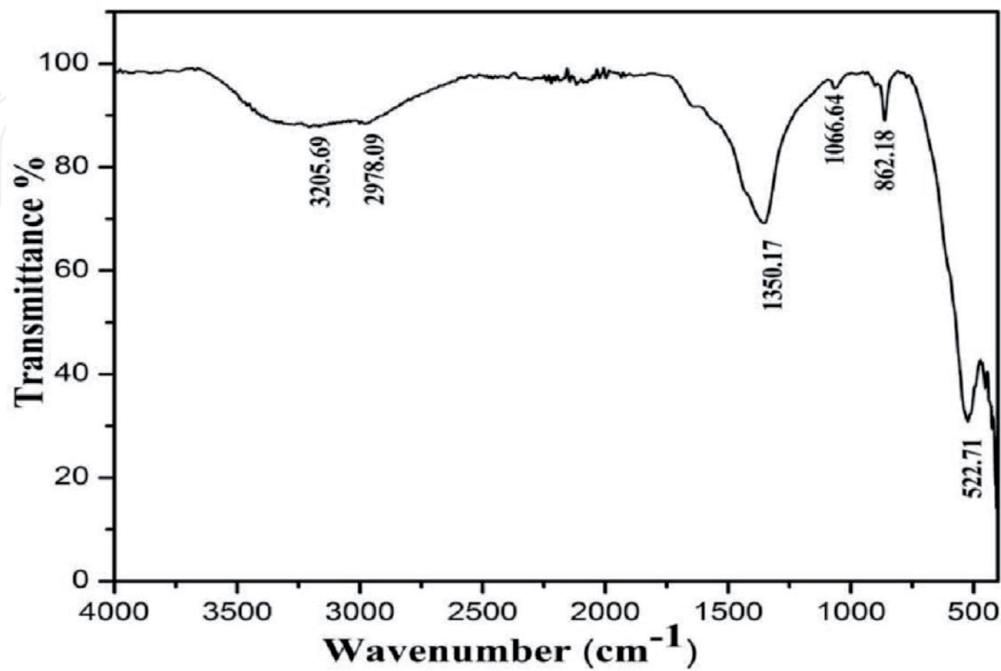


Figure 4.
FT-IR spectra of zinc copper ferrite nanostructures annealed sample at 600°C.

slightly with x . Similar results are observed in Zinc copper ferrite nanostructures prepared by the sol-gel combustion method [89, 90]. The difference in band position of ν_1 and ν_2 can be related to the difference in Fe^{3+} - O^2 bond lengths at A sites and B sites. It was found that the Fe-O distance at A sites (1.89 Å) is smaller than that of the B sites (2.03 Å) [91, 92]. When Zn^{2+} ions are replaced by Cu^{2+} ions, due to charge imbalance some Fe^{3+} ions shift from A sites to B sites, making the Fe^{3+} - O^2 stretching vibration greater in the B domain. So the decrease in peak intensity of ν_1 with increasing Cu^{2+} content is mainly attributed to the change in Fe^{3+} - O^2 bands.

3.6 Magnetic properties

The most effective technique for analyzing the magnetic properties of ferrite nanoparticles are VSM (vibrating sample magnetometer), magnetization hysteresis ($M - H$) loop. One can find saturation magnetization, remanent magnetization, and coercivity by using these characterization techniques. The interior of the magnetic substance is normally divided into several domains, as the external magnetic field increases the domain walls may move and the magnetic field rotates within domains, resulting in a single-domain state. The magnetization saturation is attained if the magnetization axis and the external magnetic field direction are similar. The spontaneous magnetization (M_s) was obtained by extrapolating the high-field part of the loop to the zero applied field [93–97]. A similar variation of magnetization of ZnCu ferrite with the increase in Zn²⁺ concentration up to a particular x value has been reported in the literature [98–100]. Najmoddin et al. [101] observed the highest M_s value of 52 emu/g at room temperature for $x = 0.25$ in ZnCu nanoferrites prepared by wet chemical method. Retentivity is the value of magnetization that is retained in the absence of an induced magnetic field. Coercivity is defined as the caliber of a ferromagnetic material to withstand an external magnetic field without demagnetizing it. In the case of a ferromagnetic material, it is defined as the intensity of the applied magnetic field that is required to reduce the magnetization to zero after the saturation state. The materials which have high coercivity are called hard materials and one with a low magnitude are soft materials. Hard materials are preferred for making permanent magnets whereas soft materials are used for making transformers, inductor cores, and microwave devices.

Figure 5 shows a typical hysteresis loop of all the Zinc copper ferrite nanostructures compositions which are annealed at 600°C. By using a vibrating sample magnetometer, the measurements of magnetization for all the compositions were carried out under the applied magnetic field of range ± 10 k Oe at room temperature. It is observed that the magnetic properties such as saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) values are closer to the values inscribed in the literature. [102–106]. The structure of spinel ferrite is ferrimagnetic, the magnetic moments of A and B sites are coupled antiparallel to each other. Since there are doubly filled B sites, the net magnetic moment is the difference between the two sites. The magnetization behavior of spinel ferrite can be understood in Neel's model [107, 108]. The composition of Zinc copper ferrite nanostructures and cation distribution among the A and B sites will to a large degree, influence the magnetic properties of samples. According to this, in any ferrite, the magnetic order of tetrahedral clusters (A-site) and octahedral clusters (B-site) was found to be anti-parallel to each other. In this, the A-A and B-B superexchange interaction was predominated by the A-B superexchange interaction. According to Neel's model, the net magnetic moment of the composition per formula is expressed as:

$$\mu_B = M_B(x) - M_A(x), \quad (1)$$

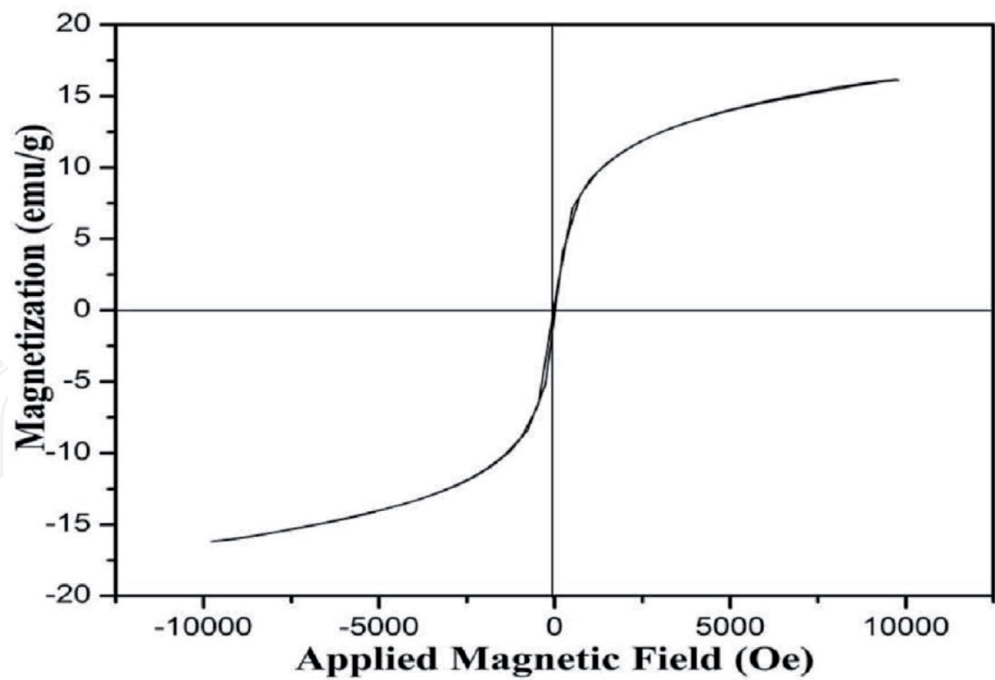


Figure 5.
Magnetic hysteresis loops for zinc copper ferrite nanostructures annealed sample at 600°C.

where M_B and M_A are the magnetic moments of B and A sublattices respectively. The squareness ratio or remnant ratio (M_r/M_s) of a material is one of the important characteristics which depends on its anisotropy. The values of the squareness ratio represent the random arrangement of uniaxial particles along with the cubic magnetocrystalline anisotropy [109, 110]. In the study, the squareness ratio of pure $ZnCuFe_2O_4$ is 0.54, at room temperature. And it has been observed from the literature that the squareness, indicates the presence of non-interacting single domain particles with cubic anisotropy in the respective compositions [111].

The values of Bohr Magneton (μ_B) of these samples were also evaluated by using the following Equation.

$$\mu_B = \frac{M_s M_w}{5585}$$

Where M_w is the molecular weight of the sample and M_s is saturation magnetization.

$5585 = \beta \times N$ [β is Conversion factor (9.27×10^{-21}); N is Avogadro's number].

It is observed that the value of Bohr Magneton is 1.56. One can adapt the composition of ferrite materials by squareness ratio (S) for the development of new electro-magnetic materials and as per the need of the hour [112]. In the present work, the variation in the magnetic properties of Zinc copper ferrite nanostructures is obtained.

4. Photocatalytic degradation

The magnetic material $ZnCuFe_2O_4$ with the spinel structure has been proven effective in the application of dye removal. The visible light exposes, excellent photochemical stability. $ZnCuFe_2O_4$ has grabbed massive attention in the conversion

of solar energy and photochemical hydrogen production from water. Also, the $\text{ZnCuFe}_2\text{O}_4$ magnetic particles possessed intrinsic peroxidase-like activity, which could react with H_2O_2 to produce $\bullet\text{OH}$. Zinc Copper ferrite is one of the most important ferrites. $\text{ZnCuFe}_2\text{O}_4$ nanoparticles were found to be photo-sensitive in the visible light region (1.92 eV) with exceptional photochemical stability which paves way for them to act as gas sensors and photocatalysts [113, 114]. Photooxidation and photoreduction refer to the initiation of oxidation and reduction reactions by light energy. When irradiated with light energy, an electron (e^-) is excited from the valence band (VB) to the conduction band (CB) of the photocatalyst, leaving a photogenerated hole (h^+). Photogenerated electron and holes are capable of oxidizing/reducing adsorbed substrates. The $\text{ZnCuFe}_2\text{O}_4$ NPs promote a photocatalytic reaction by serving as agents for the charge transfer between two adsorbed molecules. The charge transfer at the semiconductor–electrolyte interface is followed by bandgap excitation of a semiconductor nanoparticle. At the later stage, the nanoparticle quenches the excited state by accepting an electron, either transferring the charge to another substrate or generating photocurrent [115]. In both cases, the sensitivity of the semiconductor is retained which describes it as photocatalytic.

The photo-degradation phenomenon of methylene blue by Zinc copper ferrite nanocrystal is evaluated and the observed absorption spectra are presented in **Figure 6(a)**. It is clearly shown in the figure that the characteristic absorption

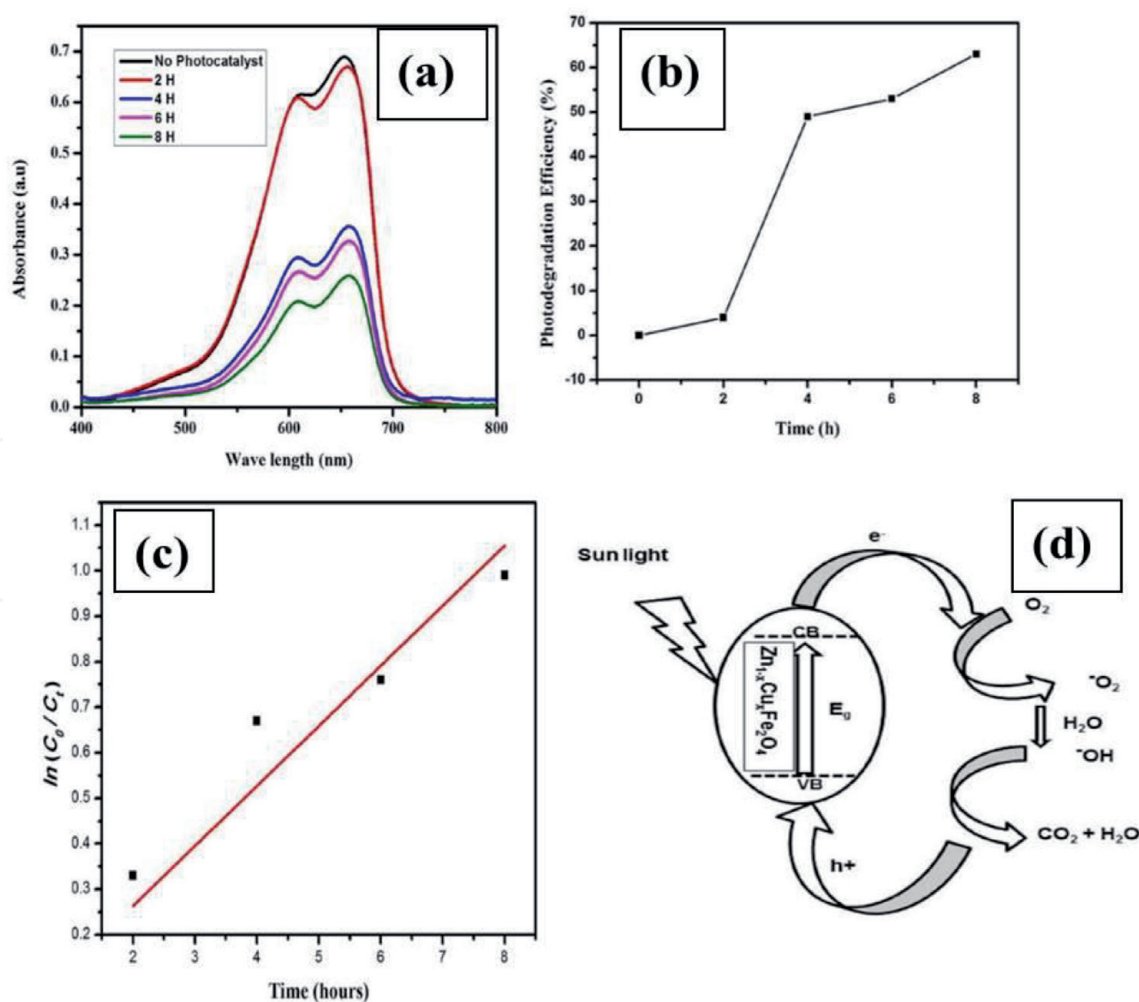


Figure 6. Zinc copper ferrite annealed at 600°C under UV-light irradiation. (a) Absorption of MB solution during the photo-degradation (b) photo-degradation percentage (c) plots of $\ln[C_0/C_t]$ versus irradiation time (d) photocatalytic mechanism of MB in the catalyst.

peak of the methylene blue (MB) at about 664 nm decay gradually with an enhanced exposure time of 8 hours and almost disappears after the irradiation time. This indicates that the MB dye has almost degraded. The photocatalytic performance of the NPs is observed by plotted (C/Co) as a function of time for MB dye and the same is shown in **Figure 6(b)**. The presence of Zinc copper ferrite nanocrystal emphasizes the effective photo-degradation activity for MB, and no degradation of dye molecules was observed in the darkness. However, the Zinc copper ferrite sample exhibited 65% photodegradation. The variation of MB photo-degradation on the crystallite size of Zinc copper ferrite nanocrystals is shown in **Figure 6(c)**. Further, it reveals that the degradation percentage of MB and their kinetics [116, 117]. Photocatalytic reaction mechanisms for oxidation of MB dye by Zinc copper ferrite are presented in **Figure 6(d)**. Photocatalytic activities have been proved to advance by Zinc copper ferrite and it can be ascribed from the photo absorption spreading even up to the visible region, minimizing the electron-hole recombination rate.

4.1 ZnCu ferrites for ongoing COVID-19 pandemics

Nanomaterials are making a global impact on the health system and socio-economic progress. Nanoparticles of ZnCu have unique physical and chemical features that can be coupled with the development of potential therapeutic drugs, nanomaterial-based antiviral sprays, anti-viral surface coatings, and drug delivery. The study emphasizes the choice of synthesis method which decides the size and charges tunability properties to the ZnCu ferrites. The size tunability ensures that a large amount of drug can be fused into anatomically privileged sites of the virus, while charge tunability would facilitate the entry of the drug into charged parts of the virus. In addition, biosensors for the early detection of viral strains such as the COVID-19 can also be developed with ZnCu ferrites. For instance, ZnCu ferrites can be used to develop Giant magneto resistance-based sensors which have been applied in virus detection, earlier [114].

5. Outlook

The synthesis of ZnCu NPs among the soft ferrites with high saturation magnetization, low retentivity, low coercivity, high initial permeability, narrow size distribution, attracted scholars towards the fabrication of these ferrites. Co-precipitation is the most suitable strategy to obtain fine crystalline size among all the techniques. The XRD pattern of the ZnCu ferrites has characteristic peaks, reveals the cubic spinel phase having an Fd3m phase group. The shape of the prepared ferrite is nearly spherical but some distortion may be observed after doping. FTIR spectra confirmed the spinel phase of the ferrite nanoparticles having tetrahedral and octahedral sites. ZnCu ferrites have a lot of applications in the field of biomedicine, electronics, and for making ferrofluids, etc. To enhance the application of ZnCu ferrite nanoparticles, continuous and effective studies are required. The electrical and magnetic properties of ZnCu ferrites can be improved by doping with other functional metals such as cobalt, zinc, copper, and can be tested for agricultural and electrical applications. The nanoparticles during the pandemic outbreaks, like COVID-19, can play a significant role in the development of high contrast imaging dyes for viral strains in body fluids. ZnCuFe can also be preferred for developing nanomaterial-based medicines and therapeutics to serve the human community.

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