Controllable Synthesis and Characterization of Cu-CoZnFe$_2$O$_4$ Nano Ferrites by Auto-combustion Route

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ABSTRACT

A detailed investigation of the effect of the preparation method on the structural, thermal and morphology Cu-Co ferrite nanoparticles prepared by the auto-combustion method. The resulting ferrites were calcined at 450 ℃ and 750 ℃. Sharper X-ray diffraction (XRD) peaks were observed for the samples calcined at 750 ℃, indicating greater crystallinity of the samples calcined at higher temperatures. Average crystallite sizes fell in the ranges of 30.4–42.1 nm for the samples calcined at 450 ℃ and 750 ℃, respectively. Agglomeration of particles was observed in the scanning electron microscopy (SEM) images. Cumulative acidity decreased for the samples calcined at higher temperatures. The results underline the effect of preparation conditions on the morphology, crystallite size, and magnetic properties of nano ferrites.

Keywords: XRD, DSC, TGA, SEM

I. INTRODUCTION

Nanotechnology, shortened to "nanotech", is the study of the controlling of matter on an atomic and molecular scale. Generally, nanotechnology deals with structures of the size 100 nanometers or smaller in at least one dimension, and involves developing materials or devices within that size. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on the atomic scale.

Nanotechnology has the potential to create many new materials and devices with a vast range of applications, such as in medicine, electronics and energy production. On the other hand, nanotechnology raises many of the same issues as with any introduction of new technology, including concerns about the toxicity and environmental impact of nanomaterials and their potential effects on global economics [1]. Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); stable materials turn combustible (aluminium); insoluble materials become soluble (gold). A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale.

Ferrites, such as spinel ferrite, have a crystal structure with two interstitial sites - tetrahedral and octahedral - that can support a variety of cations. This allows for a wide range of characteristics in ferrites as other divalent metal ions can be substituted for ferrites. Previous literature has indicated that substituting Al^{3+} in cobalt ferrite nanoparticles can alter their electromagnetic characteristics, making them a potential candidate for microwave and power devices applications. However, substituting Zn in $MgFe_2O_4$ can increase resistivity while decreasing magnetic properties. Semiconducting behavior becomes a trend after Cr^{3+} substitution. Substituting Cr^{3+} ions in the nickel-zinc ferrite system can also increase resistivity, making the prepared samples suitable for higher frequency ranging systems. Ferrites can also improve the activation energy and thermal decomposition of propellants and can be easily separated using an external magnet [24]. To synthesize ferrite nanoparticles, various methods such as sol-gel, hydrothermal, and coprecipitation are utilized. This article reports on the effect of cobalt copper zinc ferrite (Co-$CuZnFe_2$O4) using a low-cost sol-gel method.

II. MATERIALS AND METHODS

All the chemicals used were of analytical grade without further purification and available from commercial sources: cobalt (II) nitrate hexahydrate [$Co\text{-}(NO_3)_2.6H_2O$, 99%], copper (II) nitrate trihydrate [$Cu\text{- }(NO_3)_2.3H_2O$, 95%], zinc (II) nitrate hexahydrate [$Zn\text{- }(NO_3)_2.6H_2O$, 99%], ferric (III) nitrate nonahydrate [$Fe\text{- }(NO_3)_3.9H_2O$, 98%], and sodium hydroxide (NaOH), Glycine. Laboratory-setup triple distilled water was used as a solvent.

Cobalt copper zinc ferrite powder was synthesized by auto-combustion method in which stoichiometric amounts of nitrates to the fuel are taken as 1:3. Initially all the nitrates were separately into the distilled water and fuel is added to solution. These solutions are mixed using a magnetic stirrer and heated for about 45 min. The solution is continuously stirred till the temperature reaches 80 ^{0}C and pH 7 is maintained by using ammonia of suitable quantity, then the mixed solution is transferred into a heating mantel which is maintained at a temperature of about 100 ^{0}C. Upon heating the solution is turned into dried gel. The dried gel undergoes auto-combustion and forms foam like structure. Upon cooling the obtained foam is converted into ash and it is poured into mortar and will be grinded to form fine powder. The obtained fine powder is kept under sintered at 600 ^{0}C temperature of about 6 hours using muffle furnace. Finally the Cobalt Copper Zinc Ferrites are obtained.

III. CHARACTERIZATION:

The X-ray diffraction patterns of the synthesized samples were recorded using Panalytical X-Pert Pro MPD instrument. The samples were analyzed in the 2θ range of 10-80°, with a scanning speed of 5°/min and step size of 0.02°. The morphological analysis of the synthesized samples were performed using the FESEM CARL ZEISS instrument. This microscope is equipped with a field emission gun, operating with accelerating voltage variable from 0.5 to 30 kV, with 2 nm resolution. Thermal properties of the prepared samples were carried out using TGA/DTA.

A. X-Ray Diffraction Studies on as prepared $CuZnFe_2O_4$ and $CoZnFe_2O_4$ Nano Ferrites

Structural analysis of the $CoZnFe_2O_4$ and $CuZnFe_2O_4$ Nano Ferrites samples has been performed using the powder XRD patterns and is presented in Fig. 1 and 2. The XRD peaks (111), (022), (113), (222), (004), (224), (333), and (044) indicate that the prepared sample has a single-phase spinel cubic structure. The other prepared samples have partial formation of secondary hematite phase with spinel-phase cubic structure. In the reported literature, it has been found that the Co-Zn ferrite nanoparticles prepared using a sol gel method and annealed below 600 °C have single-phase [17, 18]. The diffraction peaks have good agreement with standard JCPDS card nos. 52-0277 and 89-0599 corresponding to spinel Co-Zn ferrite and secondary hematite phase, respectively. The peak intensity of secondary hematite phase and it also found that secondary phase diminished at high concentration of cobalt doping. The average crystallite size of all prepared samples has been calculated from full width at half maximum (FWHM) of most prominent peak (113) of XRD patterns using Scherer's equation [19].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the average crystallite size, β is the FWHM of the peak intensity measured in radians, λ = 1.54 Å is the wavelength of X-ray, and θ is Bragg's angle.

It is found that crystallite size (*D)* increases with cobalt doping from 25 to 31 nm. The crystallite size (*D)* obtained at x = 0.5% (28 nm) and x = 0.5% (30 nm) is nearly the same. Also, other calculated structural parameters at x = 0.03 and 0.09 possess approximately the same values by virtue of this small dopant variation. Hence, the calculated crystallite size (*D*). The effect of Co doping on structural parameters includes d spacing (*d)* [20] and lattice constant (*a)* [21] that have been calculated using the following relations:

$$2d \sin \theta = n\lambda$$

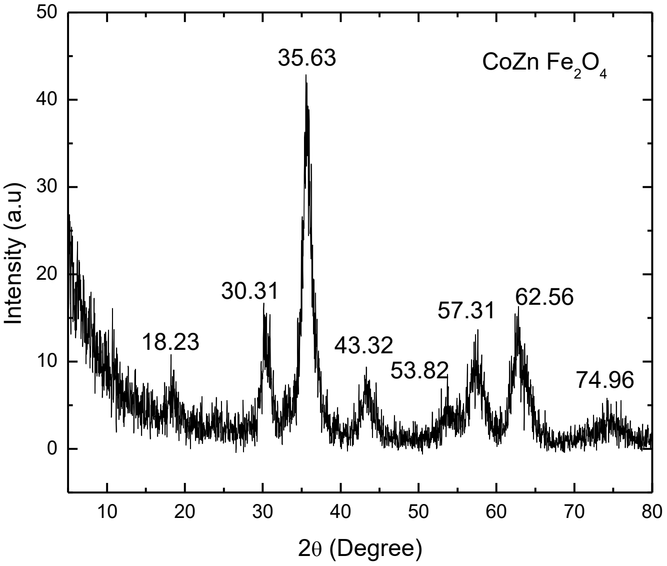

Figure 1: XRD pattern of $CoZnFe_2O_4$ Nanoferrite

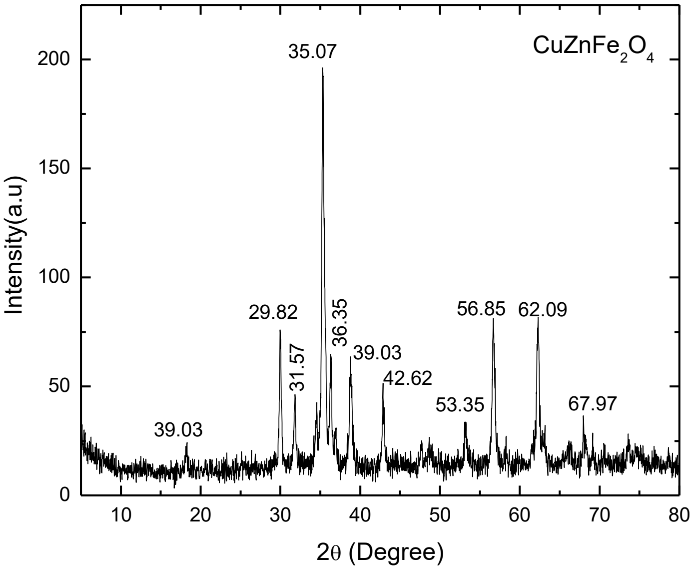

Figure 2: XRD pattern of $CuZnFe_2O_4$ Nanoferrite

B. FESEM Analysis

Figure 3 shows the SEM images of $CuZnFe_2O_4$ and $CoZnFe_2O_4$ Nano Ferrites synthesized powder dried at 90 ^{0}C in vacuum (Fig. 3a) and calcined at 500 ^{o}C for 45 min (Fig. 3b), respectively. In Fig. 3a, it is seen that agglomeration of crystals takes place. Usually, agglomeration is formed by smaller size of crystals. There are vary large number of spherical crystals with much smaller size i.e., nanometer dimensions below 100 nm. This agrees well with XRD pattern where peak broadening appeared for these powder specimens. The fine particles and their agglomerates are clearly seen in the SEM image [31].

However, after the heat treatment at 500 ^{0}C, the crystal size increases and the grain size was measured from SEM micrograph (Fig. 3b). This value is in agreement with the results obtained from XRD data where sharp peaks are the indication of well define crystallization of $CuZnFe_2O_4$ and $CoZnFe_2O_4$ Nano Ferrites. The XRD peaks are very narrow indicating the higher grain size falls beyond the nano-scale region. The effect of heat treatment (500 ^{0}C) on specimens' morphology are very obvious from the low-resolution micrographs, the specimens have small grains (Fig. 2b). The effect of these partial meltings causes dramatic changes in impedance results [22].

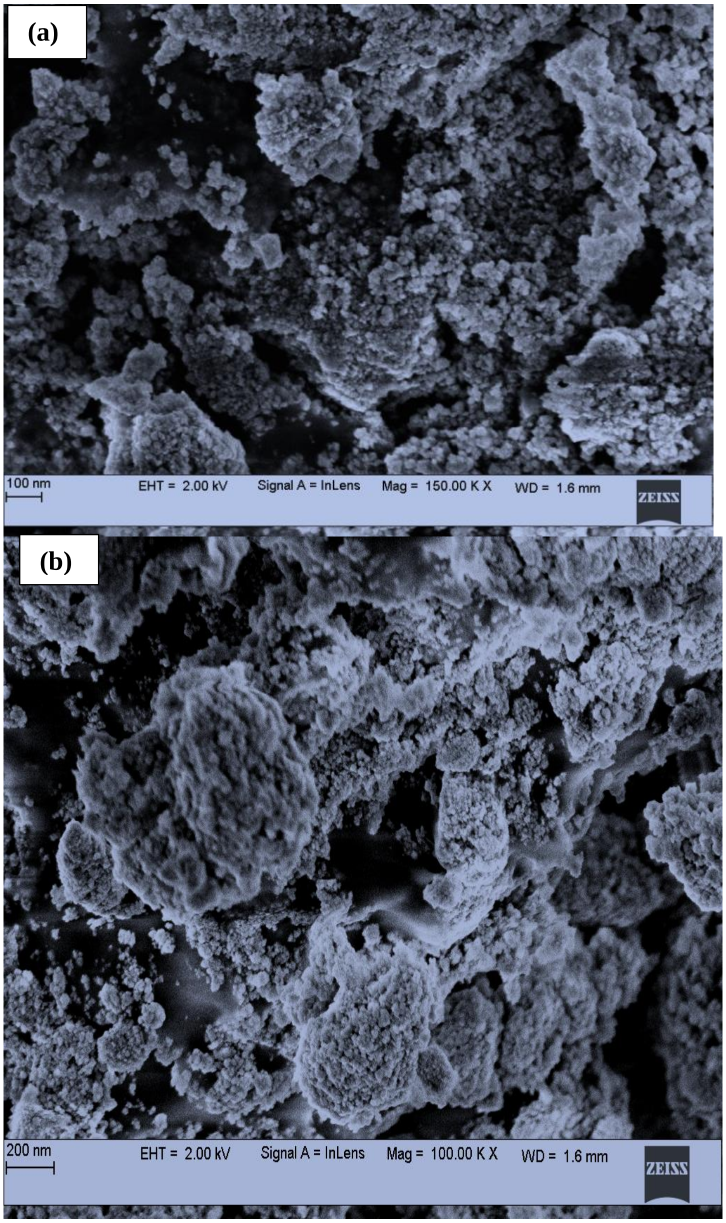

Figure 3: FESEM micrograph of (a) $CuZnFe_2O_4$ and (b)$CoZnFe_2O_4$ sintered at 500 ^{0}C.

C. DSC and DTG Analysis

Figure 4 shows the DSC/TGA curve of $CuCoZnFe_2O_4$ Nano Ferrites. The DSC/DTG curve shows that there were about initial 10% weight loss at lower temperature (less than 100 ^{0}C) due to the vaporization of water in the $CuZnFe_2O_4$ and $CoZnFe_2O_4$ Nano Ferrites. The weight change was not significant and the sample was thermally stable. In the second step there is a weight loss of about 50% in the temperature range 100°C to 450°C, which is ascribed to the degradation of the polymer chains and larger weight loss (about 68%) at the temperature between 500°C to 800°C.

The decomposition temperature of the $CuCoZnFe_2O_4$ Nano Ferrites was found to depend on the amount of $CuCoZnFe_2O_4$ Nano Ferrites present in the composite [13, 14].

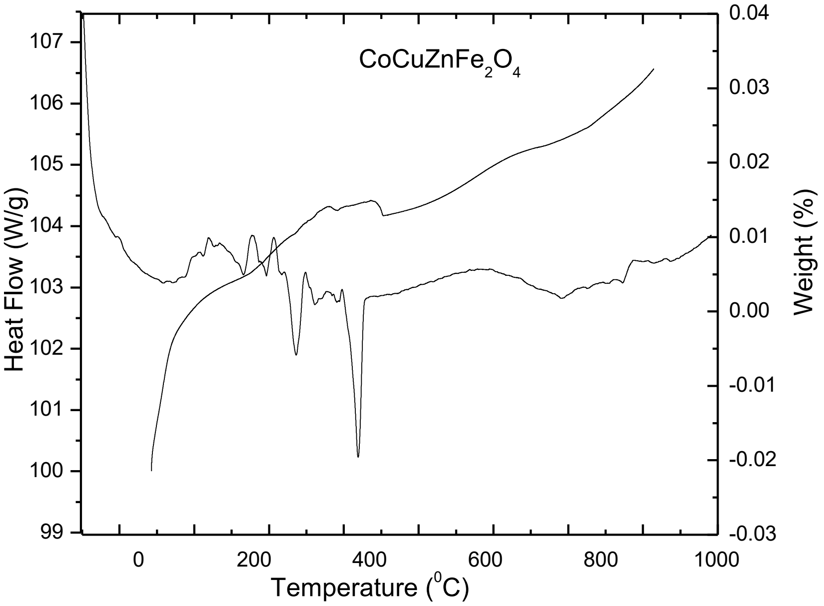

Figure 4. DSC/TGA Spectra of $CoCuZnFe_2O_4$ Nanoferrite.

IV. CONCLUSIONS

The present study demonstrated the structural, chemical and thermal properties of $CuZnFe_2O_4$ and $CoZnFe_2O_4$ Nano Ferrites synthesized using a solution combustion method. Significant results obtained are summarized below:

As-prepared samples were examined by using XRD, FE-SEM and DSC analysis techniques. XRD study revealed that samples have single phase spinel cubic structure. There is partial formation of secondary hematite phase (α-Fe_2O_3) with spinel phase cubic structure of $CuZnFe_2O_4$ and $CoZnFe_2O_4$ Nano Ferrites. The crystallite size (*D*) increases with Co and Cu because of larger ionic radii of Co^{2+} ions as compared to Cu^{2+} ions. The crystallinity of prepared samples increases and has been investigated by FESEM. Thermal stability of the samples was analyzed using TGA.

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