Synthesis of Ce$^{3+}$ doped with Cu-Zn Ferrite Nanoparticles and study of Structural, Morphological Properties

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ABSTRACT

Nanoparticles of Ce$^{3+}$doped Cu$_{0.5}$Zn$_{0.5}$Ce$_x$Fe$_{2-x}$O$_4$ (x = 0.0, 0.025 to 0.10) samples prepared by using sol-gel auto combustion technique. This prepared sample sintering temperature is confirmed by TGA. The prepared samples sintered at 600℃ at 4 hours. The prepared samples phase was confirmed by considering the XRD analysis technique. Structural parameter like lattice, porosity, density, length, etc., was measured with composition x by using XRD. The dopant concentration increases, the lattice constant in increases while crystallite size decreases. The surface morphology was confirmed by scanning electron microscopy (SEM). The Cu, Zn, Ce, Fe and O elements are existence in the composition confirmed by EDAX spectra. The cation distribution revealed that Zn$^{2+}$ion primarily on tetrahedral-A sites, the octahedral-B site shows high preference to copper (II) and Ce (III) ions. Fe (III) ions are constantly distributed on both sites tetrahedral-A and octahedral-B sites. Indication of two vibrational spectra between 400 to 600 cm$^{-1}$ corresponding to the tetrahedral and octahedral sites occurs by the analysis of FT-IR.

Keywords: Cu-Zn ferrite, Ce$^{3+}$ion, Sol-gel method, XRD, SEM, FT-IR.

INTRODUCTION

The wide use in a variety of technologies such as magnetic sensitive storage chip, microwave base systems, electronic generator, nano material-based medicine, drug also other pharmaceutical application gives the opportunity to researcher in synthesis of spinel shape ferrites nanoparticles. The general formula for spinel ferrite nanoparticles is $\text{AB}_2\text{O}_4$ whereas letter A represents divalent like Co, Ni, Fe, Sn, and Cu in (+II) states and B represents trivalent like Fe, Al, La, In, Cr and Ho in (+III) states. Due to their soft magnetic action ferrites is called as soft ferrite. Ferrimagnetic behavior in cubic spinel ferrites cause super exchange (A–O–B) through oxygen anions by tetrahedral and octahedral sub lattices. $\text{MeO.Fe}_2\text{O}_3$ has eight formula units, resulting in a 56-atom arrangement within a single unit cell. Soft ferrites have a cubic structure with 32 oxygen ions. The A and B sublattices are filled...
by these oxygen ions\textsuperscript{7-8}. Various ferrites with minor component substitutes demonstrating to give materials for an assortment of utilizations. Contingent upon the structure and measure of uncommon earth components utilized, adding a modest quantity of uncommon earth particles to a ferrite test changes its electrical, attractive properties. There are two types of rare-earth ions: those with a radius equal to Fe(III) ions and those with a range more noteworthy than Fe\textsuperscript{3+} ions particles\textsuperscript{9}. Owing to their strong ionic radii, the replacement of uncommon earth particles into ferrite brought about the substitution of Ferric ion by uncommon earth particles and decreased solvency in the spinel grid\textsuperscript{10}. Unpaired 4f electrons are found in rare-earth ions. The particles in the fourth shell are secured by the particles in the fifth shell, and the possible field of the encompassing particles has no impact on them\textsuperscript{11}.

The Ce\textsuperscript{3+}-Fe\textsuperscript{3+} cooperation’s show up (3d–4f coupling) when uncommon earth Ce\textsuperscript{3+} particles are subbed, influencing the electrical and attractive properties of spinel ferrites. As uncommon earth particles are substituted into spinel structure, structural distortion occurs; altering the electrical transport properties\textsuperscript{12-13}. The synthesis of ferrites using traditional methods is often limited by factors such as experimentation time, high temperature, grain size and solution PH. Composition, sintering temperature and sintering time can all be used to tailor the properties of ferrites\textsuperscript{14-15}. Exploratory strategies for the amalgamation of ferrite nanoparticles incorporate the two-fold sintering fired strategy\textsuperscript{16}, flash combustion technique\textsuperscript{17}, a sol-gel technique\textsuperscript{18}, electrospinning process\textsuperscript{19}, and micro emulsion technique\textsuperscript{20}. Roman T.\textit{ et al.}, investigated primary changes and magneto-electrical properties of cerium doped copper ferrites during the sintering framework\textsuperscript{21}. Ghosh M.\textit{ et al.}, studies microstructural, magnetic, optical characterizations of Ce\textsuperscript{3+} doped nanocrystalline cobalt–zinc ferrite\textsuperscript{22}. Current project is about synthesis of Cu\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2–x}Ce\textsubscript{x}O\textsubscript{4} (x=0.0,0.025,0.050,0.075,0.10) ferrites synthesized by using the sol-gel auto combustion techniques.

The insightful grade reagent of Copper Nitrate, Zinc nitrate, ferric nitrate, Cerium nitrate and citrus extract were utilized as beginning materials. Metal nitrate broke up in stoichiometric extent in deionized refined water, and afterward the citrus extract changed up to 7, by adding fluid smelling salts, then, at that point, the blended arrangement warmed on the hot plate persistently mixing at 90°C, at last because of auto burning, brown-shaded debris got. The sintering not set in stone from TGA/DTA and arranged powders of all the forerunner tests were sintered at 600°C for 4 hours.

Characterization

Utilizing a Shimadzu SDT Q600 warm analyzer, the dried powder was described utilizing TGA/DSC at a warming pace of 10°C/min in nitrogen (N\textsubscript{2}) air to decide the crystallization temperature. EDAX (energy dispersive X-beam investigation) was utilized to decide the assessed measure of component and stoichiometry in the arrangement The Rikagu Miniflax X-beam Diffractometer was utilized to record the X-beam diffraction (XRD) examples of tests at room temperature utilizing Cu–K radiation. With a checking pace of 2°/min, X-beam diffraction information were gathered in the 200–70° territory. Checking Electron Micrograph (SEM) was utilized to play out the morphological examination. Oxygen location, lattice parameters, and cation distribution were all determined. A Perkin Elmer infrared spectrophotometer was used to measure infrared spectroscopy (IR) in the range of 800–200 cm\textsuperscript{-1}.

RESULT AND DISCUSSION

Thermogravimetric analysis (TGA)

Figure 1 shows the standard TG/DTA bend
of test 0.075. The deficiency of translucent water is seen in the temperature scopes of 120–140°C and 420–470°C, as indicated by the investigation, all things considered. The metal hydroxides are changed over into relating metal oxides, which then, at that point, go through strong state response with the development of nanocrystalline ferrite at temperatures somewhere in the range of 550 and 650°C. As a result, for this sequence, we chose a sintering temperature of 600°C for 4 hours.

**Fig. 1. The typical curve of TGA/DTA of sample x = 0.075**

**Scanning electron microscope and energy dispersive X-ray analysis**

The basic investigation of all examples Cu_{0.5}Zn_{0.5}Fe_{2-x}Ce_xO_4 (x=0.00,0.025,0.05,0.075,0.1) were done by the EDAX strategy as displayed in Fig. 2. The EDAX spectra got from the focal point of Zn substituted Ni Ce ferrite grains demonstrated the presence of an enormous centralization of n inside the energy range of 1.2 keV, 9 keV, and 10 keV, Cu in between 0.9 keV, 8.1 keV and 8.4 keV and Ce was seen between 4.25 keV, 5.8 keV and 6.25 keV whereas Fe was seen between the energy range of 0.7 keV, 6.25 keV, and 7 keV. Fig. 3. The ferrite powder has agglomerated because of the hotness treatment, demonstrating that the pre-arranged examples have a high reactivity. SEM and EDAX of all examples had the very component that is exemplified, which is important.

**X-ray diffraction Study**

The X-beam diffraction (XRD) examples of strengthened Cu_{0.5}Zn_{0.5}Fe_{2-x}Ce_xO_4 (x=0.0,0.025,0.050,0.075,0.10) are shown in Fig. 4. X-beam diffraction tops identified with Bragg's appearance from (220), (311), (400), (422), (511) and (440) planes relate to the standard design of Cu_{0.5}Zn_{0.5}Fe_{2-x}Ce_xO_4 (x=0.0,0.025,0.050,0.075,0.10). The obtained pattern was indexed using JCPDS Card No. 897409 (CuZnFe_2O_4) and uncovers the way that the orchestrated example is of face-focused cubic design with space bunch Fd"m. Also, weak Secondary peaks corresponding to CeO_2 were reflected in the XRD diffractogram shown in Fig. 3. The cubic CeO_2 phase appears because of the bigger ionic radii of cerium ion particle (1.020 Å) contrasted with the ferric ion particles (0.645 Å). The literature writing revealed that the rare earth (RE) components into the spinel lattice cause phase isolation and precipitation of additional phase.
U. B et al., Orient. J. Chem., Vol. 38(1), 37-43 (2022)

The cross-section steady 'a' was controlled by the situation 1:

$$a = d \sqrt{(h^2 + k^2 + l^2)}$$  

Where h, k, l are Miller indices and d is interplanar spacing. The determined upsides of the grid consistent are summed up. It is seen that the grid consistent increments from 8.368 Å to 8.421Å with Ce$^{3+}$ concentration x the upsides of lattice constant 'a' are classified in Table 1. The expansions in lattice constant are because of the distinction in ionic radii, the more modest ionic radii of Fe$^{3+}$(0.645Å) replaced by larger Ce$^{3+}$ion (1.02Å)$^{22}$.

The X-density ($d_x$) of the examples was dictated by condition 2$^{23}$,

$$d_x = \frac{8M}{Na^3}$$  

Where M-atomic mass of the relating synthesis, N-Avogadro's number, and a$^3$- the volume of unit cell. The value of ‘dX’ are introduced in Table 1. It is seen that x-beam densities increment from 5.292 to 5.791 g cm$^{-3}$ with Ce$^{3+}$concentration x, this might be on the grounds that Ce$^{3+}$ has more prominent nuclear weight m (140 g/mol) supplant more modest Fe$^{3+}$ (55.84amu), and its outcome expansions in nuclear load with Ce$^{3+}$ substance$^{24}$.

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The particle bounce length at A (LA) and B-destinations (LB) were determined by formulae 6 and 7;

$$L_A = a \sqrt{\frac{3}{4}}$$  

$$L_B = a \sqrt{\frac{2}{4}}$$  

Utilizing the connection talked about somewhere else$^{22}$, Hopping lengths (LA, LB) between magnetic ions (the distance between the ions) in the tetrahedral (A) and octahedral (B)
The alloyed parameters like octahedral bond and tetrahedral length, tetrahedral edge, shared and unshared octahedral edge (dAXE, dBXE, and dBXE0) still up in the air utilizing oxygen positional boundary 'u' (0.375 Å) and grid boundary 'a',

\[ d_{AXE} = a \sqrt[3]{(u-1/4)} \]  

(8)

\[ d_{BXE} = a \sqrt[3]{(3u^2-(1/4)u+43/64)} \]  

(9)

\[ d_{AXE} = a \sqrt{(2u-0.5)} \]  

(10)

\[ d_{BXE} = a \sqrt{(1-2u)} \]  

(11)

\[ d_{AXE0} = a \sqrt[4]{(4u^2–3u + (11/16))} \]  

(12)

In Cu-Zn ferrite, the variations of alloyed parameters with Ce3+ concentration are shown in Fig. 5. The radii of Ce3+ and Fe3+ ions are related to the alloyed parameters. The composition of Ce3+ in Cu-Zn ferrite raises the alloyed parameters. The dopants used in the doping process, as well as the cation distribution within prepared compositions, cause this increase in edge lengths.

![Fig. 5. Allied parameter of Cu0.5Zn0.5Fe2-xCexO4.](image)

The cation flows were constrained by researching the x-bar diffraction patterns' strength. The saw power extent was diverged from the intentional force extent in this collaboration. Method for Ber inflexible23. Table 2 shows the cation flow of the 600°C examples. The outcomes show that Cu2+ and Ce3+ cations will in general involve octahedral location, while Zn2+ and Fe3+ particles move toward tetrahedral destinations [A]. The ionic reach (rA and rB) for both tetrahedral (A) and octahedral (B) worked with objections submitting to ideal cationic not actually settled using the going with associations21,22. With an increment in Ce3+ replacement in Cu-Zn ferrite, both rA and rB stay steady while rB increments. The increment in rB is because of the substitution of more modest Fe3+ (0.645) particles by bigger Ce3+ (1.02) particles at an octahedral B site, as displayed in Table 2.

![Table 2. shows the upsides of oxygen positional boundaries, and it is found that the worth of 'u' diminishes with the substitution of Ce3+ in Cu-Zn ferrite. The metallic particles in spinel oxide are smaller than the oxygen ions. Spinel lattice value slightly deviated from the actual value of spinel lattice24.](table)
Table 2: Composition x, Cation appropriation, band position ($u_1$, and $u_2$), mean ionic radii (rA and rB), theoretical lattice constant constant($a_0$), Oxygen boundary (u) of Cu$_{0.5}$Zn$_{0.5}$Fe$_{2-x}$Ce$_x$O$_4$

| Compound X | Cation appropriation | Band Position | Mean ionic radii | $a_0$(Å) | u(Å) |
|------------|----------------------|---------------|------------------|---------|-----|
|            | (A) Position Conc.     |               |                  |         |     |
|            | of Zn$^{2+}$ and Fe$^{3+}$ |               |                  |         |     |
|            | [B] Position Conc.     |               |                  |         |     |
|            | of Cu$^{2+}$ = 0.5, Fe$^{3+}$ |               |                  |         |     |
|            | = 0.5                  |               |                  |         |     |
|            | = 1.5, Ce$^{3+}$ = 0.0 to 0.1 |               |                  |         |     |
| 0.0        | (Zn$^{2+}$ and Fe$^{3+}$) |               |                  | 566.41  | 362.45 |
| 0.025      | (Zn$^{2+}$ and Fe$^{3+}$) |               |                  | 570.63  | 367.92 |
| 0.050      | (Zn$^{2+}$ and Fe$^{3+}$) |               |                  | 571.3   | 395.51 |
| 0.075      | (Zn$^{2+}$ and Fe$^{3+}$) |               |                  | 575.17  | 399.64 |
| 0.1        | (Zn$^{2+}$ and Fe$^{3+}$) |               |                  | 627.14  | 418.34 |

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 6 depicts the FT-IR spectral analysis of samples. FT-IR analysis is often used to assign vibrational bands to a specific group in compounds 25-27. There are three retention groups in the scope of 200–800 cm$^{-1}$ in the current example. The absorption bands 1 and 2 in the ranges of 566.41 cm$^{-1}$–627.14 cm$^{-1}$ and 362.45 cm$^{-1}$–418.34 cm$^{-1}$, respectively, were allocated shown in Table 2. The intrinsic vibrations of tetrahedral and octahedral are due to the band 1 and 2 bands, respectively. For the A–B site, the Fe$^{3+}$ ± O$^{2-}$ distance is the most important factor. In Table, the band frequency values are tabulated. 2. Show that the frequency of the bands increases as the Ce$^{3+}$ content rises. The as of now researched ferrite framework Ce$^{3+}$ occupied B-site by supplanting Fe$^{3+}$ ions which influence the band positions28,29.

CONCLUSION

The Cerium ion doped Cu-Zn ferrite nanoparticles of different concentration synthesized by using the sol-gel method and it confirmed by XRD analysis. The XRD pattern of prepared samples revealed the formation of cubic spinel structure. The lattice constant increases in the range (8.364 Å to 8.412 Å) and average crystallite size decreases in the range of (14nm-10nm). The hopping lengths of both sites increases. The allied parameter was increased with increase in Ce-content.

In cation distribution of Zn$^{2+}$ prefer to tetrahedral sites, while Cu$^{2+}$ and Ce$^{3+}$ ions prefer to octahedral sites. Ferric (Fe$^{3+}$) ions occupy both tetrahedral and octahedral sites. EDAX spectra shows all the elements are confirmed. Spinel Structure and distribution of ions between two sites confirmed by IR spectra.

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Conflicts of interest

The present research work had no conflict of interest.

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