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SYNTHESIS AND CHARACTERIZATION OF NANO FERRITES BY CITRATE GEL METHOD

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ABSTRACT

Nano size nickel ferrite, copper ferrite, zinc ferrite, nickel copper ferrite, nickel zinc ferrite and nickel copper zinc ferrite powders have been prepared by citrate gel precursor method and calicinated at 800^{o}C temperature. The resulting powders were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The ferrite powders showed XRD line broadening and sizes of the crystals were calculated 20-65 nm at 800^{o}C temperature. Comparing the size of ferrites by addition of transition metal were discussed.

Key words: Nano ferrite, Citrate gel method.

INTRODUCTION

Ferrospinel compounds are a very important group of magnetic materials due to their extensive use in a wide range of applications from low to high permeability devices including electronics, ferrofluid, magnetic drug delivery microwave devices and high density information storage devices[1-5]. They have the general formula of AFe_2O_4 (where A: Co, Ni etc.) a unit cell contains 32 O-atoms in a cube close packing with 8 T_d (tetrahedral) and 16 O_h (octahedral) occupied sites. Recently, surface mounting devices (SMD) have been rapidly developed using multilayer chip inductors (MLCI). Among the nano magnetic materials, ferrites are of special interest stemming, from their applications for high-density information storage media in[6] and electromagnetic wave absorption[7]. Ferrites in nanometer scale size show many unusual and interesting properties.

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Transition metal ferrites MFe_2O_4 represent an important class of technological materials, due to their remarkable properties which render them suitable for many applications in the next generation of electronics, catalysis and magnetic information storage. Although ferrites are traditionally prepared in bulk, the minimization of magnetic and electronic devices has demanded advanced materials with new forms and shapes, nano particles or thin films. Some spinel ferrites, MFe_2O_4 (M = Cu, Cd and Zn), having submicron grain sizes (0.1-0.7 μm) were prepared by sol gel self combustion and their sensing properties to reducing gases were investigated[8]. The sensitivities of the three ferrites to reducing gases like acetone, ethanol and LPG were been compared. It was revealed that $CuFe_2O_4$ is the most sensitive to LPG and $ZnFe_2O_4$ is sensitive and selective to ethanol. Zinc containing binary oxides are active catalysts for methane combustion[9]. Nickel ferrite ($NiFe_2O_4$) is an inverse spinal in which half of the ferric ions fill the tetrahedral sites (A-sites) and the rest occupy the octahedral sites (B-sites). Mg-Cu-Zn ferrite was prepared[10] through a wet synthetic method by self-combustion reaction directly from a citrate precursor. The synthesized powders were sintered at 750°C for 2 h. XRD patterns and FTIR spectra confirm the formation of single phase Mg-Cu-Zn ferrite after combustion. Among the Ferro spinels, the inverse type is particularly interesting due to its high magneto crystalline anisotropy, high saturation magnetization, and unique magnetic structure. Nickel ferrite ($NiFe_2O_4$) with an inverse spinel structure shows ferri magnetism that originates from magnetic moment of anti-parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} ions at octahedral sites[11]. Jahanbin and Hashim[12] presented nano crystalline nickel zinc ferrite ($Ni_{0.8}Zn_{0.2}Fe_20_4$) by co-precipitation technique. The dried powder has passed into the torrid and pellet forms, then sintering them at sintering temperatures of 1100°, 1200° and 1300°C. The samples were characterized by X-ray diffraction, initial permeability and relative loss factor. The initial permeability values were in the range of 10-17 due to the small particle size. The relative loss factor was in the order 10^{-3} –10^{-5} in the frequency range of 1 MH_Z to 1 GH_Z. In our laboratory work on (Mn-Zn and Ni-Zn) ferrites by two different methods viz, co-precipitation method and ball milling method[13] and Ni-Zn ferrites by co-precipitation method and sol gel method have been studied and the results are published. In this paper, we report citrate precursor synthesis of nano nickel ferrite, copper ferrite, zinc ferrite, nickel copper ferrite, nickel zinc ferrite, nickel copper zinc ferrite and characterized by XRD, SEM.

EXPERIMENTAL

Materials

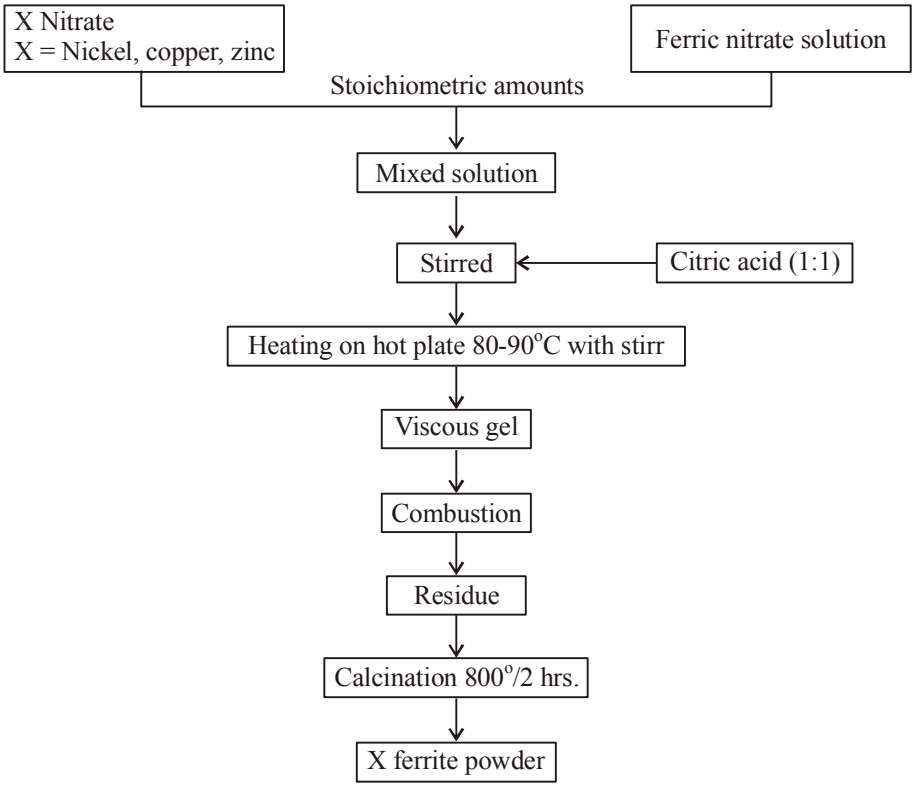
All the chemicals used in this study are of analytical reagent grade. Nickel nitrate, copper nitrate, zinc nitrate, ferric nitrate, citric acid and ammonia produced from M/s. Merck and BDH (Analar) have been used as received.

Synthesis: In this paper we report the spinal ferrites of composition MFe_2O_4 (M = Ni, Cu and Zn), $Ni_{0.5}$ $Cu_{0.5}$ Fe_2O_4, $Ni_{0.5}$ $Zn_{0.5}$ Fe_2O_4 and $Ni_{0.5}$ $Cu_{0.25}$ $Zn_{0.25}$ Fe_2O_4 and characterized by XRD and SEM.

Synthesis and characterization of nickel ferrite ($NiFe_2O_4$), copper ferrite ($CuFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$)

Citrate gel mehtod

The synthesis was carriedout using standard process. The reagents were obtained from commercial sources and used after purification. The polycrystalline nickel ferrite, copper ferrite, zinc ferrites was synthesized by citrate precursor method and procedure was presented in Scheme I.



Scheme I

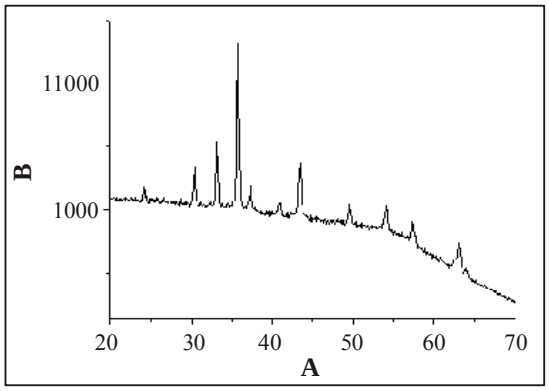
The sizes of particles are calculated by X-ray diffraction (XRD) patterns and scanning electron microscope (SEM) and presented in Fig. 1 and Fig. 2.

Synthesis of $Ni_{0.5}$ $Cu_{0.5}$ Fe_2O_4, $Ni_{0.5}$ $Zn_{0.5}$ Fe_2O_4 and $Ni_{0.5}$ $Cu_{0.25}$ $Zn_{0.25}$ Fe_2O_4

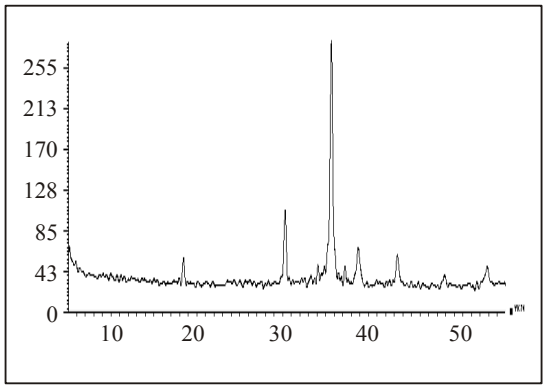
The polycrystalline nickel copper ferrites, nickel zinc ferrites and nickel copper zinc ferrites was synthesized by non-conventional citrate precursor method. Stoichiometric amounts of cationic salts were weighed separately and dissolved in minimum amount of deionised water to make clear solution, they are mixed and stirred for 1 hr to get a homogenous solution. Citric acid solution is prepared in deionised water and 1 : 1 molar ratio of metal nitrates to citric acid solutions were mixed and stirred. A small amount of NH_3 was added to the solution to adjust the pH value at 7.0. The solution was heated, stirred continuously to transform into a highly viscous gel. The gel was heated gradually up to 90°C, to evolve reddish brown color gases and finally the dried gel was finally burnt-out completely to form loose powders. These particles are further purified by acetone and toluene to get dark brown precipitate or black precipitate. Finely powdered materials were annealed at 800°C temperatures for further crystallization. The sizes of particles are were calculated by X-ray diffraction patterns and scanning electron micrograph studies.

RESULTS AND DISCUSSION

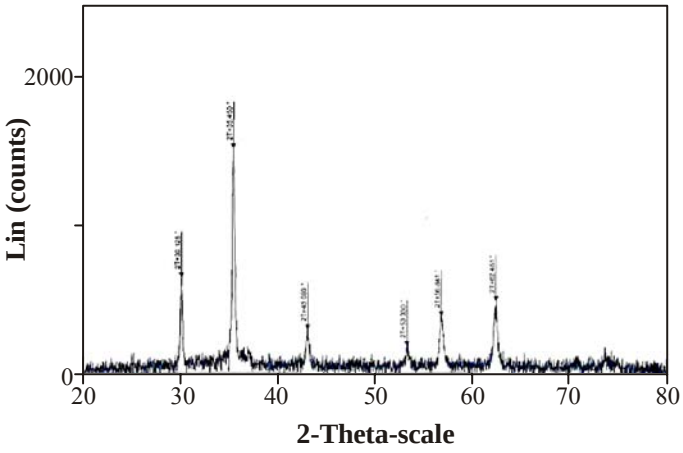
The XRD peaks in Fig. 1 represent that the nickel ferrites, copper ferrites and zinc ferrites in which spinal crystals are formed during the crystallization (at 800°C). From the XRD data, Ni ferrite particle size are calculated by using Sheerer formula and the particle size are calculated as 27 nm, copper ferrite at 20 nm and zinc ferrite around 30-31 nm. This shows that the synthesized powder has nano size crystalinity. Further the samples exhibit (active single phase) spinal crystal structure, with increase in the crystalinity. From Scanning electron microscope (SEM) (Fig. 2), studies are carried out on the ceramic samples. For nickel ferrites, SEM micrograph produced number of pores with smaller lump size.



XRD Patterns of $NiFe_2O_4$ at 800°C

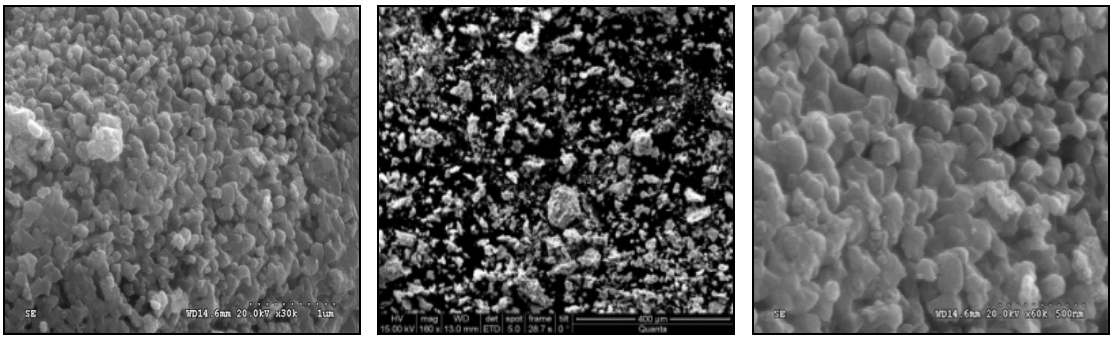


XRD Patterns of $CuFe_2O_4$ at 800°C



XRD Patterns of $ZnFe_2O_4$ at 800°C

Fig. 1: XRD Patterns of ferrites at 800°C



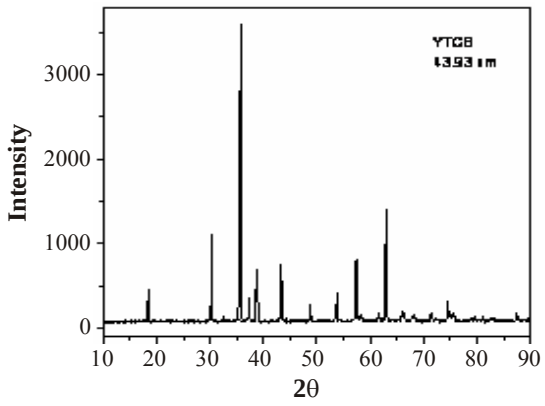
SEM image of $NiFe_2O_4$(800°) **SEM image of $CuFe_2O_4$(800°)** **SEM image of $ZnFe_2O_4$(800°)**

Fig. 2: SEM Images of ferrites at 800°C

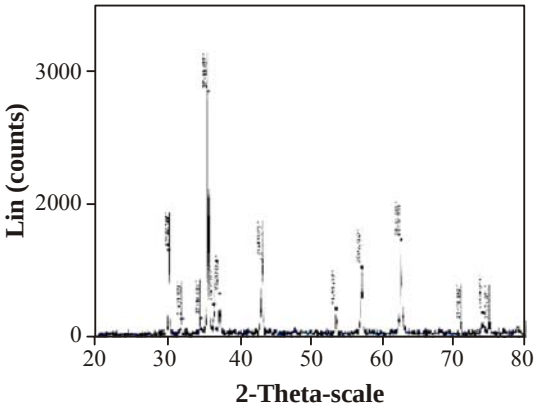
The grain size of ferrite formed in the 500 nm (smaller grain size) in groove form. Scanning electron microscope (SEM) studies for copper ferrite and zinc ferrites are carried out on the ceramic samples sintered at 800°. We can observe the formation of soft agglomerates with irregular morphology constituted with the quite fine particles.

Powder X-ray diffraction studies (XRD) (Fig. 3) for nickel copper ferrite, nickel zinc ferrite and nickel copper zinc ferrite have been carried out on the ceramic sample sintered at 800°C temperatures for 2 hrs, respectively. XRD peaks represent that the nickel copper ferrites, nickel zinc ferrites and nickel copper zinc ferrites in which spinal crystals are

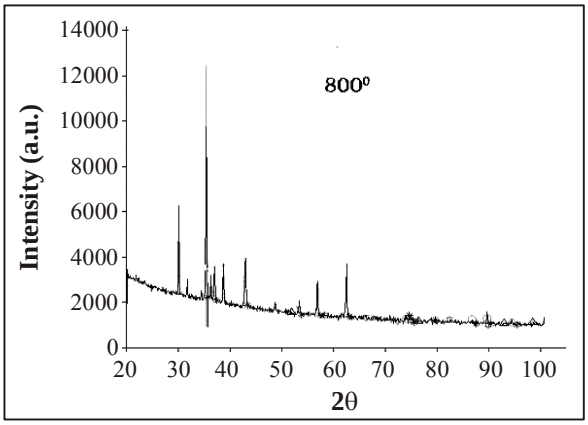
formed during the crystallization (calcination at 800^o temperature). From the XRD data, the sizes of particles are calculated by using sheerer formula are 44 nm for nickel copper ferrite, 45.58 nm for nickel zinc ferrites and nickel copper zinc ferrites is 65 nm. This shows that the synthesized powder has nano size crystalinity. Active single phase is observed as spinal crystal structure, with increase in the crystalinity. From the SEM diagrams (Fig. 4), in nickel copper ferrites, the grains and grain boundaries are larger with intergrannular pores. From the study of SEM micrographs of these samples produced less number of pores with smaller lump size and exhibiting fine grained microstructures with respect the ferrites prepared by the conventional route.



XRD patterns of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ at 800^{o}C

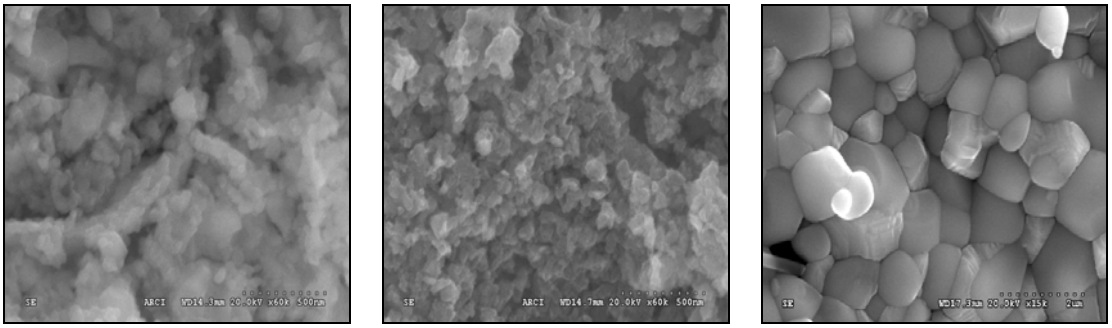


XRD patterns of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at 800^{o}C



XRD patterns of $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_2O_4$ at 800^{0}C

Fig. 3: XRD Patterns of ferrites at 800^{o}C



SEM image of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ | SEM image of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ | SEM image of $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_2O_4$

Fig. 4: SEM Images of ferrites at 800°C

The particle size of copper ferrite (20 nm) is less (Table 1) than that of nano nickel ferrite (27 nm) because meta stable Cu^{3+} ions (low spin 54 pm) occupy in tetrahedral sites (A site) and also it has less size than Ni^{2+} ion (69 pm). Further, observed that the particle size increases as doping of large sized ions such as Cu^{2+}, Zn^{2+} ions and it is also observed that the doping of more transition metal ions (Ni^{2+}- 69 pm, Cu^{2+}-73 pm, Zn^{2+}-74 pm) increases the sizes of the nano ferrite particles (Table 1).

Table 1: Comparison of particle size of different ferrites synthesized by citrate gel method

Ferrite	Particle size in nm
$NiFe_2O_4$	27
$CuFe_2O_4$	20
$ZnFe_2O_4$	31
$Ni_{0.5}Cu_{0.5}Fe_2O_4$	44
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	45.58
$Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_2O_4$	65

From the above results, we plot a graph between ferrite systems against the size of the particle (type of ferrite on X-axis and particle size on Y-axis). As the adding of a transition metal increase the particle size is shown in Fig. 5. In the above results, copper ferrite possess the smallest size 20 nm and $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_2O_4$ (65 nm) do possess largest nano size.

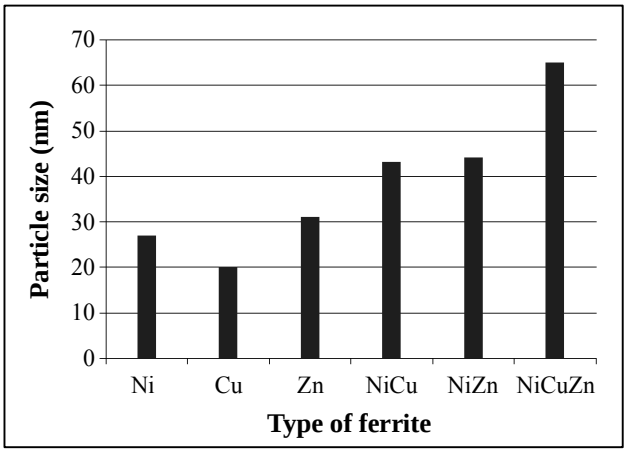


Fig. 5: Ferrites particle size (nm)

CONCLUSION

The citrate gel precursor method is convenient for the synthesis of nano sized above ferrites. X-ray diffraction patterns confirm that the synthesis of fully crystalline ferrites nano particles, which seems to be very promising.

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