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Synthesis and Characterization of Nanocrystalline Zn Doped Magnesium Ferrite Via Sol-Gel Route

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ABSTRACT

The present investigation deals with the synthesis of nanocrystalline $Mg_{1-x}Zn_xFe_2O_4$ (x = 0.5) mixed ferrite was successfully prepared by sol-gel method using citric acid as anionic surfactant followed by calcination at 700°C for 2h. The resultant powder was characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) to study the crystallite size, phase compositions, structure and morphology. The nano size was confirmed by the XRD and SEM micrographs. XRD indicated the formation of nanocrystalline single-phase cubic spinel structure with average crystallite size is 30 nm. Fourier Transform Infrared Spectroscopy (FT-IR) confirms the formation of $Mg_{0.5}Zn_{0.5}Fe_2O_4$. Energy Dispersive X-ray Analysis (EDX) determined the concentration of constituents involved in the synthesized material. The crystallite size from TEM analysis matches well with XRD results confirming the usefulness of sol-gel method for the synthesis of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$. DC conductivity of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ thick film shows semiconducting in nature

Keywords: Nanocrystalline mixed ferrite, XRD, SEM, EDX, FT-IR, TEM.

I. INTRODUCTION

During the last decade, the world has seen huge interest in developing and understanding the matter of nanometric scale. It has allowed the scientists to develop and characterize materials with prominent properties and nanometric sizes. Due to the note-worthy properties, exhibited by nonmaterial, they have become centre of attention in the scientific community. The fabrication of spinel-structured ferrite nanoparticles has been intensively investigated in recent years due to their unique physical and chemical properties, as well as technological applications in ferrofluids [1], high-density magnetic recording media [2], biomedicine [3] and radar-absorbent materials [4].

Spinel ferrites, MFe_2O_4 (M = Mg, Mn, Fe, Co, Ni, Zn, Cu, Cd, etc.) are a technologically important group of materials. Among different ferrites, magnesium ferrite ($MgFe_2O_4$) enjoys a special attention because of its vast applications in high density recording media, heterogeneous catalysis, adsorption, sensors and magnetic technologies. $MgFe_2O_4$ is a partially inverse spinel and its degree of inversion is sensitive to the thermal history of the sample, microstructure and preparative parameters. Nanoparticles of $MgFe_2O_4$ have good photo electrical properties [5-7]. To fabricate various types of nanoparticles, a large number of methods are used such as physical, chemical, biological and hybrid methods. The nanoparticles synthesized using each method exhibit particular properties. So, the synthesis of nanostructured materials has become a particularly important area of research.

There are several methods for synthesizing nanosized spinel ferrite particles such as hydrothermal, co-precipitation, combustion, sol–gel, precursor, spray drying and freeze drying, microemulsion and reverse micelle method [8–15]. To prepare nanoferrites with simple routes by using cheap, non-toxic and eco-friendly precursors are still the core issue, among other proven synthesis methods [16]. Among these methods, the

nanoparticles prepared by sol-gel method have been studied, although this synthesis provides a quick and easy way to prepare nanoparticle, it usually produces sample with large size distribution and less defined crystal chemistry.

Herein, the purpose of this work is to prepare nanocrystalline Zn doped Mg spinel ferrite by a sol-gel method with a low calcination temperature involving low cost metal nitrates as raw materials and study of their structural properties.

II. EXPERIMENTAL

Preparation of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$ powder was synthesized by the sol-gel technique. All chemicals were of analytical grade and were used without further purification. The stoichiometric molar amounts of Ferric nitrate [$Fe(NO_3)_3.9H_2O$], Magnesium nitrate [$Mg(NO_3)_2.6H_2O$], Zinc nitrate [$Zn(NO_3)_2.6H_2O$] and Citric acid [$C_6H_8O_7.H_2O$] were weighed separately with a ratio 0.5M:0.25M:0.5M. These reagents were mixed with distilled water and volume made up to 100 ml. The solution mixture was stirred and heated at 60^{o}C for 3 h and followed by 80^{o}C, until the mixture changed to gel form. The gel was then dried in an oven at 100^{o}C for 24 h. The obtained powder was then calcined in a muffle furnace at 700^{o}C for 2 h to improve the crystallinity of the prepared material. Finally, brown colour powder was obtained. Taken solid phase sample was grinded in a mortar to make it powder for further analysis.

The phase confirmation was determined using XRD (Bruker, AXD D8-Discover using Cu Kα radiation with an accelerating voltage 40 kV). FT-IR image was recorded using 3000 Hyperion Microscope with Vertex 80 (Bruker, Germany) to provide information about the structural coordination in the powder sample. The TEM image was recorded using CM 200 (Philips) with an accelerating voltage of 20-200 kV.

Appropriate quantity of mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol was added to the mixture of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ and a solution of ethyl cellulose (a temporary binder). The mixture was then ground to form paste. The paste obtained was screen printed onto a glass substrate in desired patterns. The thick films so prepared were fired at 500°C for 1 h. Surface morphology of thick film was observed by using SEM (JSM-7600F microscope) with an accelerating voltage of 0.1 to 30 kV.

III. RESULT AND DISCUSSIONS

3.1 XRD analysis

The X-ray diffraction pattern of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ calcinated at 700^{o}C for 2 h was exhibited in Figure 1. Main peaks were found at 2θ values = 29.90^o, 35.21^o, 56.58^o, 62.14^o and 73.48^o which were identified as corresponding to Miller index (220), (311), (400), (511) and (440) respectively (JCPDS card no. 73-2211). The XRD peaks and their positions with the calculated lattice parameter confirm that all the compositions exhibit single-phase cubic spinel structure with Fd3m space group. No peaks from other phases are detected, indicating high purity of the products.

The average crystallite size (D) was calculated from XRD peaks broadening using the Debye-Scherrer approximation, which is defined as

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

where, D is the average crystallite size, k is a constant equal to 0.9, λ is the X-ray wavelength and β is the peak full width at half maximum (FWHM) and θ is the angle of diffraction.

However, the lattice constant of as-synthesized ferrite powder was a= 8.421A˚. A similar linear variation of lattice constant with Zn content has been observed by El-Sayed [17] and Kakatkar et al. [18] for M–Zn ferrites with M = Ni, Co, Cu, Mg. The average crystallite size was determined from the XRD powder pattern using Debye–Scherrer formula and was found to be 30 nm.

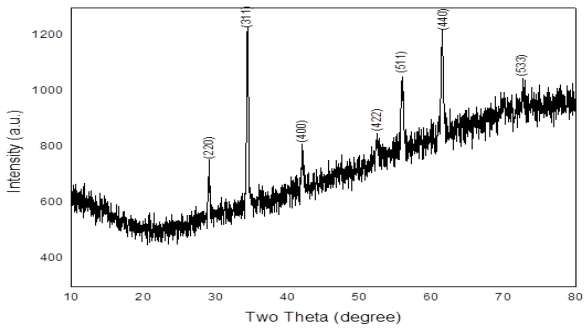

Figure 1. XRD pattern of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ calcined at 700^{o}C.

3.2 FT-IR analysis

FT-IR spectrum of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticle was presented in Figure 2. Vibrations of ions in the crystal lattice were usually observed in the range of 4000 - 400 cm^{-1} in IR analysis. Two main broad metal-oxygen bands were seen in the IR spectra relative to spinel ferrite compounds. Infrared spectrum shown in Figure 2 had two absorption bands near about 400 cm^{-1} and 600 cm^{-1} for octahedral and tetrahedral sites respectively. Waldron [19] attributed the higher absorption band position (600 cm^{-1}) to the intrinsic stretching vibrations of tetrahedral complexes and the lower absorption band position (400 cm^{-1}) to octahedral-metal stretching because of the difference in Fe^{3+}– O^{2-} distances for the octahedral and tetrahedral sites respectively. The Mg^{2+} ions occupy mainly the octahedral sites but fraction of these ions may be migrated into tetrahedral sites. This would explain the existence of a weak shoulder in the range of 690 –710 cm^{-1}. This confirms that the Mg ferrite has a partially inverse spinel structure.

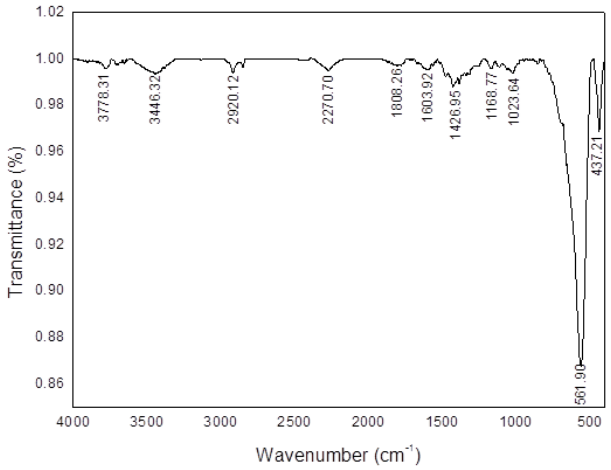

Figure 2. FTIR spectrum of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

3.3 TEM analysis

The size and morphology of the obtained $Mg_{0.5}Zn_{0.5}Fe_2O_4$ nanocrystal was characterized by TEM observation. Figure 3(a) shows TEM image of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticle. The corresponding SAED pattern is shown in Figure 3(b). As can be seen from Figure 3(a) and (b), the prepared product consists of small sized nanocrystals with irregular shapes. It appears that a higher temperature reaction favors a particle with larger grain sizes, because a higher temperature enhanced the atomic mobility and caused the grain growth to result in a better crystallinity. As it can be seen that the result estimated from TEM micrograph was in good accordance with the XRD analysis. The selected area aperture used in this study sufficed to reveal all the corresponding bright rings of the spinel structure. It was observed that the spot type pattern which is indicative of the presence of single crystallite particles and no evidence was found for more than one pattern, suggesting the single phase nature of the material.

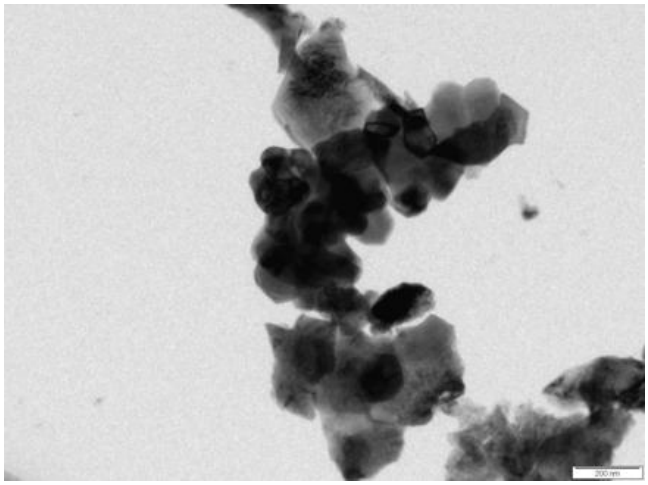

Figure 3(a). TEM image of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

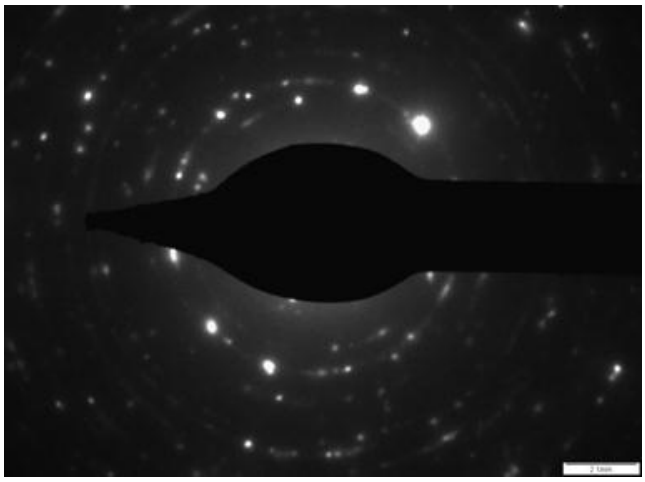

Figure 3(b). SAED micrograph of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

3.4 SEM analysis

SEM technique was employed for finding morphology of the thick film. Figure 4 shows SEM image of the nanocrystalline spinel $Mg_{0.5}Zn_{0.5}Fe_2O_4$. The SEM technique was employed for finding morphology of the powder; it shows formation of the agglomerated particle. SEM image shows that the sample exhibit large grains structure having irregular morphology (polygons) with the presence of soft agglomerations.

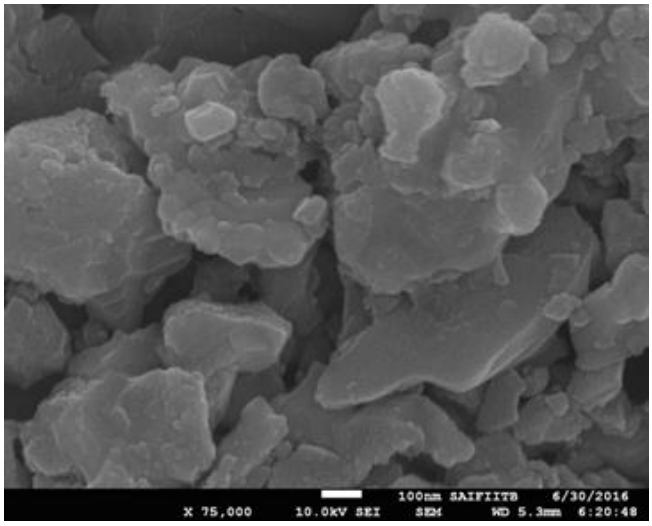

Figure 4. SEM image of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

3.5 Energy dispersion X-ray analysis

Energy dispersion X-ray analysis (EDX) was investigated the elemental composition of synthesized $Mg_{0.5}Zn_{0.5}Fe_2O_4$ thick film. EDX spectrum of the nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$ is as shown in Figure 5. The EDX analysis exhibit the presence of Mg, Zn, Fe and O and EDX spectrum reveal almost the same ratio of Mg/Zn/Fe for the nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$ as they were actually added during synthesis process. Hence, confirms the purity of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

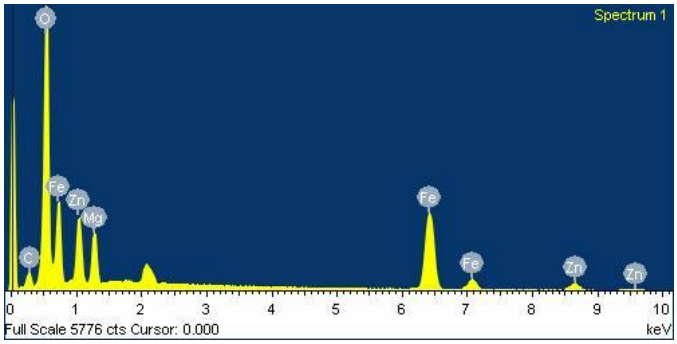

Figure 5. EDX spectrum for nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

IV. CONCLUSIONS

Zinc doped magnesium ferrite nanoparticles ($Mg_{0.5}Zn_{0.5}Fe_2O_4$) was prepared using less expensive, environment-friendly and low temperature sol-gel method using citric acid as anionic surfactant calcined at 700^{o}C. XRD pattern reveals that the synthesized ferrite consists of nano crystalline particle with average crystallite size 30 nm. The FT-IR spectrum exhibits main absorption bands around 561 cm^{-1} and 437 cm^{-1} corresponding to the vibration modes of the tetrahedral and octahedral sites respectively. The crystallite size from TEM analysis matches well with XRD results confirming the usefulness of sol-gel method for the synthesis of nanocrystalline $Mg_{0.5}Zn_{0.5}Fe_2O_4$. The morphological investigations from SEM showed the sample surface is fully covered by grains with irregular shape. The EDX confirmed the presence of Mg, Zn, Fe and O with values as per the initial precursor concentration.

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