STUDY ON THE EFFECTS OF NICKEL SUBSTITUTION IN SOL-GEL SYNTHESIZED CADMIUM SPINEL FERRITE NANOPARTICLES

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Abstract: Magnetic materials are necessary for many aspects of our daily life. Therefore the demand of advance magnetic materials progresses in the industrial and medical purposes.Cadmium ferrite nanoparticles ($CdFe_2O_4$) are well known for some unique characteristics such as good saturation magnetization, excellent physical and chemical stability, which make them so attractive for various biomedical and industrial applications.In this study, nickel doped cadmium ferrite nanoparticles ($Ni_{1-x}Cd_xFe_2O_4$) (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were synthesized by sol-gel auto combustion method. Then, using X-ray diffraction (XRD), scanning electron microscopy (FESEM), and structural properties were investigated. XRD analyses show a single-phase spinel structure for annealed samples at 800°C. The crystallite sizes increasesslightly by decreasing concentration of Ni doping from 20 to 40 nm, in agreement with FESEM micrographs. The lattice parameter value was between 8.4 and 8.7 Å. The Rietveld analysis showed that $Ni_{1-x}Cd_xFe_2O_4$ nanoparticles have a mixed spinel structure. Then, by using the vibrating sample magnetometer (VSM), we obtained the magnetic parameters of the samples.

Key words:Spinel ferrite, Sol-gel auto combustion method, XRD, SEM, VSM.

Introduction:

In recent years, spinel ferrite nanomaterials have emerged as a prominent class of functional materials with vast potential across diverse scientific and technological domains[1]. These nanomaterials, composed of transition metal ferrites with a spinel crystal structure, exhibit a rich array of magnetic, electrical, optical, and catalytic properties, making them highly sought after for a wide range of applications[2]. As a result, significant research efforts have been dedicated to the synthesis, characterization, and exploration of the multifaceted properties of spinel ferrite nanomaterials.

Spinel ferrites are a family of compounds with the general formula AB_2O_4, where A and B represent divalent and trivalent metal ions, respectively, occupying tetrahedral and octahedral sites within the spinel crystal lattice [3-4]. Common examples include magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and various mixed metal ferrites such as cadmium ferrite ($CdFe_2O_4$), nickel ferrite ($NiFe_2O_4$), and manganese ferrite ($MnFe_2O_4$). The unique arrangement of metal ions in the spinel structure gives rise to fascinating magnetic properties, including high saturation magnetization, tunable magnetic anisotropy, and excellent chemical stability, which are highly desirable for applications in magnetic recording, data storage, magnetic resonance imaging (MRI), and magnetic hyperthermia [5-7].

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The advent of nanotechnology has revolutionized the field of spinel ferrite research by enabling the synthesis of nanoscale particles, thin films, and composite structures with tailored size, shape, composition, and surface properties. These advances have not only enhanced our fundamental understanding of spinel ferrite nanomaterials but also opened up new avenues for their utilization in cutting-edge technologies. Nanosized spinel ferrite particles exhibit enhanced magnetic properties compared to their bulk counterparts due to size-dependent phenomena such as superparamagnetism, exchange bias, and quantum confinement effects, which are instrumental in various applications including high-density magnetic recording, biomedical imaging, and targeted drug delivery [8].

Furthermore, the versatile nature of spinel ferrite nanomaterials allows for the integration of additional functionalities through surface modifications, doping, or composite formation, thereby expanding their applicability in fields such as catalysis, sensors, energy storage, and environmental remediation. Functionalization of spinel ferrite nanoparticles with organic ligands, polymers, or noble metal nanoparticles can impart improved dispersibility, biocompatibility, and selectivity, enabling their deployment in biomedical applications such as magnetic resonance imaging contrast agents, magnetic hyperthermia therapy, and drug delivery carriers [9-10].

In this research paper, we present a comprehensive overview of the synthesis strategies, structural characterization techniques, magnetic properties, and emerging applications of spinel ferrite nanomaterials. By elucidating the fundamental principles underlying their behavior and highlighting recent advancements in the field, we aim to contribute to the collective understanding of spinel ferrite nanomaterials and inspire further exploration of their potential in addressing current technological challenges and societal needs.

Synthesis Method:

The sol-gel microwave auto-combustion synthesis method offers a rapid and efficient route for the preparation of ferrite nanoparticles with controlled properties. By optimizing the synthesis parameters, such as precursor concentration, pH, calcination temperature, and microwave power, it is possible to tailor the characteristics of the synthesized nanoparticles for specific applications in fields such as electronics, catalysis, and biomedicine. Here, we present a detailed protocol for the synthesis of ferrite nanoparticles using the sol-gel microwave auto-combustion method [11].

Step I- Dissolve the appropriate amount of metal nitrates in a suitable solvent 30 ml distilled water to achieve the desired metal ion concentration. Add a 5 ml chelating agent (e.g., citric acid or ethylene glycol) to the solution to complex metal ions and prevent their precipitation.

Step II -Now slowly add ammonia solution dropwise to the metal precursor solution under continuous stirring until the pH reaches about 7-8. Continue stirring the solution on hot plate magnetic stirrer for a few hours until a homogeneous gel forms.

Step III - Transfer the crystalline gel beaker into a scientific microwave oven (400 to 800 W)for few minutes until self-sustaining combustion occurs. The exothermic combustion reaction will lead to the formation of ferrite nanoparticles with a high degree of crystallinity.

Step IV –Ground and Calcine the dried gel in a furnace at elevated temperatures (typically 400-800°C) for four hours to initiate the reaction and convert the grounded ash into a crystalline ferrite phase. Allow the obtained nanoparticles to cool to room temperature naturally.

Step V - Characterize the synthesized nanoparticles using various techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and vibrating sample magnetometry (VSM) to assess their crystalline structure, morphology, size distribution, and magnetic properties.

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Result and Discussion:

1. XRD Analysis

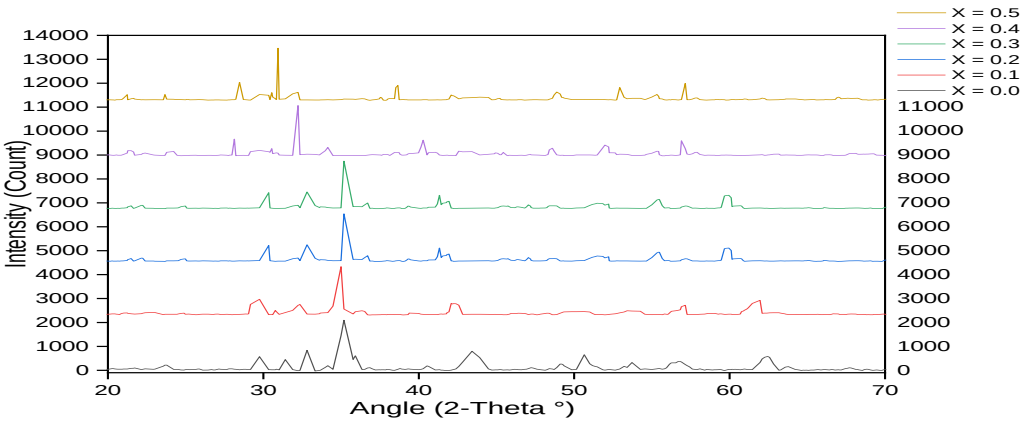

Figure 1 XRD Patterns of $Ni_{1-x}Cd_xFe_2O_4$

Comparative study of XRD phases of a synthesized Cadmium substituted Nickel (Cd-Ni) ferrites were elucidated by X-ray diffraction pattern (Fig). The formation of cubic phase spinel ferrite with space group Fd3m (227) is confirmed from the XRD, revealing the highly crystalline character of the sample. The peaks could be indexed as (111), (220), (311), (222), (400), (422), (511), (440), (620) and (533) are major lattice planes, which are characteristics of single-phase cubic spinel structure. To analyse the X-ray diffraction (XRD) data of Ni1-xCdxFe2O4 (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5), we'll focus on several key parameters. The lattice parameter refers to the constant distance between unit cells in a crystal lattice. It can be determined from the XRD data by analysing the peaks and their positions. The lattice parameter for given compound has been found between from 8.35 to 8.64. It has observed that the lattice parameter varies with the concentration of cadmium. Itincreases in the lattice constants 'a' is due to the larger ionic radii of the doped ions Cd^{2+} (0.97 Å) as compared to that of the Ni^{2+} (0.69 Å). The volume of the unit cell can be calculated from the lattice parameter [12]. It gives insight into the spatial arrangement of atoms within the crystal structure. The bulk density is the mass of the material per unit volume. It can be calculated using the volume and the mass of the sample.X-ray density is the theoretical density calculated based on the crystal structure and atomic composition [13]. It can be derived from the lattice parameter and the atomic weights of the elements. Particle size can be estimated from the broadening of the XRD peaks using techniques like the Scherequation [14-15]. The Strain refers to the distortion or deformation within the crystal lattice. It can be determined from the peak broadening in the XRD pattern. It has observed from table that all the various parameters are depends on doping concentration [16-17].

SEM Analysis:

Formula	Lattice Parameter	Volume	Bulk Density	X-Ray density	Porosity	Particle Size	Strain
	Å	10^{-30} m^3	g/cm^3	g/cm^3	%	nm	
$NiFe_2O_4$	8.35	582	3.44	5.35	35.00	12.81	0.145
$Cd_{0.1}Ni_{0.9}Fe_2O_4$	8.38	588	3.28	5.33	33.40	14.10	0.147
$Cd_{0.2}Ni_{0.8}Fe_2O_4$	8.42	596	5.50	5.5	32.10	14.47	0.158
$Cd_{0.3}Ni_{0.7}Fe_2O_4$	8.51	616	3.45	5.55	31.80	19.48	0.187
$Cd_{0.4}Ni_{0.6}Fe_2O_4$	8.56	627	3.37	5.67	30.45	21.66	0.198
$Cd_{0.5}$-$Ni_{0.5}Fe_2O_4$	8.64	644	3.59	5.73	27.34	23.19	0.215

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Typical FE-SEM image of the sample Cd-Ni synthesis via chemical route annealed at 800^{o}C is shown in Fig.2. The image reveals that the particles have an almost regular shape and homogeneous distribution in the range of 12 to 40 nm shown. The FESEM micrographs show that the particle size microstructures were affected by theCadmium concentration with increasing particle size listed in Table 1 [16]. Interactions between magnetic nanoparticles showed agglomeration area in images explain by M. G. Naseri (2013) [17]. It is clear from the images that the microwave induces sol-gel combustion technique has yielded; less agglomerated, steady grain growth, uniformly distributed and homogenous spherical particles. The porosity of given Cd-Ni and Cd-Zn nano ferrites samples has been calculated from XRD data which clearly shown by SEM images.

As reported by Ahamadet al. (2017) [21], grain morphologies of Cd-Ni doped spinel Nanoparticles indicate improvement in inter-grain connectivity with Cu^{2+} ions substitution. The electrical and magnetic properties of ferrites are found to be largely influenced by the homogeneity of shape and grain size of the particles [22].

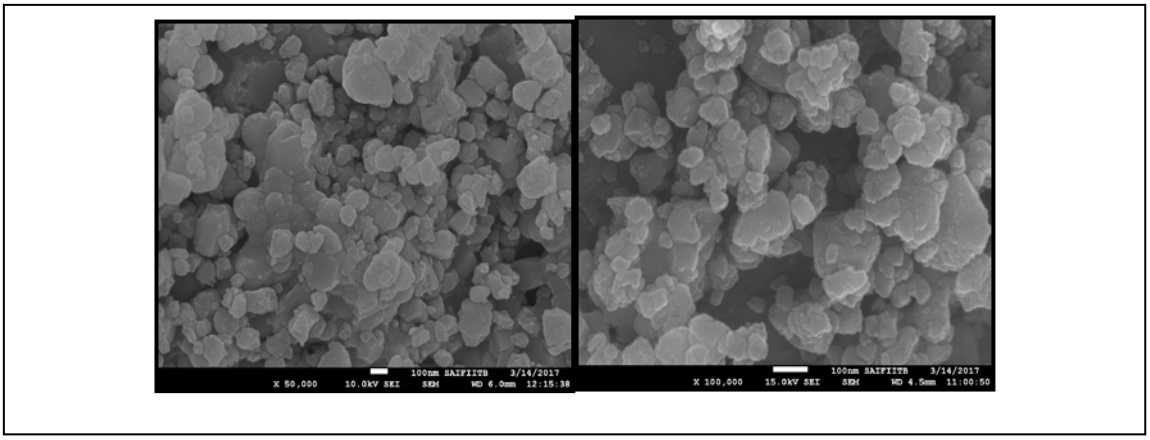

Figure 2Scanning Electron Microscope Images of Cd-Ni Ferrites

VSM Magnetic Analysis

The magnetic properties of the synthesized nanoparticles are analyzed using a Vibrational Sample Magnetometer (VSM) at room temperature (300 K) in the range of approximately −15000 to +15000 Gauss. Figure show the M-H curves of the prepared Cd-Ni nanocrystals. The coercivity (Hc) and saturation magnetization (Ms) values have been directly extracted from these curves and have been listed for various concentrations of Ni^{2+} contain in table. These tables indicate that Ms decreasing while increasing the Cd^{2+} concentration of both series, i.e. the minimum value of Ms is found in the $NiFe_2O_4$nanocrystals [23-25].

The relation between magnetization and applied field (M-H loops) can be attributed to the competition of ferromagnetic ions such as Fe^{3+}, $Ni^{2+}$and nonmagnetic ions such as Cd^{2+} ions in the occupancy of the tetrahedral and octahedral sites [26]. The variation in the value of the H_C with Ni^{2+} is depends on the concentration and particle size. It can be explained on the basis of domain structure, cation distribution and the anisotropy of the crystal [27]. The narrow loop area of the magnetization curve shows the soft magnetic nature of the sample [28].Thus, the decrease of the saturation magnetization with the increase of particle sizes can be attributed to surface effects that are the result of finite-size scaling of nanocrystallites, which in turn leads to a non-colinearity of magnetic moments on their surface [29] and can also be explained by core-shell morphology of the nanoparticles consisting of ferrimagnetically aligned spins core and spin-glass-like surface [30-31]. Due to the above mentioned effects, when the calcination temperature is below 900°C, the coercivity shows lower values than that of bulk nickel ferrite.

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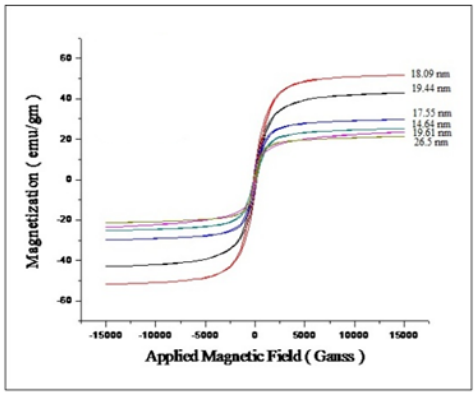

Figure 3Hysterisis Curves of Cd-Ni Ferrites with Different Concentration

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