Characterization of nanostructured spinel NiCr$_x$Fe$_{2-x}$O$_4$ obtained by sol gel auto combustion method

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Abstract: The samples of Cr$^{3+}$ substituted Nickel ferrite with composition NiCr$_x$Fe$_{2-x}$O$_4$ were synthesized by employing sol gel auto combustion method. The ferrite powder materials were subjected to X-ray diffraction spectroscopy (XRD) analysis and Transmission electron microscopy (TEM) analysis for the study of structural as well as morphological characteristics. The X-ray diffraction pattern at the room temperature showed the formation of a cubic spinel ferrite having a single phase. Moreover, the values of lattice parameters (a) counter verified the same. TEM imaging demonstrated the formation of nanosize particles and the presence of all constituent elements were confirmed by energy dispersive X-ray (EDAX) analysis. Vibrating Sample Magnetometer (VSM) was used to study the magnetic properties of the samples. The magnetic properties showed low saturation magnetization (Ms), Remnance (Mr) as well as Coercivity (Hc). This confirmed the viability of such materials in the various applications of such as water treatment, microwave device materials, permanent magnets and storage recording devices.

Key words: cubic spinel ferrite, XRD, TEM, VSM, sol gel auto combustion etc.

1. Introduction

Nanotechnology is often referred to as the technology of the century and deals with the design, fabrication and application of nanostructures or nano materials. It also embraces the fundamental knowledge of the relationship between different physico-chemical properties and size of the material. Nanotechnology is often considered as an evolving interdisciplinary technology that has contributions in many fields, including physics, materials science, optics, electronics, electricity, mechanics, aerospace, plastics and medicine, over the past decade. Its strong social influence has been seen as the tremendous momentum to begin another industrial revolution [1-5].

Various magnetic materials have fascinated mankind for over centuries. Later, they have found their way into almost every part of our civilization. Every day we are using magnetic materials in computer HDD, credit ID cards, loudspeaker, permanent magnet motors, refrigerator door seals and a lot more. In the last 50 years, the production of new materials on a smaller and smaller scale has been at the centre of advances in material science [6-9].

2. Synthesis

In this method, a conventional heating element is replaced by a coherent microwave producing magnetron. It releases the required amount of heat in less time and in a more focused way. To some
better extent, this method is being improvised by controlling the operation of magnetron by incorporating digital circuits including frequency modulator, time counter, etc. Because of the additional circuits supported with the basic circuit of microwave oven, it is observed that the entire set up operates in a more suitable way to synthesize samples having particle size in the nano scale. The earlier demerit of fluctuating frequency around 2.45 GHz of magnetron is overcome in this method. The additional digital set up cares to maintain the frequency of the magnetron constant throughout the cycle of synthesis of a sample.

The sol gel method of synthesis comprise of various steps as given below;
Step I – A homogeneous solution is prepared in the deionized water by dissolution of the precursor metal ions in an organic solvent. In the given synthesis method, during the initial stages of preparation, blending of metal ions on an atomic scale in solution state helps to obtain homogeneous mixtures. For example: Nickel nitrate (Ni(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O), Chromium nitrate (Cr(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O) and iron nitrate (Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O), in their respective molar ratios have been dissolved in 40 ml deionized water to prepare a homogeneous solution.
Step II – The solution so prepared is transformed to a sol if it is not already a sol. A colloid in which solid particles are suspended in a liquid is referred to as a sol. The resultant sol is generally stabilized by adjusting the pH, or else, the particles would expand into agglomerates which can further precipitate and thus don’t allow for the acquisition of specific powder chemistry.
Step III – Gel formation is the most important step in the process and essentially aimed at the removal of the majority of the deionized water (solvent) so that a formation of rigid body with a well defined chemistry takes place. This aqueous sol of metal ions is steadily heated for 2 hours at around 80°C by using a magnetic stirrer hot plate to convert it into a gel which is kept in plastic or highly viscous form by maintaining processing variables like temperature, pH and time.
Step IV – The gel is transformed into the correct morphology, may be in the form of spheres, fibers or coatings. The gel is fired in the microwave oven at power 800 watt for three minutes which results in the formation of dry ash. These ash forming compounds are grounded by a using a mortar pestle or ball-milling process to obtain fine nano size powder.
Step V – Traditional grinding is performed for a powder calcined in muffle furnace for 4 hours at around 800°C in order to obtain a spinel ferrite material NiCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} for the intended application, in which x varies as 0.2, 0.4, 0.6, 0.8 and 1.0 [9-14].

3. Characterization

3.1. Powder XRD analysis
The use of XRD analysis is done to calculate the grain size of the material prepared. Debye Scherer formula is employed to determine the grain size of all the synthesized compounds from the most intense peak as; D= 0.9λ/βcos, where, λ is the wavelength of used X-ray beam, β is the full width at half maxima (FWHM) and Ө is the corresponding angle.
Table 1 summarizes the Lattice parameters, x-ray and bulk density and the porosity of these samples [15-17]. Similarly, Figure 1 explains the XRD pattern of chromium substituted nickel spinel ferrite samples. The study of NiCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} samples reveals the formation of cubic crystal structure with space group Fd3m. PowderX software was used to index the miller planes indices [18-20].
Figure 1. Powder XRD of NiCr$_x$Fe$_{2-x}$O$_4$ spinel ferrite

Table 1. Lattice parameter of NiCr$_x$Fe$_{2-x}$O$_4$

| Series      | Conc . (x) | Fe$_{2-x}$ | Molecular wt | Lattice parameter ($\text{Å}^0$) | X ray density (gm /cm$^3$) | Bulk density (gm /cm$^3$) | Porosity (%) |
|-------------|------------|------------|--------------|---------------------------------|---------------------------|--------------------------|--------------|
| NiCr$_x$Fe$_{2-x}$O$_4$ | 0.2 | 1.8 | 233.6 | 8.2950 | 5.44 | 3.897 | 28 |
|              | 0.4 | 1.6 | 232.83 | 8.3123 | 5.38 | 3.797 | 29 |
|              | 0.6 | 1.4 | 232.06 | 8.3545 | 5.29 | 3.697 | 30 |
|              | 0.8 | 1.2 | 231.29 | 8.3712 | 5.24 | 3.573 | 31 |
|              | 1   | 1   | 230.52 | 8.3912 | 5.18 | 3.457 | 33 |

3.2. EDAX analysis

The energy dispersive X-ray (EDAX) study was also carried out for the synthesized samples and is shown in figure 2. The EDAX spectrum of Nickel ferrite nanoparticles, calcined at 800°C divulged the information about presence of Ni, Cr, Fe and O peaks. EDAX analysis confirmed that all the constituent elements are present in the synthesized ferrite samples in the desired ratio. The pattern that is obtained also validate that the crystal structure of Cr$^{3+}$ spinel ferrite was reduced after being doped with Nickel ferrite [18-21]. Powder XRD analysis.

Figure 2. EDAX analysis of NiCr$_x$Fe$_{2-x}$O$_4$
3.3. VSM analysis
The Vibrating sample magnetometer (VSM) study was done to study the magnetic properties ferrite samples at room temperature. Magnetic hysteresis (M-H) loops of measurements of synthesized NiCrXFe2-xO4 samples with different concentrations were carried out and the observed values of saturation magnetization (Ms), remanent magnetization (Mr) as well as coercivity (Hc) were noted and plotted as seen in figure 3 and reported in Table 2 [21-22].

![Figure 3. VSM of NiCrXFe2-xO4 spinel ferrite](image)

Table 2. Magnetic properties VSM of NiCrXFe2-xO4

| Series     | Conc. (x) | Fe2-x | Magnetization (Ms) (emu/gm) | Retentivity (Mr) (emu/gm) | Coercivity (Hc) (Gauss) | Squareness ratio (Mr/Ms) |
|------------|-----------|-------|-----------------------------|---------------------------|------------------------|--------------------------|
| NiCr_xFe_2O_4 | 0.2       | 1.8   | 5.7                         | 2.11                      | 435.35                 | 0.37                     |
|            | 0.4       | 1.6   | 5.26                        | 2.05                      | 432.75                 | 0.39                     |
|            | 0.6       | 1.4   | 4.68                        | 1.87                      | 429.60                 | 0.40                     |
|            | 0.8       | 1.2   | 4.29                        | 1.59                      | 426.80                 | 0.37                     |
|            | 1         | 1     | 3.15                        | 1.40                      | 423.15                 | 0.45                     |

3.4. TEM analysis
The Transmission Electron Microscopy (TEM) analysis was done to confirm the particulate size of the materials. The TEM pictures revealed that the particle size of the mechanically milled and annealed samples is well consistent with the grain size (crystallite size). Debye-Scherer formula was applied to calculate the grain size by using prominent XRD peaks corresponding to the cubic spinel phase. The grain size was found to be in the range of 22- 60 nm approximately for the synthesized samples and is shown in figure 4 [23-26].
3.5. Electrical Properties
In case of ferrites, which are mostly low mobility semiconductors it is observed that rather than the concentration, it is the activation energy of the charge carriers, which is normally associated with the mobility of these charge carriers. Figure 5 illustrates the relation of the temperature with DC electrical conductivity. In case of NiCr$_x$Fe$_{2-x}$O$_4$ ferrite samples it is also observed that the DC electrical conductivity attains a peak value at a particular temperature, which is termed as the transition temperature. Metallic character of the materials can be indicated by the initial increasing trend of conductivity with temperature and the subsequent increase of the same represents a semiconductor nature. A graph between conductivity and temperature with temperature was used to calculate the activation energy of synthesized nickel ferrite samples and is tabulated in the table 3 [27-33].

![Figure 4. TEM of NiCr$_x$Fe$_{2-x}$O$_4$ spinel ferrite](image)

![Figure 5. Electrical study of NiCr$_x$Fe$_{2-x}$O$_4$ spinel ferrite](image)
Table 3. Transition temperature of NiCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4}

| Series       | Conc. (x) | Resistivity (x 10\textsuperscript{-7} ohm/cm) | Activation energy para (eV) | Activation energy ferri (eV) | Transition Temp. (\textdegree\text{K}) | GOUY’ Balance (\textdegree\text{K}) |
|--------------|-----------|---------------------------------------------|----------------------------|----------------------------|----------------------------------------|----------------------------------------|
| NiCr\textsubscript{0.2}Fe\textsubscript{2-0.2}O\textsubscript{4} | 0.2       | 3.95                                       | 1.754                      | 0.154                      | 637                                    | 640                                    |
|              | 0.4       | 3.37                                       | 2.245                      | 0.134                      | 621                                    | 632                                    |
|              | 0.6       | 2.63                                       | 1.934                      | 0.193                      | 614                                    | 625                                    |
|              | 0.8       | 2.22                                       | 1.034                      | 0.134                      | 609                                    | 612                                    |
|              | 1         | 1.35                                       | 1.132                      | 0.124                      | 602                                    | 603                                    |

4. Conclusion
In summary, spinel NiCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} nanoparticles were successfully synthesized by sol gel auto combustion route by using urea as a fuel. The formation of single phase, well crystallized cubic spinel ferrite powder with general formula NiCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} was confirmed by XRD, Rietveld refinement XRD as well as EDAX analysis. The size of the synthesized nanocrystals calculated by the Debye-Sherrer formula was in the range of 22 to 60 nm. HR-TEM images of the samples also confirmed the size in the nanometer range confirming to the particle morphology with slight agglomeration.

The ferromagnetic behavior was confirmed by VSM technique as it is observed that the Ms values of the undoped sample is 66.93 emu/g, which shows a decreasing trend with the increase in Cr\textsuperscript{3+} content. The inclusion of Cr ion in the NiCr\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} lattices plays a crucial role in electrical behavior and result in proportionate increase in electrical conductivity. Size dependence of electrical properties was well established and it is found that grain and grain boundary kinetics regulate these properties in the material. It is assumed that the interchange of cations from their respective tetrahedral (A) and octahedral (B) sites along with hopping of holes (Cr\textsuperscript{3+}→Cr\textsuperscript{2+}) and electrons (Fe\textsuperscript{2+}→Fe\textsuperscript{3+}) among cations of B site affect the electrical properties to a larger extent. Activation energy was decreased with increasing Cr ion concentration which confirmed the transition from ferromagnetic region to paramagnetic. The decrease in transition temperature with the increase in concentration of Cr ion was supported by Gouy’s balance data.

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