Influence of fuel to metal nitrate ratio on the structural properties of nickel ferrite

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Abstract: Sol-gel auto combustion synthesis is one of the best chemical methods for the synthesis of ferrite nano-particles. The ratio of fuel to nitrate is an important parameter in obtaining nano-particles of high quality. In the present paper we communicate our experimental results based on the influence of fuel to metal nitrate ratio on the structural properties of nickel ferrite. Nickel ferrite (NiFe₂O₄) nanoparticles were prepared by a well-known sol-gel auto combustion method taking citric acid as a fuel. We have prepared nano-particles of nickel ferrite using different ratios of fuel to metal nitrate 1:1, 1:2, 1:3, and 1:4. These samples are named as NF1, NF2, NF3 and NF4 respectively. All the samples are thermally characterized by TG-DTA. The TG-DTA analysis confirmed the ferritization temperature, which varies slightly as the ratio of fuel to metal nitrate varies. All the samples were sintered at an average temperature of 560 °C for 4 hours and used for further study. XRD was used to study the structure and phase purity of prepared nanoparticles. It has been concluded from XRD analysis that all the samples NF1, NF2, NF3 and NF4 show single phase nature with cubic structure. The crystallite size was obtained by Scherrer’s formula. It is found that the fuel to nitrate ratio influences the structural properties of nickel ferrite.

1. Introduction

Ferrites are the prominent magnetic materials consist of iron oxide (Fe₂O₃) and metal oxide (MO, M = Co, Ni, Zn, Cd, Cu, Mg, etc.). They possess both the electric and magnetic properties which make them different from all other magnetic materials. Their high electrical resistivity, high saturation magnetization, high Curie temperature, low eddy current and dielectric losses, high magnetocrystalline anisotropy constant etc. makes them useful in many technological applications. They can be used in antenna rod, transformer core, information storage device, sensors, catalysts etc [1, 2]. Ferrite crystallizes in three
groups as spinel ferrite, garnet and hexagonal ferrite. Spinel ferrite is represented by MFe$_2$O$_4$ where M is a divalent metal cation like Co, Ni, Mn, Mg, Cu, Cd, etc. Owing to their excellent electrical and magnetic properties spinel ferrites are currently being investigated on large scale for their possible use in several technological applications. In the recent years, spinel ferrite in nanocrystalline form have gained lot of importance due to their smaller size of the nanometer dimension, large surface to volume ratio, reactivity at atomic scale, more chemical stability, high homogeneity. Nanocrystalline spinel ferrites are therefore useful in drug delivery, hyperthermia, sensor, catalyst, water purification etc. areas [3, 4]. Many reports are available in literature on the synthesis and characterization of nickel spinel ferrite [5, 6]. In the family of spinel ferrite, (NiFe$_2$O$_4$) Nickel ferrite is a unique which exhibits excellent properties that are useful for many technological applications. Thus, the nickel ferrite has been investigated for its electrical and magnetic properties by many researchers [7-9]. The interest of researchers in nickel ferrite is increasing day by day and therefore their synthesis and properties are of prime importance. The properties of spinel ferrite can be improved lot by choosing appropriate synthesis method apart from synthesis method, synthesis parameters are also important in governing the properties of spinel ferrite. NiFe$_2$O$_4$ has been prepared by ceramic technique, chemical co-precipitation, hydrothermal, sol gel auto-combustion methods. The synthesis parameters such as pH, fuel, fuel to metal nitrate ratio, annealing temperature, annealing atmosphere etc are important and play important role in controlling size and shape of the nanoparticles. In the present study, we have prepared nickel ferrite nanoparticles by using sol-gel auto-combustion method and effect of fuel to metal nitrate ratio on the structural properties of nickel ferrite has been undertaken.

2. Experimental

Nickel nitrate (Ni(NO$_3$)$_2$.6H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O), and citric acid (C$_6$H$_8$O$_7$) of analytical reagent (AR) grade were used as received without any further purification. The metal nitrate to citric acid ratio was taken as 1:1, 1:2, 1:3 and 1:4 (metal nitrate to fuel ratio). The above precursors were dissolved separately in distilled water with constant stirring and then mixed together and stirred for 30 minutes and then adjusted the pH by adding ammonium solution drop by drop in it. The pH of solution is maintained to neutral (pH = 7). The neutralized solution was evaporated to dryness by heating at 80°C with continuous stirring. The solution become viscous and finally formed a very viscous brown gel. The viscous gel then burnt and forms floppy foam like structure in beaker. Thereafter a mortar and pestle was used to obtain a very fine powder after grinding. The fine powders were calcined at 560°C for 4 hrs in a muffle furnace. The prepared powder was characterized by different characterization techniques.

Characterization

To confirm the phase purity and to study the change in mass of a sample, NiFe$_2$O$_4$ ferrite as the function of temperature was investigated by TG-DTA (Thermal gravimetric analysis). The thermal analysis (TG-DTA) was carried out under varying temperature from 20°C to 1000°C. The phase purity and structural properties of prepared samples studied by recording the X-ray diffraction (XRD) pattern at room temperature by X-ray diffractometer (Bruker) with Cu K$_\alpha$ ($\lambda = 1.5406\AA$) radiation operated at 40 mA current and 40 kV voltage and 2$\theta$ scanning range from 20$^\circ$ to 80$^\circ$, at a speed of scanning ~2$^\circ$/min.

3. Results and discussion

3.1 Thermal studies
The material properties like TGA –DTA was investigated for all samples i.e. NF-1, NF-2, NF-3 and NF-4. Here in figure 1, TGA- DTA curve for a typical sample NF-1 is shown.

![Fig. 1: TG-DTA curve of a typical sample (1:1) of NiFe$_2$O$_4$](image.jpg)

It is observed from fig. 1 that peak at around 100$^\circ$C belongs to removal of water molecule. The second peak at around 300$^\circ$C corresponds to removal of impurities. There is no further weight loss above 600$^\circ$C. Therefore the decomposition temperature of the NiFe$_2$O$_4$ nanoparticles was considered here as 600$^\circ$C. Similar kind of change occurred in all remaining samples.

### 3.2. Structural studies

Fig. 2 represents the X-ray diffraction pattern of a typical sample NF-3 recorded at room temperature.

![Fig. 2: XRD pattern of a typical sample (1:3) of NiFe$_2$O$_4$](image.jpg)
The XRD pattern shows the reflections (220), (310), (311), (222), (400), (422), (511), (440) and (533). These reflections belong to cubic spinel structure. In addition to these planes, few impurity peaks are observed in XRD pattern. The impurity peak diminishes as fuel to metal nitrate ratio increases as 1:1 to 1:4. The ratio of fuel to oxidizer i.e. metal nitrate can be obtained from propellant chemistry approach the best ratio of metal nitrate to fuel is 1:3 in the present study. However, the ratio 1:4 is also good. The lower ratio 1:1 and 1:2 do not provide the sufficient energy required for the combustion process also it required more time as compared to ratio 1:3 and 1:4. Using ratio 1:3, we obtained very fine and more homogenous powder as can be seen from the XRD pattern. The XRD was used to determine the crystallite size and the structural parameters like lattice constant, X-ray density etc. The crystallite size (t) was calculated considering the most intense peak (311) and by using the relation

\[ t = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

Where, \( t \) = crystallite size, \( \theta \) = Diffraction angle and \( \beta = \) FWHM

The lattice constant (a) was determined by the relation,

\[ a = \frac{d\sqrt{N}}{g} \]  

(2)

Where, ‘a’ is lattice parameter, ‘d’ is inter-planer distance and ‘N’ is Miller indices

The other structural parameters are also calculated from standard relation [10] reported in the literature. The values of lattice constant (a), unit cell volume (v), X-ray density and crystallite size (t) calculated for all the four NF-1, NF-2, NF-3 and NF-4 sample are given in table 1. It can be observed from the table that, the structural parameter as get affected by the metal nitrate to fuel ratio. The lattice constant found to increase with increase in metal nitrate to fuel ratio.

| Sample   | a (Å)  | t (nm) | dX (g/cm³) | V (Å³) |
|----------|--------|--------|------------|--------|
| NF -1 (1:1) | 8.3321 | 19.958 | 5.3827 | 578.4 |
| NF -2 (1:2) | 8.3344 | 20.985 | 5.3783 | 578.9 |
| NF -3 (1:3) | 8.3364 | 22.157 | 5.3743 | 579.3 |
| NF -4 (1:4) | 8.3369 | 22.223 | 5.3714 | 579.7 |

4. Conclusion

In the present study, the NiFe₂O₄ spinel ferrite in nanocrystalline form have seen successfully prepared by sol-gel auto-combustion method for varying metal nitrate to fuel ratio. The decomposition temperature was confirmed through thermal study. The structural properties studied by X-ray diffraction analysis suggested the formation of single phase cubic spinel structure. There are some impurity peaks with lower intensity was observed from lower metal nitrate to fuel ratio. The lattice constant and crystallite size go on
increase with increasing metal nitrate to fuel ratio. Overall the synthesis parameter, metal nitrate to fuel ratio strongly influence structural properties.

5. Acknowledgement

Author R Dudhal is grateful to Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for TG-DTA facility and Punyashlok Ahilyadevi Holkar University, Solapur for XRD facility.

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