NANOCRYSTALLINE NiFe$_2$O$_4$ PARTICLES SYNTHESIZED BY CITRATE – UREA ASSISTED COMBUSTION PROCESS

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ABSTRACT

Nanocrystalline NiFe$_2$O$_4$ particles are prepared using citric acid urea assisted combustion process by varying the metal ions, citric acid and urea ratio as 1:1:0.5, 1:1:1 and 1:1:2. The prepared samples are characterized using XRD, FTIR, DSC and SEM-EDS techniques. The impurity free pure nanocrystalline (~20 nm) NiFe$_2$O$_4$ powder is obtained for M:CA: urea ratio 1:1:0.5 sample.

Keywords: Nanocrystalline NiFe$_2$O$_4$, SEM-EDS, DSC, XRD, FTIR

1. INTRODUCTION

Nanocrystalline ferrites (MFe$_2$O$_4$) are current focus of researchers because of their usage in numerous applications like recording media, ferrofluids, magneto optics, spintronics, microwave devices, etc. [1-3]. Apart from the electronic and magnetic applications, ferrites are also used as a gas, humidity sensor material and as an anode material for lithium ion battery [4,5]. Superior magnetic, dielectric and mechanical properties of nanocrystalline materials, compared to their respective conventional bulk, are due to the occupancy of majority of atoms at the grain boundaries. Different chemical routes are currently used for the synthesis of nanoparticles including co-precipitation, combustion, polyol, sol–gel, spray pyrolysis, micro emulsion and hydrothermal routes [6-10]. Among the available wet chemical routes, combustion route is capable of producing nanocrystalline powder at a lower temperature in a short time. In our present study, nanocrystalline NiFe$_2$O$_4$ powders are prepared using combustion process by varying the metal ions, citric acid and urea fuel ratio as 1:1:0.5, 1:1:1 and 1:1:2. The synthesized sample is calcined at different temperatures and characterized using XRD, FTIR, DSC, SEM-EDS techniques to confirm the formation of NiFe$_2$O$_4$ nanocrystals.

2. CITRIC ACID-UREA ASSISTED COMBUSTION SYNTHESIS

Nanocrystalline NiFe$_2$O$_4$ powder sample was prepared using citric acid urea assisted combustion route by varying the metal ions, citric acid and urea ratio as 1:1:0.5, 1:1:1 and 1:1:2. Analar grade precursor chemicals of nickel nitrate hexahydrate, ferric nitrate nanohydrate, citric acid and urea were used for the synthesis of nanocrystalline NiFe$_2$O$_4$ powder.

The required quantity of metal nitrate solutions were taken and sonicated for 10 minutes. The mixture of solution was continuously stirred at 353 K for an hour. The required amount of citric acid and urea solutions were added to the above solution on continuous stirring. The solution was evaporated at 353 K for 8 hours under constant stirring, which results the polymeric resin. The resins were further dried in an oven at 333 K for 24 hours to remove the excess water and the drying process caused the formation of dried foamy polymeric intermediate. Nanocrystalline NiFe$_2$O$_4$ powders were obtained by calcining the polymeric intermediates at 448 K and above. The complete process was investigated through XRD, FTIR, DSC and SEM techniques.

3. CHARACTERIZATION

The powder X-ray diffraction patterns were recorded on a PANalytical XPertPro X-ray diffractometer with Cu K$_{α}$ radiation of wavelength $λ=1.5418$ Å and scanned from 80-10$^0$. FTIR spectra were recorded on pellet samples using Shimadzu FTIR/8300/8700 spectrophotometer in the range of 4000 – 400 cm$^{-1}$ with 2 cm$^{-1}$ resolution for 20 scans. Thin transparent pellet samples were prepared using the dried gel sample, heated from room temperature to higher temperatures (623 K), and scanned with spectra pure KBr powder taken in 1:20 ratio. The DSC measurements were made on Mettler Toledo Star e System; module DSC 821e/500/575/414183/5278 under ambient air atmosphere. The polymeric intermediate sample, 3 mg, was taken in aluminium crucible and heated from 300 K to 773 K at a heating rate of 10K per minute. The microstructures of polymeric intermediate as well as the size of the NiFe$_2$O$_4$ particles and their elemental distribution were obtained.

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through SEM – EDS measurements using Hitachi S 3400N Scanning Electron microscope.

4. RESULT AND DISCUSSION

4.1 XRD

Fig 1 shows the powder X-ray diffraction patterns of NiFe$_2$O$_4$ samples of three different compositions; 1:1:0.5, 1:1:1 and 1:1:2. From Fig 1, it was observed that the XRD patterns of as synthesized NiFe$_2$O$_4$ polymeric intermediates of composition 1:1:1 and 1:1:2 calcined at 333 K showed the characteristic diffraction patterns of NiFe$_2$O$_4$. The XRD patterns of the calcined polymeric intermediate powders of compositions 1:1:0.5, 1:1:1 and 1:1:2 showed the characteristic diffraction patterns of the NiFe$_2$O$_4$ phase and further calcination increases the crystallite size of the sample. The samples of compositions 1:1:1 and 1:1:2 showed additional peak at 33$^\circ$, which corresponds to the Fe$_2$O$_3$ phase and phase pure NiFe$_2$O$_4$ was observed only for 1:1:0.5 composition. The formation of NiFe$_2$O$_4$ crystalline phase was confirmed by comparing the diffraction patterns with JCPDS # 74-2081 data. The crystallite size of the NiFe$_2$O$_4$ sample was calculated by using Scherer’s formula and it is found to be 20 nm for 1:1:0.5, 31 nm for 1:1:1 and 30 nm for 1:1:2 samples, which confirm that the prepared crystalline NiFe$_2$O$_4$ samples are in nano size. The lowest crystallite size is observed for 1:1:0.5 composition of the NiFe$_2$O$_4$ sample.

![XRD patterns](image)

Fig. 1 XRD patterns of NiFe$_2$O$_4$ samples of three different compositions (M:CA:Urea = 1:1:0.5, 1:1:1 and 1:1:2).

ammonium nitrate. This indicates that the addition of excess urea to the sample is not participated in the formation of polymeric matrix, rather it forms ammonium nitrate. The XRD patterns of the as synthesized NiFe$_2$O$_4$ sample of composition 1:1:0.5 shows complete amorphous nature, which indicate that the added urea and citric acid are completely take part in the polymeric matrix formation and hence, showed amorphous nature. The XRD patterns of the calcined polymeric intermediate powders of compositions 1:1:0.5, 1:1:1 and 1:1:2 showed the characteristic diffraction patterns of the NiFe$_2$O$_4$ phase and further calcination increases the crystallite size of the sample. The samples of compositions 1:1:1 and 1:1:2 showed additional peak at 33$^\circ$, which corresponds to the Fe$_2$O$_3$ phase and phase pure NiFe$_2$O$_4$ was observed only for 1:1:0.5 composition. The formation of NiFe$_2$O$_4$ crystalline phase was confirmed by comparing the diffraction patterns with JCPDS # 74-2081 data. The crystallite size of the NiFe$_2$O$_4$ sample was calculated by using Scherer’s formula and it is found to be 20 nm for 1:1:0.5, 31 nm for 1:1:1 and 30 nm for 1:1:2 samples, which confirm that the prepared crystalline NiFe$_2$O$_4$ samples are in nano size. The lowest crystallite size is observed for 1:1:0.5 composition of the NiFe$_2$O$_4$ sample.

4.2 FTIR

![FTIR spectra](image)

Fig. 2 FTIR spectra of NiFe$_2$O$_4$ samples of three different compositions (M: CA: Urea = 1:1:0.5, 1:1:1 and 1:1:2).
Fig. 2 shows the FTIR spectra of NiFe$_2$O$_4$ samples of three different compositions. From fig. 2, all the three different compositions of the synthesized samples showed the characteristic vibrational bands of organic groups and nitrates at 3450, 3195, 1719, 1635, 1568, 1384, 1139, 1070, 901, 834 cm$^{-1}$. The above observed IR bands confirm the presence of citric acid and urea in the sample. The FTIR spectra of calcined samples of three different compositions showed the characteristic IR bands at 600 and 430 cm$^{-1}$, which correspond to the formation of tetrahedral and octahedral structured spinel NiFe$_2$O$_4$ and also confirms the removal of organic residuals [11-12]. Nanocrystalline NiFe$_2$O$_4$ sample with high purity was observed for 1:1:0.5 composition. The organic impurity free NiFe$_2$O$_4$ sample is taken for further studies.

4.3 DSC

Fig. 3 shows the DSC thermogram of NiFe$_2$O$_4$ sample of composition (M:CA:Urea = 1:1:2) dried at 333 K. From fig. 3, it was observed that the combustion is retained up to 650 K and the organic fuels are start burning from 443 K onwards.

![Fig. 3 DSC thermogram of foamy polymeric intermediate of composition (M:CA:Urea = 1:1:2) dried at 333 K.](image)

The DSC thermogram showed two endothermic peaks one corresponds to evaporation of water and other endotherm may be due to the degradation of the sample before volume expansion. The poor exothermic reaction continues for a longer time and resulted unburnt carbon retain in the sample calcined around 623 K. This result is also reflected in FTIR analysis.

4.4 SEM

Fig. 4 shows the SEM images of as synthesized polymeric intermediate of NiFe$_2$O$_4$ samples with different citric acid urea ratios. NiFe$_2$O$_4$ sample of composition 1:1:0.5 showed better polymerization and formed very soft polymeric intermediate with high volume expansion. The NiFe$_2$O$_4$ samples of compositions 1:1:1 and 1:1:2 showed poor polymerization with less volume expansion and hard nature. The same is reflected as the formation of the crystalline phase confirmed from XRD results. The SEM images of the above compositions of NiFe$_2$O$_4$ samples showed the soft nature as well as hard flakes. The soft foamy nature of polymeric intermediate with high volume expansion avoids the agglomeration of particles during combustion reaction.

![Fig. 4 SEM images of foamy polymeric intermediates of all compositions (M:CA:Urea = 1:1:0.5, 1:1:1 and 1:1:2) dried at 333 K.](image)

4.5 SEM-EDS

The fine powdered NiFe$_2$O$_4$ sample of composition 1:1:0.5 calcined at 623 K is dispersed in acetone and poured over the aluminium stub is used for SEM-EDS measurements. Fig. 5 shows the SEM and EDS elemental mappings of NiFe$_2$O$_4$ sample of composition 1:1:0.5. From SEM image, the NiFe$_2$O$_4$ particles are dispersed uniformly and the particle size was varied form 150 to 300 nm. The elemental analysis confirmed the presence and uniform
distribution of Ni, Fe and O elements in the NiFe₂O₄ sample.

Fig. 4 SEM-EDS image of NiFe₂O₄ sample prepared with 1:1:0.5 composition

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Table 1 SEM-EDS results of NiFe₂O₄ sample prepared with 1:1:0.5 composition

5. CONCLUSION

The nanocrystalline NiFe₂O₄ sample was prepared using citric acid and urea assisted combustion process. The metal ions, citric acid and urea fuel ratio was varied as 1:1:0.5, 1:1:1 and 1:1:2. The crystalline phase formation was confirmed from XRD results. The crystallite size was calculated using Scherrer’s formula and it is found to be 20 nm for 1:1:0.5, 31 nm for 1:1:1 and 30 nm for 1:1:2 composition sample. The FTIR results confirm the bond and structural formation of citric acid, urea and NiFe₂O₄. The complete removal of impurity at 623 K for 1:1:0.5 composition is also confirmed from FTIR results. NiFe₂O₄ sample of composition 1:1:0.5 showed high pure final product at 623 K compared to other compositions. SEM image of as synthesized polymeric intermediate sample showed the foamy nature of the sample. The SEM-EDS analysis of the sample of composition 1:1:0.5 showed the uniform elemental distribution. The particle size varied form 150 nm to 300 nm. The elemental result showed the presence and uniform distribution of Ni, Fe and O elements in the NiFe₂O₄ sample.

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