

Microwave assisted sol-gel auto-combustion synthesis of NiCuFe₂O₄ nanoparticles using citric acid as an organic chelating agent: structural and optical studies

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Ferrite spinels may also contain mixture of two divalent metal ions, in which ratio of these divalent metal ions may vary, are called mixed ferrite. The cations distribution of mixed ferrite significantly affects the surface properties of ferrosinels making them catalytically active. Because of their small size and large number of cations, for co-ordination sites, nanocrystallites are capable of enhancing the rate of chemical reactions and are increasingly gaining popularity as reactive nanocrystallites.

Among the various methods, microwave combustion technique is probably opted for homogeneity, high purity and improved characteristics. The microwave energy is an internal means of heat energy generation and conversion. The microwave energy is transformed into heat energy by strong inter- molecular friction and rises the temperature of the precursor materials suddenly. The use of microwave energy as heating source, speeds up the chemical reaction and kinetics, improve the economical viability, and reduces the energy loss.

Complexant organic agents can effectively chelate metal ions with varying ionic sizes. They also serve as reductant being oxidized by nitrate ions, thus working as fuel in a synthetic method named auto combustion sol-gel. Citric acid (C₆H₈O₇) is most frequently used in producing in large variety of ferrites. It is inexpensive and is a more effective complexing agent than other complexant producing fine ferrite powder with smaller particle size.

In this present study, NiCuFe₂O₄ nanoparticles was prepared by microwave assisted sol-gel auto-combustion method employing nickel nitrate, copper nitrate, iron nitrate, ammonia and citric acid as an organic chelate agent. The nanostructured samples were characterized by XRD, SEM, DRS and FT-IR. X-ray and the FT-IR revealed the formation of cobalt ferrite cubic spinel type structure. The direct band gap was estimated using Kubelka-Munk method and is obtained from the DRS.

Keywords: microwave, sol-gel auto-combustion, NiCuFe₂O₄ nanoparticles, optical property, organic chelating agent

1. Introduction

NiCuFe₂O₄ is a member of the spinel ferrites, AB₂O₄. In spinel ferrites oxygen ions are in a fcc arrangement with the A ions in tetrahedral vacancies and B ions in octahedral vacancies. In normal spinel structure M²⁺ are in A sites and Fe³⁺ are in B sites but in inverse spinel structures M²⁺ are in B sites and Fe³⁺ are equally divided between A and B sites. The divalent and trivalent ions normally occupy the B sites in a random fashion [1]. Ferrite spinels may also contain mixture of two divalent metal ions, in which ratio of these divalent metal ions may vary, are called mixed ferrite. The cations distribution of mixed ferrite significantly affects the surface properties of ferrosinels making them catalytically active. Because of their small size and large

number of cations, for co-ordination sites, nanocrystallites are capable of enhancing the rate of chemical reactions and are increasingly gaining popularity as reactive nanocrystallites [2].

Various methods are used to synthesize ferrite nanoparticles, such as: combustion, mechano-chemical method, redox process, forced hydrolysis, co-precipitation, sol-gel, hydrothermal, polymer combustion method (PC), solid state method (SS), micro-emulsion, sonochemical, electrochemical and thermal decomposition method [3-11]. Among the various methods, microwave combustion technique is probably opted for homogeneity, high purity and improved characteristics. The microwave energy is an internal means of heat energy generation and conversion. The microwave energy is transformed into heat energy by strong inter-molecular friction and rises the temperature of the precursor materials suddenly. The use of microwave energy as heating source, speeds up the chemical reaction and kinetics, improve the economical viability, and reduces the energy loss [12].

Complexant organic agents can effectively chelate metal ions with varying ionic sizes. They also serve as reductant being oxidized by nitrate ions, thus working as fuel in a synthetic method named auto combustion sol-gel. Citric acid ($C_6H_8O_7$) is most frequently used in producing in large variety of ferrites. It is inexpensive and is a more effective complexing agent than other complexant producing fine ferrite powder with smaller particle size [13, 14].

In this present study, $NiCuFe_2O_4$ nanoparticles was prepared by microwave assisted sol-gel auto-combustion method employing nickel nitrate, copper nitrate, iron nitrate, ammonia and citric acid as an organic chelate agent.

2. Experimental

The starting materials for the synthesis of $NiCuFe_2O_4$ are $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, ammonia (30%) and citric acid monohydrate (98%) (CA). The required amount of metal nitrates and citric acid are taken so as to have a molar ratio of 1:1 and dissolved in 100 mL of deionized water. A required amount of ammonia is added into the solution in order to modify the pH value to about 7. The stoichiometric amount of surfactant was dissolved in minimum amount of water then added to the above solution. Dehydration of the solution was then done on a hotplate at $80^\circ C$ until a gel forms. Dry gels were subjected to microwave irradiation (20 at 900 W). During combustion large amounts of gas were given off and a lightweight massive powder formed quickly. The resulting "precursor" powder was lightly ground by hand, as well as calcined at $800^\circ C$ for 2 h in a furnace to remove any organic rest [15, 16].

3. Results and discussion

3.1 XRD analysis

X-ray diffraction pattern of $NiCuFe_2O_4$ is shown in Figure 1. X-ray diffraction confirms the formation of single-phase (fcc) spinel structure for $NiCuFe_2O_4$

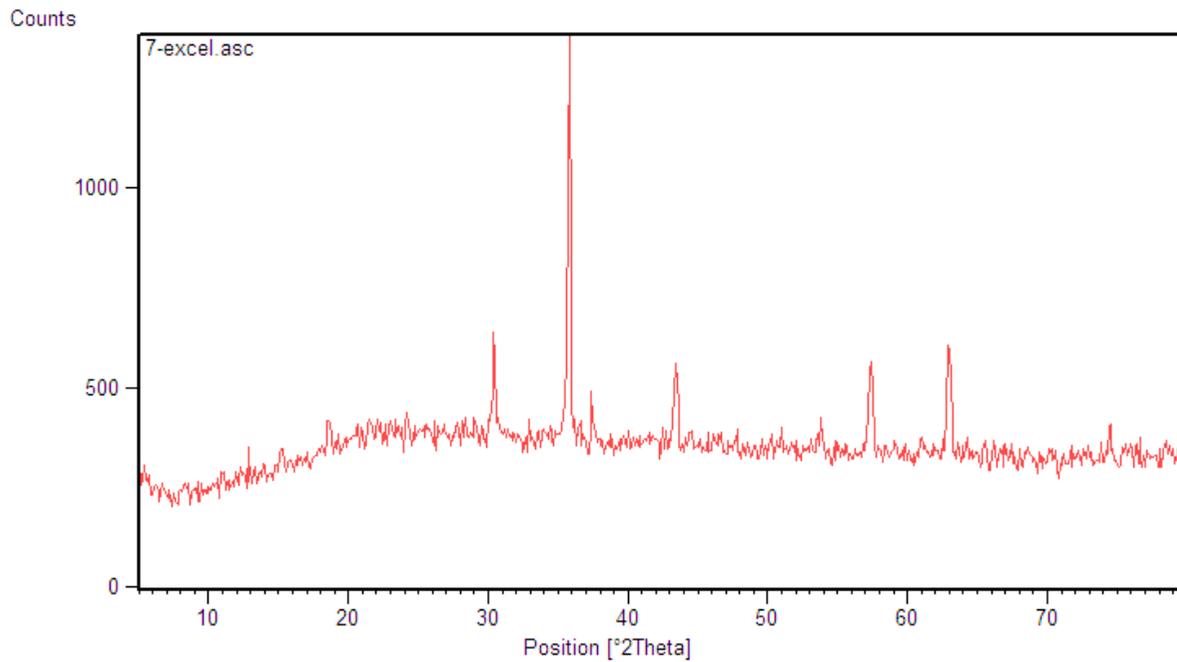


Fig. 1. XRD pattern of nanoparticles of $\text{NiCuFe}_2\text{O}_4$ ferrite.

3.2 FT-IR analysis

Figure 2 shows the FT-IR spectrum of the $\text{NiCuFe}_2\text{O}_4$ powders. The characteristic peaks of tetrahedral and octahedral complexes could be observed at 544 cm^{-1} and 450 cm^{-1} . It is clear that the normal mode of vibration of tetrahedral cluster is higher and normal mode of vibration of octahedral cluster is shorter. The tetrahedral cluster has shorter bond lengths and the octahedral cluster has longer bond lengths [15].

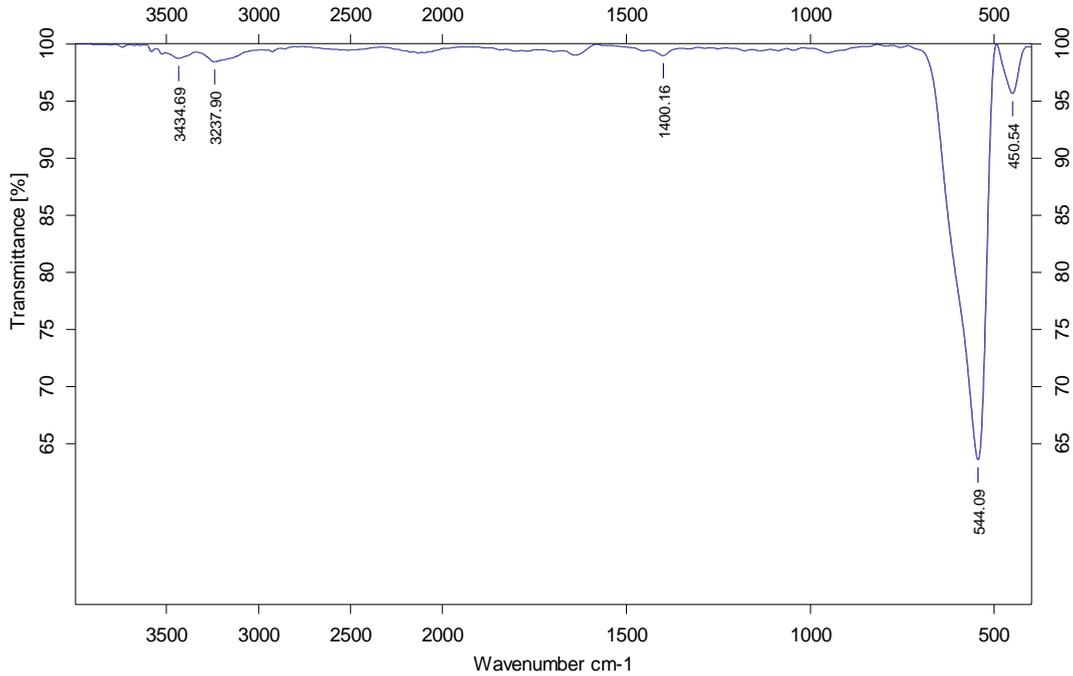


Fig. 2. FT-IR spectrum of nanoparticles of NiCuFe₂O₄ ferrite.

3.3 SEM analysis

The micrograph of NiCuFe₂O₄ ferrite is taken with SEM (Fig. 3). It is clearly seen in the micrograph that the sample possess spherical and tetragonal nanosize grains. In comparison with other samples, it was observed that the nanoparticles are single crystal, spherical and tetragonal, uniformly distributed, but not highly agglomerated.

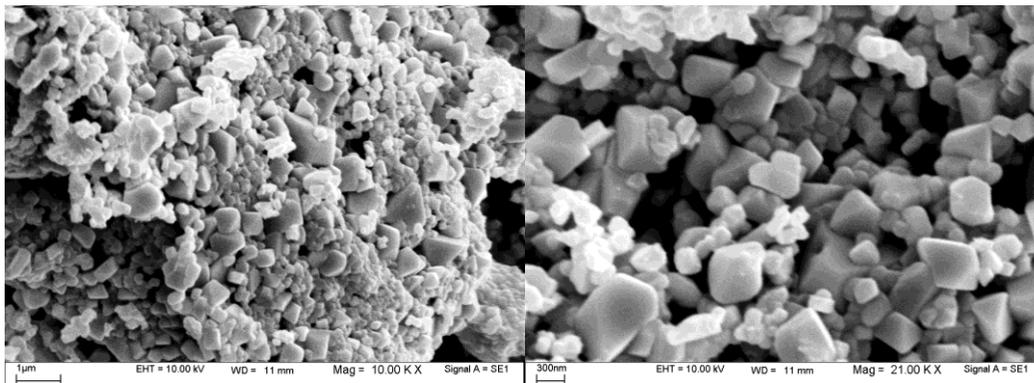


Fig. 3. SEM images of nanoparticles of NiCuFe₂O₄ ferrite.

3.4 DRS analysis

The analysis of optical absorption spectra is a powerful tool for understanding the band structure and band gap of both crystalline and noncrystalline materials. The optical properties of the ferrite samples were characterized by UV-DRS with the help of optical absorption data [17]. Optical band gap of NiCuFe₂O₄ ferrite nanoparticles was estimated using the Kubelka-Munk relationship. The Kubelka–Munk plot NiCuFe₂O₄ is presented in Figure 4. The calculated band-gap energies of NiCuFe₂O₄ was found to be 1.75 eV.

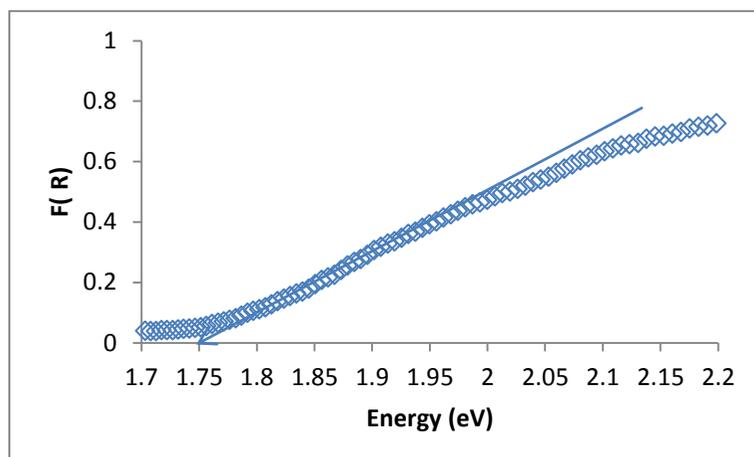


Fig. 4. The Kubelka–Munk plot for NiCuFe₂O₄.

4. Conclusion

NiCuFe₂O₄ nanoparticles have been successfully synthesized by microwave combustion technique. The nanoparticles were characterized by XRD, SEM, FT-IR and DRS. Powder XRD analysis and FT-IR spectroscopy confirmed formation of NiCuFe₂O₄ spinel phase. The particles size was estimated from SEM data. The energy band gaps were calculated by Kubelka-Munk model from UV–Vis absorption. The use of microwave energy as heating source, speeds up the chemical reaction and kinetics, improve the economical viability, and reduces the energy loss.

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