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Synthesis and Characterization of Nanostructure Copper Ferrites by Microwave Assisted Sol-Gel Auto-Combustion Method

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ABSTRACT
NanostructuredCuFe$_2O_4$ ferrites having interesting electrical, magnetic and structural propertieswere synthesized by microwave assisted sol-gelauto-combustion method. Sample was calcined at 800 ^oC.X-ray diffraction study confirms single phase, cubic inverse spinel structure of CuFe$_2O_4$. Particle size of nanoferrite was confirmed by the TEM. Lattice parameter, X-ray density, Radius of octahedral and tetra-herald sites, lattice strain, polaron hopping radius were calculated for the sample.
KEY WORDS: Spinel Ferrites, Copper ferrite, Spinel Sol-Gel Synthesis, X-RD Characterization,

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Introduction

Ferrites are important class of materials and among them, spinel ferrites are of prime importance. Spinel ferrites have high thermodynamic stability, magnetic properties, high electrical resistivity and catalytic activity in addition to their resistance to corrosion and so they are used in telecommunication, permanent magnet, electronic devices, data storage, catalyst, and drug delivery. Magnetic nanoparticles of spinel ferrites and their related structures have been investigated for nearly four decades, due to their theoretical and technological relevance, especially for addressing the fundamental relationships between various physical properties and their composition and method of synthesis [1-4].

Copper ferrite (CuFe2O4) is one of the important spinel ferrite as it has paramount advantages over other type of magnetic materials due to its unmatched flexibility in magnetic and mechanical parameters, high stability, high quality, low cost and low eddy current losses over a wide range of frequency.Copper ferrites are distinguished from the other spinel ferrites in two aspects: first they have distorted tetragonal structures and second their inability to have a cation/oxygen ratio higher than ¾ [5]. The tetragonal structure is stable at room temperature and changes into cubic phase around 400 ^oC temperature due to John-Teller distortion [6,7,8].Copper ferrite has a nearly complete inverse spinel structure and Cu^{2+} distribution between tetrahedral and octahedral sites depends on the actual heat distribution. The c/a ratio influenced by Cu^{2+} distribution [9]. The cubic structure possesses a larger magnetic moment than that of the tetragonal one, because there are more cubic ions (Cu^{2+}) at tetrahedral sites in cubic structure as compared to that in the case of tetragonal structure[10].

Copper ferrites (CuFe2O4) are used in different applications such as catalysts [11,12,13,14,15], Li-ion batteries [16,17], magnetic refrigeration,absorbent materials [18,19],sensors [20,21], inter-body drug delivery [22,23,24], magnetic refrigeration systems [25]. Unlike ferromagnetic metals, ferrites are also good electrical insulators [26]. Microstructure and magnetic performance of ferrites considerably depends upon chemical composition of sample.

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Out of these,microwave assisted sol-gel auto-combustion method is most convenient to synthesize low cost copper ferrite (CuFe2O4) because of its simplicity and results uniform and ultrafine nano particles with interesting physical, magnetic and electrical properties. In the present study, we applied microwave assisted sol-gel auto-combustion method for synthesizing the nano ferrites. The open-ended nature of the results of the earlier studies has motivated a systematic characterization of these materials using XRD, and TEM techniques.

Experimental

In current research work, cupric spinel ferrite with formula $CuFe_2O_4$ were synthesized by Microwave assisted sol-gel auto combustion method. The starting materials to synthesize nanostructure spinel copper ferrite sample were AR grade $Cu(NO_3)_2.3H_2O$, $Fe(NO_3)_3.9H_2O$, and urea, NH_2-CO-NH_2 as a fuel. All the chemicals were weighed on a digital balance. The stoichiometric amounts of AR grade metal nitrates were dissolved in 30 ml triple filtered de-ionized distilled water in a beaker and was continuously stirred for about15 minutes so that all the chemicals were dissolved and a greenish solution was obtained. The urea $CO(NH_2)_2$ as fuel was also dissolve in de-ionized water which was used as reducing agent to supply requisite energy to initiate exothermic reaction amongst oxidants. This solution of homogenous mixture was put on the magnetic hot plate at 60^0C for about 5 hours with continuous stirring. After sometime, the solution turns into gel which is placed in modified digitally controlled microwave. The gel get burnt by self propagating auto-combustion reaction evolving large volumes of gases (N_2, $NH_3$and CO_2) and finally gets converted in brown ash powder. The entire combustion process, which produces copper ferrite powder,takes about 7 min. The ash powder of samples was crushed and ground in the pestle mortar for 4 hours to have ultrafine spinel copper ferrite. The synthesized sample was calcined at 800^0C for about 8 hours in the muffle furnace to obtain monophase cubic copper ferrite.

Results and Discussion

The structural characterization was carried out using the X-ray diffractomerter with a diffracted beam of monochromatic X- ray $Cu\,K_\alpha$ -radiation (λ = 1.54056 Å) source between the Bragg Angles 10° to 80° The 2θ vs. intensity data is as shown in Figure 1. All Bragg reflections have been indexed,which include (220), (311), (400), (511) and (440) planes, which confirm the formation of cubic spinel structure with space group Fd3m in single phase without any impurity peak. The strongest reflection comes from the (311) plane, which denotes the spinel phaseconfirmed with JCPDS data (Card no. 00-025-0283). The miller planes indices are indexed by using Powder X software. The indexed *d*–values and lattice parameters of samples are summarized in table format (Table1).The crystallite size was calculated for the all the com-positions using the high intensity (311) peak and using Scherrer Formula $D = \frac{0.89\lambda}{\beta cos\theta}$ while taking into account the instrumental broadening [27].

where λ wavelength of monochromatic X- ray $Cu\,K_\alpha$ radiation (λ = 1.54056 Å), diffraction angle $2\Theta = 35.952^o$, and β is full width at half maxima (FWHM) of most intense diffraction peak corresponding to (311) plane, $\beta = 0.502^o$.The particles size was found 16.47 nm.Interplaner spacing *d* between planes was also estimated from XRD data *d* = 2.49710°A. Lattice parameter *a* was estimated using relation $a = d\sqrt{h^2 + k^2 + l^2}$. Volume of unit cell$V = a^3$ was also calculated.

Actual density (X-ray density) ρ_X of the synthesized sample was estimated using relation given by by Smith and Wijn,

$\rho_X = \frac{Z\,M}{N\,V}$.

where M is the molecular weight of the sample(239.24 gm), N_A is the Avogadro' snumber (6.023 x 10^{-23}), Z = 8 as there are 8 formula units in a unit cell and V is volume of unit cell $V = a^3$.

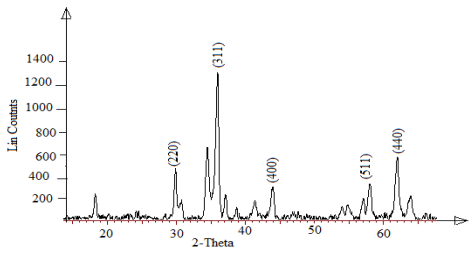


Figure1. XRD pattern of CuFe2O4 sample calcined at 800 ºC

Lattice strain was calculated using relation $\varepsilon = \frac{\beta}{4\,tan\theta}$. It was found 2.302×10^{-2}.

Table 1

Lattice parameter a (Å)	Volume $V = a^3$ (Å ^{3})	M (gm)	X-ray Density $d_x=8M/Na^3$ g/cm^3	Particle Size (nm)
8.28194	568.06327	239.24	5.5946917	16.47 nm

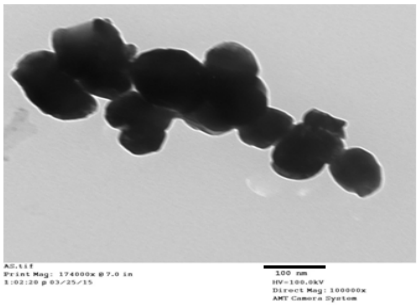
The radius of tetrahedral site (r_A) and octahedral site (r_B) has been determined using the relations given below [20]

$$r_A = \sqrt{3}\left(u - \frac{1}{4}\right)a - r(O^{2-})$$

$$r_B = \left(\frac{5}{8} - u\right)a - r(O^{2-})$$

Here, by taking the oxygen positional parameter u as 0.379 Å and radius of oxygen ion (O^{2-}) as 1.32 Å, we obtained $r_A = 0.53047\ A^o$ and $r_B = 0.71736\ A^o$.

The transmission electron micrograph (TEM) image of the sample is shown in Figure2. The nanostructure of the powder shows the cubic spheres. The surfaces of the grains are smooth and the grain edges are sharp.



Figur2 TEM image of the $CuFe_2O_4$ sample calcined at 800 ºC

Conclusion

Spinel ferrite CuFe2O4have been successfully synthesized by microwave assisted sol-gel auto-combustion method. The nanoparticles were characterized by XRD and TEM. Powder XRD analysis confirmed formation of CuFe spinel phase. The particle size, lattice strain, radius of tetrahedral site (r_A) and octahedral site (r_B) were estimated XRD data.

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