STRUCTURAL PROPERTIES AND MICROSTRUCTURE OF COBALT FERRITE PARTICLES SYNTHESIZED BY A SOL-GEL AUTO COMBUSTION METHOD

ANAND RAVAL*

[†]*Department of Physics, Gujarat University,
Ahmedabad-380009, Gujarat, India
ravalanand_30@yahoo.com*

NITAL PANCHAL

*Department of Physics, Gujarat University,
Ahmedabad-380009, Gujarat, India
nituahd@gmail.com*

RAJSHREE JOTANIA

*Department of Physics, Gujarat University,
Ahmedabad-380009, Gujarat, India
rbjotania@gmail.com*

Synthesis and characterization of Cobalt ferrite powders by a sol gel combustion process is focused in the present work. The prepared precursors was calcined at 950° C for 4 hours in order to get cobalt ferrite powder. The effect of metal nitrates/citric acid ratio (referred as x) of CoFe_2O_4 on structural and micro-structural properties was investigated. The structural characterization on CoFe_2O_4 ferrite samples were carried out using the X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques. Phase identification and crystallite size of calcined powder were determined using XRD analysis. The formation of the ferrite is confirmed by FTIR results. The morphology of prepared CoFe_2O_4 ferrite samples (with $x = 0.5, 1.0, 1.5$ and 2.0 , where x is metal to citrate ratio) was studied using a scanning electron microscopy.

Keywords: Cobalt ferrite; auto-combustion method, SEM.

1. Introduction

Ferrites are electrically insulating material and have good electrical, magnetic and mechanical properties. Among the different types of ferrites, the CoFe_2O_4 spinel ferrite is one of the most versatile from the view point of their large number of potential applications. CoFe_2O_4 ferrite possesses large crystalline anisotropy and reasonable magnetization, as potential predominant magnetic and electrical resistive material, which has been applied in high density magnetic recording media, high performance electromagnetic and spintronic devices [1, 2]. Spinel CoFe_2O_4 has Face- Centered Cubic (FCC) structure with a large unit cell. There are two kinds of lattice for cation occupancy,

mainly two sites namely A (tetrahedral) and B (octahedral). In a normal spinel structure Co^{2+} occupying tetrahedral A sites, while Fe^{3+} is sitting on the octahedral B sites. In inverse spinel structure, A site being Fe^{3+} ions, while B sites populated by Co^{2+} and Fe^{3+} ions.

Ferrite can be prepared by using various experimental techniques like ceramic, hot spraying, evaporation condensation, matrix isolation, laser-induced vapour phase reactions and aerosols but most types of nano-particles prepared by these methods, gives broad particle size distribution and coarse particles so additional milling is required. Other chemical methods are co-precipitation, sol-gel, ball milling, citrate precursor, hydrothermal, microemulsion [3-11]. Among above mentioned methods; a sol-gel process is less complicated and inexpensive method than the others.

In present work we focused on the synthesis and physical properties of cobalt ferrite powders prepared by a sol gel auto combustion technique. This is unique combination of the chemical sol-gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of desired metals and some organic fuel, giving rise to porous fluffy product with large surface area. The effect of different metal to nitrate ratio on crystallite size and structural properties of prepared cobalt ferrite particles has been investigated.

2. Experimental procedure

A sol- gel auto combustion method [3] is used to prepare CoFe_2O_4 particles with different metal nitrate/citric acid ratio referred as x (1:x, where $x = 0.5, 1.0, 1.5, 2.0$). Starting materials are Cobalt (II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Mw = 291.04 g/mol.), Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Mw = 404.00 g/mol.) and Citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Mw = 210.14 g/mol.). An aqueous solution of citric acid was mixed with metal nitrates solution under vigorous stirring. To adjust pH of 7.0, the ammonia solution was slowly added in mixture. The solution was heated on hot plate at 80°C to evaporate the water. During evaporation, the solution become viscous and finally formed a gel and by continuous heating the gel is ignited, the combustion rapidly propagated forward until all the gel burnt out completely to form ash and porous product was obtained. The as – burnt obtained powder was calcined at 950°C for 4 hours to get final product of cobalt ferrite powder.

3. Characterization

The structural characterization on CoFe_2O_4 ferrite samples ($x = 0.5, 1.5$ and 2.0) were carried out using the X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). Microstructures of prepared CoFe_2O_4 powder samples ($x = 0.5, 1.0, 1.5$ and 2.0) were studied using a scanning electron microscopy.

4. Results and discussion

4.1. XRD analysis

XRD measurements were carried out at room temperature on X-ray diffractometer model no. Make – Seifert; XRD 3000 PTS with scanning rate of 0.08°/min using CuK_α radiation ($\lambda=1.5406 \text{ \AA}$). The 2θ Bragg angles were scanned over a range of 20°–80°. The XRD patterns of CoFe_2O_4 powders sintered at 950°C for 4 hours with different metal to citrate ratios; $x = 0.5, 1.5, 2.0$ are shown in figure 1. The crystalline phases of the sintered samples were identified by X-ray powder diffraction using a Powder-X software. The obtained [hkl] planes of CoFe_2O_4 samples are in agreement with reported data (JCPDS card no. 77-0426) are illustrated in Table 1. XRD patterns show that all prepared samples have a single spinel phase. The characteristic reflection of the spinel phase is clearly evident in the XRD pattern. Cobalt ferrite phase has an inverse spinel structure with Co^{2+} ion occupying half of the octahedral (B) sites, i.e. $\text{Fe}^{3+}(\text{Co}^{2+}\text{Fe}^{3+})_2\text{O}_4$. The XRD broadening lines show that produced grains are very fine.

Fig. 1 XRD patterns of CoFe_2O_4 samples calcined at 950°C for 4 hours

The crystallite size of CoFe_2O_4 powder samples were calculated by the X-ray line broadening technique employing the X-ray Debye-Scherrer formula [12], using most intense XRD [311] peak;

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad (1)$$

Where, D is the crystallite diameter in nm, λ is the radiation wavelength ($\lambda = 1.5406 \text{ \AA}$ for CuK_α radiation), β is the corrected half width and θ is the diffraction peak angle. The calculated crystallite size, lattice parameter a ($\text{\AA}$), volume V ($\text{\AA}^3$) of CoFe_2O_4 ferrite samples with different metal to citrate ratios are listed in Table 2. It is clear from table 2 that there is not much change in crystallite size, but there is slight increase of lattice

constant and cell volume for X = 0.5, 1.5 and 2.0 samples; also believe these concentration (ratios) of are suitable to form nano particles.

Table 1. Diffraction angle and [hkl] of CoFe₂O₄.

No	x = 0.5		x = 1.5		x = 2.0	
	Diffraction angle (2θ°)	[hkl]	Diffraction angle (2θ°)	[hkl]	Diffraction angle (2θ°)	[hkl]
1	30.06	220	35.40	311	30.02	220
2	35.43	311	43.05	400	35.38	311
3	43.09	400	53.42	422	43.02	400
4	53.44	422	56.97	511	53.43	422
5	57.00	511	62.58	440	56.94	511
6	62.61	440	74.02	533	62.53	440

Table 2: The crystallite size, lattice parameters and cell volume of CoFe₂O₄

Sr. No.	Metal to Citrate Ratios (1: x), x	Lattice Parameters, a = b = c (Å)	Cell Volume V (Å ³)	Crystallite Diameter D (nm)
1.	0.5	8.3880	590.17	23.82
2.	1.5	8.3921	591.04	22.61
3.	2.0	8.4000	592.70	23.64

Fig. 2 FT-IR spectra of CoFe₂O₄ powders calcined at 950°C for 4 hrs in air atmosphere.

Infrared absorption spectra (FT-IR) of calcined CoFe₂O₄ powders with different metal to citrate ratio x =0.5, 1.5, 2.0 were recorded on a Bruker Tensor 27 spectrometer in wave number range of 400-4000 cm⁻¹. FTIR spectra of all samples are shown in figure 2. The

existence of strong absorption bands around 560 cm^{-1} and 450 cm^{-1} are due to stretching of metal oxygen (M-O), which attributed to the formation of the ferrite phase.

Micrographs were recorded on a LEO SEM model no. S - 440i. The SEM images of all CoFe_2O_4 ferrite samples are shown in figure 3 (a-d). It is clear from Fig. 3(a-d) that grown CoFe_2O_4 particles are well developed; having non-uniform morphology with the individual particles are typically less than one micron size but there is agglomeration of particles. It is well known that the magnetic inter-particle interaction is dominant between larger magnetic particles due to the magnetic attractive force. There is the magnetic attractive force among non-uniform, coarse crystals lead to the formation of agglomeration. We conclude from SEM analysis that non-uniform morphology and grown CoFe_2O_4 particles have agglomeration due to magnetic force.

Fig. 3 SEM micrographs of CoFe_2O_4 powders sintered at 950°C for 4 hrs in air atmosphere for metal to nitrate ratio, x (a) $x=0.5$, (b) $x=1.0$, (c) $x=1.5$ and (d) $x=2.0$.

5. Conclusions

Spinel ferrite CoFe_2O_4 powders with different metal to citrate ratios were successfully synthesized using a sol-gel auto combustion method. Experiments results of XRD, FTIR and SEM summarized as follows:

- (i) The characteristic reflection of the spinel phase is clearly evident in the XRD pattern.
- (ii) FT-IR results confirm the formation of the ferrite.
- (iii) SEM micrographs show non-uniform morphology and grown CoFe_2O_4 particles have agglomeration due to magnetic force.

Acknowledgments

This work was carried out under DRS-SAP program of UGC.

References

1. T. M. Whitney, J. S. Jiang, P. C. Searson, C. Chien, *Science* **261**, 1316 (1993).
2. J. J. Versluijs, M. A. Bari, J. M. D. Coey, *Phys. Rev. Lett.* **87**, 026601 (2001).
3. S. Albuquerque, J. D. Ardisson, W.A.A. Macedo, M. C. M. Alves, *J. Appl. Phys.* **87**, 4352 (2000).
4. B. Jayadevan, K. Tohji, K. Nakatsuka, A. Narayanasamy, *J. Magn. Magn. Mater.* **217**, 99 (2000).
5. M. Mozaffari, J. Amighian, *J. Magn. Magn. Mater.* **260**, 244 (2003).
6. Upadhyay, H.C. Verma, *Appl. Phys. Lett.* **85**, 2074 (2004). doi:10.1063/1.1786368
7. L. J. Cote, A. S. Teja, A. P. Wilkinson, Z. John Zhang, *Fluid Phase Equilibria* **210**, 307 (2003).
8. Y. Okazaki, M. Lixin, Y. Ohya, Sh. Yanase, Sh. Hashi, *J. Mater. Process. Technol.* **181**, 66 (2007).
9. X. Li, C. Kutal, *J. Alloys Compds.* **349**, 264 (2003).
10. N. Moumen, M.P. Pileni, *Chem. Mater.* **8**, 1128 (1996).
11. D.S. Mathew, R.-S. Juang, *Chem. Eng. J.* **129**, 51 (2007).
12. B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA, 102 (1978).