SYNTHESIS OF NANOCRYSTALLINE Cd-FERRITE PREPARED BY OXALATE CO-PRECIPITATION METHOD

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ABSTRACT

Cadmium ferrite was synthesized by oxalate co-precipitation method using high purity sulphates. The synthesized material is characterized by X-ray Diffraction studied (XRD), Scanning Electron Microscopy (SEM) and Fourier Trans formed Infrared Radiation (FT-IR) techniques. The samples were sintered at 500^0 C for 4hr. The X-ray diffraction analysis confirms the formation of single phase cubic spinal structure of the sample. The FT-IR spectra show two strong absorption bands around in the range of $400cm^{-1}$ and $800cm^{-1}$ on the tetrahedral and octahedral respectively. The lattice constant, X-ray density, physical density, crystallite sixe , site radi (r_A, r_B) bond length(A-O,B-O) on tetrahedral (A- site) and octahedral (B- site) were calculated for the sample. The lattice constant and crystallite size are 8.69 and 33.4 nm respectively. The SEM study shows that the grain size is 0.15µm.

Keywords: Chemical synthesis, Crystallite size, Bond length, XRD.

1. INTRODUCTION

Now-a-days the vast growing industries, various machines and an increasing large number of vehicles are responsible for spoiling the healthy life of human begins and all living organisms. Air pollution is found to be very dangerous as it is related to the respiratory system [1]. Cadmium ferrite is spinel ferrite and antiferromagnetic [2]. Magnetic spinel ferrites are used in ferrite cores, transducers, electromagnetic wave absorbers, magnetic recorders, drug delivery, magnetic fluids [3]. Cadmium ferrite despite its non-magnetic behaviour has attracted interest in the last decade due to its potential applications as gas sensors [4] and photocatalysts [5]. These materials need to be nanostructure with a high specific surface area.

The ferrite powders are prepared by the high temperature solid state reaction, sol –gel method, ball milling and co-precipitation method [6-9]. The solid state sintering route of producing these materials requires high sintering temperature, as well as long sintering time. The ferrites in present work have been synthesized by chemical solution method known as oxalate co-precipitation method. The advantage of this method is that it results in very fine, reactive, high purity and homogenous powers.

In the present study, we report preparation of $CdFeO_4$ by oxalate co–precipitation method their characterization by XRD, SEM and FTIR techniques.

2. MATERIALS AND METHODS

Synthesis of $CdFe_2O_4$ ferrites were prepared by the oxalate co precipitation method the high purity starting materials $CdSO_47H_2O$ (purity 99.99%) and $Fe_2SO_47H_2O$ (purity 99.5%, Thomas baker). These chemical were weighed in desired stoichimetric proportional and dissolved in distilled water. The pH of the solution was maintained at 4.8 by drop wise addition of concentration H_2SO_4. The resulting solution was heated at 80^0 C for 1 hr in order to complete the ionization of metal surfaces. The precipitating reagent was prepared in distilled

water by adding required proportion of AR grade ammonium oxalate. The precipitating reagent was added by drop in to metal sulfate solution with constant stirring until the process in precipitation was complete. The process of precipitation can be explained by following chemical reaction

$CdSO_4 + 2 H_2O + C_2O_4 \rightarrow CdC_2O_4 2H_2O + SO_4^{---}$

$FeSO_4 + 2H_2O + C_2O_4 \rightarrow FeC_2O_4 2H_2O + SO_4^{---}$
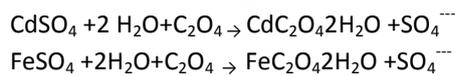
The resultant precipitation was solid solution of cadmium oxalate and ferrous oxalate. The precipitate along with solution was digested on sand bath for 1h in order to settle down the precipitate at the bottom of the beaker. The precipitate was filtered by using what's man filter paper no. 41 with help of distilled water in order to remove sulphate ions. The absence of sulphate ion in the filtrate was conformed with a barium chloride test. The co precipitate product was dried and present at 400^{0}C for 2 h in air. The presinterted powder was milled in an agate mortar. The AR grade acetone was used as a base. The powder was finally sintered at 500^{0}C for 4h followed by slow cooling the furnace. The rate of heating and cooling was 80^{0}C/h. The sintered power was milled and pressed in the pellets of 0.13 m diameter by applying pressure of 5.3n/m^{2}using a hydraulic pressure machine. Polyvinyl alcohol wt% was used as a binder. The pellets were finally sintered at 500^{0}C allowed to cool naturally.

The X-ray powder diffraction (XRD) patterns were obtained at room temperature by using philps PW-3710 X-ray powder diffracto meter. The diffraction patterns were recorded at steps size of 0.02^0 in angular range of 20^0-100^0. The crystallite size was calculated by Scherrer formula. The scanning electron microscopy was carried by analyze the microstructure of fractured surface of the pellets using the SEM JEOL-JSM 6360 MODEL, JAPAN. Infrared absorption spectra of powered samples were record in the range of 350-800 cm^{-1} using perkin-Elmer FT-IR spectrum one spectrometer by KBr pellet technique.

3. RESULT and DISCUSSION

3.1 X-ray diffraction

The X-ray diffractograms of CdFe$_2$O$_4$system is present in Fig. 1. The presence of (220), (311), (222),

(400), (420) and (511) planes in the diffraction patterns conforms formation of cubic spinel structure. The lattice constant 'a' of the samples was calculated by using the formula [10].

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

Where, d$_{hkl}$ is the observed inter planer distance of or hkl planes. The calculated value of lattice constant of ferrite is 8.34 A^0. The average crystallite size of all samples is determined for the (311) peak using Debye scherrer formula [11].

$$D = \frac{0.94\lambda}{\beta\cos\theta} \qquad (2)$$

Wavelength of X-ray (λ = 1.54439A^0)

The average crystallite size 'D' of the sample is 35.96 nm. The average crystallite size of studied sample is smaller than that prepared by ceramic method [12]. Using lattice constant data the 8.34 A^0 X-ray density for sample was calculated by using the relation

$$\rho_x = \frac{8M}{Na^3} \qquad (3)$$

Where, M is the molecular weight of the sample (kg). N is Avogadro's number (per mole) and 'a' is lattice constant (A^0). The X-ray density of sample is 5.64gm/cc. The X-ray diffraction data are further used to calculate the ionic radii (r$_A$, rB) and bond lengths (A-O and B-O) on tetrahedral A-sites and octahedral B- sites of cubic spinal structure by using the relation from literature [13].

$$A - o = (u - \frac{1}{4})a\sqrt{3} \qquad (4)$$

$$B - O = (\frac{5}{8} - u)a \qquad (5)$$

$$r_a = (u - \frac{1}{4})a\sqrt{3} - r(O^{2-}) \qquad (6)$$

$$r_B = (\frac{5}{8} - u)a - r(O^{2-}) \qquad (7)$$

Where, a is the lattice constant (A^0), r(O^{-2}) is the radius of oxygen ionic radii (4.96A^0) and u is the oxygen ion parameter u=0.382 for CdFe$_2$O$_4$. The values of site radii (r$_A$, r$_B$) and bond length (A-O and B-O) are summarized in the table. The A-site and B-site radii are found to be in good agreement with those reported by Standley [13]. The bond length on

A-site is less than that on B-site. From table the calculated of bond length is A-O = (1.88) and B-O = 2.00 and ionic radii r_A =0.53 A^0 and r_B =0.65 A^0

3.2 Scanning Electron Microscopy

SEM microphotographs of fractured surface of pellet sintered at 500^{0}C for all the compositions are shown in the Fig.2. The average grain size of the sample is calculated by the equation [14]

$$G_a = \frac{1.5L}{MN} \qquad (8)$$

Where, L is total test line length (m), M is the magnification and N is the total number. The reduction in grain size is found due to method of preparation.

3.3 Infrared spectroscopy

The infrared spectrum of $CdFe_2O_4$ is shown in Fig. 3. The FT-IR spectra are found to exhibit two major absorption bands in the range 350 cm^{-1} to 800 cm^{-1} the high frequency band (υ_1) in the range 565.1cm^{-1} And lower frequency band (υ_2) is the range 425.7 cm^{-1}. According to Waldron [15] the vibration of unit cell of the spinal can be constructed in the tetrahedral (A) sites and octahedral (B) sites. So the absorption (υ_2) is caused by scratching vibration of the tetrahedral metal - Oxygen vibration in octahedral sites. The band position of υ_1 and υ_2 for the sample is given in table.

Crystallite size (nm)	Lattice constant (A^o)	Grain Size (μm)	Absorption bands		X-ray Density (ρ_x)	Ionic radii (A^o)		Bond length (A^o)	
			υ_1	υ_2		r_A	r_B	A-O	B-O
35.96	8.34	0.15	565.1	425.7	4.96	0.531	0.65	1.88	2
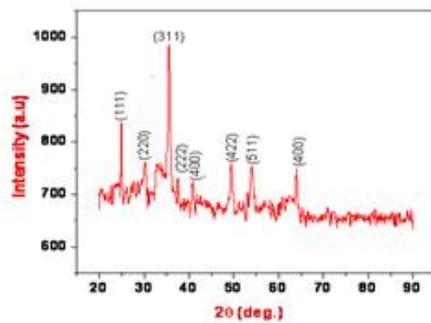
Fig. 1 XRD patterns of CdFe$_2$O$_4$
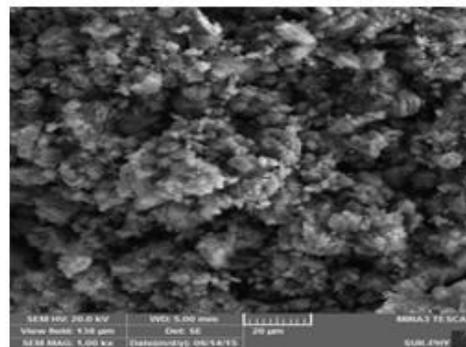
Fig. 2 SEM patterns of MgFe$_2$O$_4$
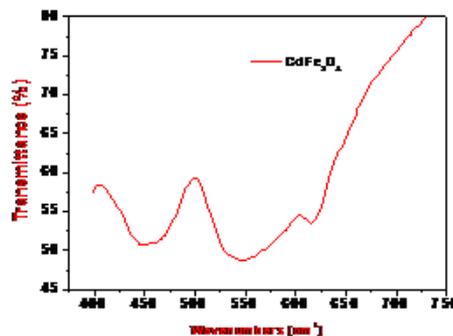
**Fig. 3 FT-IR of CdFe$_2$O$_4$**

4. CONCLUSION

The Cd ferrites have been prepared successfully by using oxalate co-precipitation method at sintering temperature 500^0 C for 4 h. The average crystallite size and lattice constant is 35.96 nm and 8.34 A^0 respectively. The grain size is smaller than that prepared by ceramic method. The values of site radii (r_A, r_B) and bond length (A-O and B-O) are found to be in good agreement with those reported by Standley . Two major absorption bands are found in frequency range.

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