



PHYSICAL CHARACTERISTIC OF COMPOSITES $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ PREPARED BY SOL-GEL METHOD.

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ABSTRACT :

High Temperature properties in nanocomposites have received significant attention in recent years due to its widespread applications. Several synthesis techniques have been employed to develop these spinel nanopowders. Sol-Gel synthesis provides lower processing temperatures, control over purity, composition and easy introduction of doping elements. In this work an sol-gel route was adopted for preparation of nanocrystalline $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. The gels of compositions were developed by copper nitrate, zinc nitrate, ferric nitrate and ethyl alcohol as precursors. The gel obtained is dried to room temperature and heated to 850⁰c in atmospheric temperature. The structure and thermal behavior of these nanopowders was studied by utilizing various characterization techniques. X-ray diffraction spectra were studied for confirming the formation of crystalline $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ phase. The mean crystal size calculated using Scherrer's equation was 290 nm. Fourier Transfer Infrared spectra was recorded to understand the various bond-formations during the transformation. This approach may enable rapid and cost-efficient manufacturing of bulk nanocomposite for supporting the industrial demands of stringent continuous processes with higher availability.

KEYWORDS : Nanomaterial, Sol-gel, Physical properties

1. Introduction

Nano-composite materials are being developed in order to meet stringent demands in high temperature processes, which could offer improved service life. Spinel presents itself as a promising structural material for mechanical and thermal applications because of its excellent high-temperature properties such as strength, hardness and chemical stability.

Synthesis of nanostructured spinel based composites have drawn great interest of research owing to their potential applications in refractories, high alumina cement, optical and as oxidation catalysts [1-4]. These materials are found to exhibit enhanced properties such as thermal shock resistance, wear resistance and increased hardness [5-6]. Synthesis of nanomaterials depends on the ability to control the size and distribution of the particles in the host matrix, the mixing modes of the reactants and drying techniques [7]. The advantages of Sol gel synthesis route are lower processing temperatures, control over purity, composition and easy introduction of doping elements [8-10]. In this paper, we are presenting a sol gel route for $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

(0.0<x<0.5) nanocomposite and its characterization using x-ray diffraction, infra-red spectroscopy.

2. Experimental Techniques:

Sol-gel synthesis route was adopted for developing gel samples with the composition was made by mixing $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water according to their respective molecular weight percentages. In the solution ethyl alcohol is added as pressures. The solutions obtained is stirred at 500 rpm at 298 K for one hour and then allowed to age at the same temperature for 24 hours for gel formation. The gel was then dried. The gel was calcined at 850 K for 2 hours and then sintered at 1100 K for 5 hours at a heating rate of 1 K/min.

X-ray diffraction spectra were studied for samples in the range 20° to 70°, 2θ with CuKα radiation wavelength $\lambda = 1.540598 \text{ \AA}$ in steps of 0.1°. Fourier Transfer Infrared spectra (FTIR) was recorded to understand the mechanism of development various bond-formations during the transformation.

3. Result and Discussions :

The X-ray diffraction pattern of sample shows clear diffraction peaks. On comparison with

JCPDS data, these peaks confirm to the formation of crystalline spinal phase.

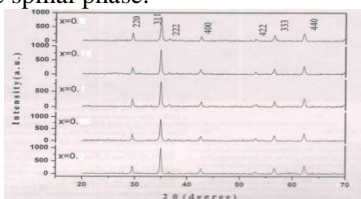


Fig 1 X-ray pattern of the system $Cu_{1-x}Zn_xFe_2O_4$ ($0.0 < x < 0.5$)

The average crystallite size was calculated from the diffraction peak broadening with the use of Scherrer's equation (4). Using the Scherrer's equation, the calculated average crystallite size is 290 nm.

The lattice parameter of the samples was determined using the relation (11)

$$a_{exp} = d_{hkl} \sqrt{h^2 + K^2 + l^2}$$

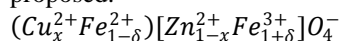
All the parameters are tabulated in Table 1 from table it is observed that all the samples show narrow size distribution, also the lattice constant increases as Zn concentration increases this may be fact that ionic radii of Zn (0.84) is large compare to ionic radii of Cu (0.89) and it is expected range with lattice parameters of spinel cubic ferrites. (12,13)

The theoretical lattice parameter (a_{th}) is calculated using the relation

$$a_{th} = \frac{8}{3\sqrt{3}} [(r_A + r_B) + \sqrt{3}(r_B + r_O)]$$

Where r_o is radius of oxygen ion (0.138 nm), and r_a , r_b are ionic radii of tetrahedral (A-site) and Octahedral (B-site) sites, respectively. The r_A and r_B will depend critically on the cation distribution of the metals present in the systems.

To calculate r_A and r_B following cation distribution is proposed.



The cation distribution is based on the following:

a) $NiAl_2O_4$ is inverse spinel in structure in which half of the ferric ions occupy the tetrahedral side (A site) and the other half occupy the octahedral site (B site) (14)

b) On the other hand, Cu ions prefer to occupy the tetrahedral site.(15)

c) During the sintering process, oxygen loss occurs, leading a part of Fe^{3+} ions to transform to Fe^{2+} for charge compensation. (16)

The data in table 1 reveals that the values of the theoretical lattice parameter (a_{th}), calculated assuming the suggested cation distribution formula, agree well with those experimentally obtain (a_{exp}).

The mean radius of the ions at the tetrahedral site r_{tet} and octahedral site r_{oct} has been calculated using the relation (17).

The X-ray density was calculated using the formula

$$D_{hkl} = \frac{ZM}{Na^3}$$

Where Z is the number of molecules per unit cell ($Z=8$), M is the molecular weight, a is the lattice parameter and N is Avogadro's number.

The theoretical density of the sample was calculated using the formula (18)

The porosity of the sample was calculated using the formula-

$$P = (1 - \frac{D_x}{D_{hkl}}) \times 100$$

The apparent density of the specimens is about 90% to 94% of the corresponding X-ray density. The data in the table show that both densities decreases with increasing Zn concentration i.e. the apparent density nearly reflects the same general behavior with the X-ray density.

Fig 2 : FT-IR spectra of the system $Cu_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 0.5$)

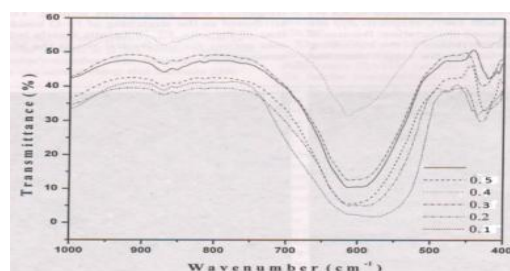


Table 1 : Grain Size, lattice parameter and Ionic radii data of $Cu_{1-x}Zn_xFe_2O_4$ ($0.0 < x < 0.5$) ferrite system.

Zn conc. (x)	Grain size D nm	Lattice constant		Ionic radius	
		Aexp (Å)	Ath (Å)	rA (Å)	rB (Å)
0.0	289.4	8.372	8.459	0.688	0.749
0.1	290.3	8.375	8.465	0.723	0.745
0.2	290.7	8.381	8.479	0.736	0.748
0.3	290.9	8.391	8.483	0.741	0.751
0.4	290.9	8.392	8.485	0.745	0.751
0.5	290.9	8.392	8.447	0.746	0.571

FTIR spectra of the gel sample and heat treated samples in the wave number range 3800 to 600 cm^{-1} is shown in Figure 4. The spectrum has strong and broad absorption peak between 3500 cm^{-1} and 3380 cm^{-1} indicating the vibration modes of metal hydroxyl groups. The peaks of metal hydroxyl and nitrate groups are not present for heat treated samples. The peaks between 1650 to 1635 cm^{-1} and between 950 and 940 cm^{-1} may be attributed to stretching and bending vibrational modes of O-H of molecular water.

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