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Synthesis and characterization of $Ni_xCu_{1-x}Fe_2O_4$ as fillers for conductive polymer composite in EMI shielding application

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Abstract **— High-performance electromagnetic (EM) interference shielding materials have become indispensable to prevent the adverse effect of EM pollution on human beings and safeguard electronic equipment from EM interference. This research proposes a new route to regulate the percolation threshold of conductive fillers in conductive polymer composites. Nano-size nickel copper ferrite nanoparticles ($Ni_xCu_{1-x}Fe_2O_4$) were prepared by a facile Co-precipitation method at different stoichiometric ratios and can be used to change the chemical vicinity of other conductive materials in conductive polymer composites. The resulting nanoparticles were characterized by X-ray diffraction (XRD) to depict their crystallinity and a scanning electron microscope (SEM) to study their surface morphology. The result showed nanosized $Ni_{0.75}Cu_{0.25}Fe_2O_4$ has a crystalline size of 38.4nm with nanorod bundle-like structures surrounded by small, uniform nanocrystals. This unique morphology will be favorable for EMI shielding application.**

Keywords—Conductive Polymer composite, Nanocomposite, $Ni_xCu_{1-x}Fe_2O_4$, Characterization, EM shielding effectiveness.

I. INTRODUCTION

The upsurge in the use of electronic devices has resulted in electromagnetic pollution due to the increased manufacture of enhanced operational-performance miniature devices [1, 2]. Excessive usage of these miniature devices inevitably generates Electromagnetic interference (EMI) [3, 4]. EMI shielding has become an effective method and key technology to protect humans and the environment from unwanted EM radiation, which is of great importance in both the civil and military fields [2, 5]. EMI shielding materials eliminate EM pollution through three mechanisms: shielding by absorption loss (SE_A), reflection loss (SE_R), and multiple reflection loss (SE_M). EMI shielding materials unavoidably should be lightweight, have high conductivity, corrosion resistance, superior shielding performance, easy processability, and a wide absorption bandwidth [6]. Numerous materials have been employed for EMI shielding in recent years [7, 8], among which are traditional metals. Traditional metals can achieve excellent EMI shielding due to their high conductivity. However, their high density, easy corrosion, and difficult processing restrict their applications in EMI shielding [9, 10]. The major route for EMI shielding material design is via material combinations (composites). The ferrites AB_2O_4, where A is a first-row 3d metal (= Fe, Ni, Zn, Cu, Mn) crystallizing in the spinel structure, are gaining popularity. Ferrites are among the most appealing oxides due to their microstructural, optical, electrical, magnetic, and dielectric characteristics. Ferrites are also gaining prominence among these options due to their intriguing electromagnetic properties. $CuFe_2O_4$ and $NiFe_2O_4$ crystallize in the form of an inverse spinel with cubic symmetry and soft magnetic characteristics [11].

Composite materials are viable for achieving manufacturability [12, 13]. Polymer-matrix composites are the most common composite materials, with substantially lower manufacturing costs than carbon-matrix, ceramic-matrix, and metal-matrix composites [14]. Conductive polymer composites (CPCs) are advanced types of

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functional materials. They possess a stimulating combination of properties including light weight, ease of processing, high specific toughness and ductility, tunable electrical conductivity, and environmental-sensitive resistivity compared to conventional metallic and ceramic composites. [15]

II. MATERIAL AND METHODS

A. Materials

Iron nitrate nonahydrate ($Fe(NO_3)_2.9H_2O$) 99% purity, Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) 98% purity, Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) 99% purity, and Sodium hydroxide 98% purity. All chemicals are analytical-grade.

B. Methods

Preparation of $Ni_xCu_{1-x}Fe_2O_4$

$Ni_xCu_{1-x}Fe_2O_4$ was synthesized using the co-precipitation method at different stoichiometric ratios (X= 0, 0.5, 0.75, and 1). Stoichiometric amounts of $Ni(NO_3).6H_2O$, $(Cu(NO_3)_2.3H_2O)$ and $(Fe(NO_3)_2.9H_2O)$ were dissolved in distilled water, and 0.1M NaOH was added dropwise until a pH of 13 was reached. The resulting solution was stirred vigorously for 1 hour and allowed to age for 6 hours. After aging, the solution was heated in a water bath at 90°C for 120 minutes. The precipitate was dried overnight at 80°C. After drying the dark-coloured crystals obtained were crushed and then calcinated at 900°C for 3 hours and post-calcinated at 1000°C for 2 hours in the air.

III. CHARACTERIZATION:

The crystalline structure and phase information of samples were analysed using X-ray diffraction spectroscopy. The scanning electron microscope SEM was used to investigate the morphology of the prepared nanoparticles at different magnifications.

IV. RESULTS AND DISCUSSION

A. Chemical Composition

1). Phase Crystallinity (XRD)

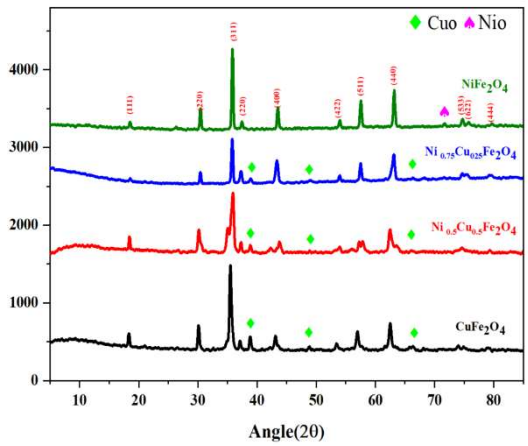

Figure 1: XRD Spectra of NixCu1-xFe2O4

The crystal structures of the prepared ferrites were analyzed using XRD pattern as shown in Fig.1. Distinct spinel peaks were observed along (111), (220), (311), (222), (400), (422), (511) and (440) were observed at 18.41°, 30.40-30.16°, 35.52°-35.76°, 37.26°, 43.34°-43.93°, 53.04°-54.11°, 57.07°-57.54° and 62.44°-63.15°, 74.47°, and 79.30°. The miller indices that were observed in the XRD analysis graph are (111), (220), (311), (220), (400), (422), (511), (440), (533), (622) and (444). This proves the synthesized samples are single-phase cubic spinel Ni-Cu ferrite particles with an FCC structure [16, 17]. This correlates with the results obtained in the literature [17, 18]. In addition to the spinel ferrite peaks, a peak was observed at 71.73° in x=1 and x= 0.75. Also, at x=0, 0.5 and 0.75, 2 peaks were observed at 38.99 and 48.83. This could be attributed to the presence of CuO. In x=0.5, a peak was found attached to the plane (311) and (440). This could be ascribed to the insufficient reaction between several oxides such as CuO (copper oxide) during composite formation [19]. The presence of sharp diffraction peaks in the sample indicates the high crystallinity of the nanocomposite. The crystallite size was calculated using Scherrer's equation.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

In addition to the crystallite size, the lattice constant and micro strain were also calculated. The calculated lattice constant, Micro strain, and crystallite size are presented in Table 1

Lattice constant (a) = $\{4xr/(3)^{1/2}\}$

$$a= D_{hkl}(h^2+k^2+l^{2+})^{1/2}$$

Micro strain

$$\varepsilon = \frac{\beta}{4\tan\theta}$$

TABLE I. CRYSTALLINE SIZE, LATTICE CONSTANT, X-RAY, AND MICRO STRAIN FOR THE SYNTHESIZED $Ni_XCu_{1-x}Fe_2O_4$ NANOCRYSTALS.

Sample	Crystalline size (nm)	Interplanar spacing (Dhkl)	Lattice constant	Dislocation Density	Micro Strain (10-4)
X=0	25.7 nm	2.53 Å	8.40 Å	1.51E-03	4.53
X=0.5	32.5 nm	2.53 Å	8.38 Å	9.47E-04	6.07
X=0.75	38.4 nm	2.53 Å	8.33 Å	6.78E-04	3.07
X=1	45.6 nm	2.53 Å	8.32 Å	4.80E-04	2.58

The Lattice parameter showed a linear dependence as the ration of Cu increased in the composite. This correlates with Vegard's law of XRD which states that the lattice parameter of a substitutional solid solution varies linearly between the lattice parameter values of the components [20]. The Dislocation density decreases with increasing concentration. This gives information on the number of dislocations per unit volume of the synthesized material. The microstrain shows the variation in the lattice parameter across the nanocomposite [16].

2). Surface Morphology

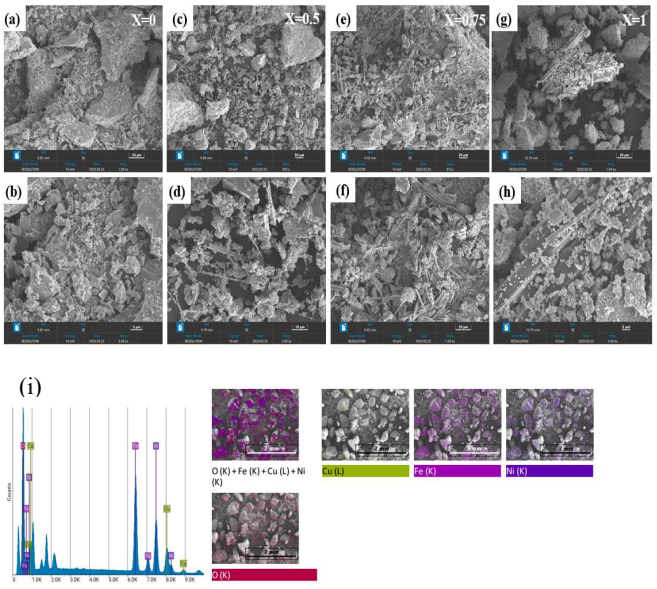

Figure 2(a)-(h):SEM images of the prepared nanocomposite and (i) EDX result of the studied sample.

The morphology of the synthesized nanocomposites was analyzed using SEM. From the SEM images, it was observed that the addition on Ni resulted in the formation of nanorods in the samples. Figure 2a&b shows the formation of irregular nanocrystals whereas in Figure 2c, it was observed that the addition of Ni resulted in the formation of tiny nanorods attached to the nanocrystals. Figure 2e shows the agglomeration cubic spinel structure and formation of nano rod bundles. Whereas in figure 2g&h, small cubic spinel spheres were observed on broader nanorods. The EDX showed the elemental distribution, whereas the mapping showed the distribution of each element on the composite's surface. Based on the EDX and Mapping result, it can be concluded that there was a successful composite formation with the elemental distribution shown in table 2.

TABLE II: WEIGHT PERCENTAGE OF THE ELEMENTS PRESENT IN THE PREPARED $Ni_XCu_{1-x}Fe_2O_4$ COMPOSITE.

Sample	Nickel (%)	Copper (%)	Iron (%)	Oxygen (%)	Ratio (Ni/Cu)
X=0.5	14.62	28.52	30.70	24.33	0.51
X=0.75	24.45	16.68	27.11	31.76	0.68

V. CONCLUSION

In this study, the percolation threshold of Conductive Polymer Composite (CPC) has been proved to be altered by surface modification with other conductive materials for effective EMI shielding. Polymer/carbon nanofiller nanocomposites can be used as effective shielding materials, but carbon-based materials have less mechanical flexibility, whereas metal-based shielding materials are heavyweight, corrosive, and it is very difficult to tune their shielding efficiency. The prepared nanocrystals showed high crystallinity and presence of nanorod bundles with attached nanocrystals. This will help in the alteration of the chemical vicinity of the CPC by attaching the nanorods and crystals to the polymer matrix. The EDX and mapping confirmed the presence of the element. This shows that $Ni_{0.75}Cu_{0.25}Fe_2O_4$ can be used as the magnetic composite (fillers) for conductive polymer composites in EMI application. In EMI shielding, the most important is designing the structure and development of new materials with improved shielding performance.

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