



# Article Fabrication of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> Nanoparticles Using One Step Self-Assembling Route to Enhance Energy Consumption

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**Abstract:** The preparation of copper manganite (hopcalite,  $Cu_{1.5}Mn_{1.5}O_4$ ), as a single phase, was achieved by using a sustainable method of green synthesis. This method is based on the replacement of the conventional "brute force" ceramic preparation by the recent "soft force" green synthesis via the egg white assisted one-step method. In other words, we present a facile and rapid methodology to prepare the nanocrystalline  $Cu_{1.5}Mn_{1.5}O_4$  spinel as a single phase, compared to our previous work using ceramic and glycine-assisted combustion methods. The as-synthesized copper manganite was characterized using X-ray diffraction (XRD), Fourier-transform infrared (FTIR), energy-dispersive spectroscopy (EDS), and scanning electron microscope (SEM). We used a vibrating sample magnetometer to determine the magnetic properties of the prepared sample (VSM). XRD, FTIR, SEM, EDS and transmittance electron micrograph (TEM) resulted in synthesis of a successful cubic spinel  $Cu_{1.5}Mn_{1.5}O_4$  system with a sponge crystal structure. The particles of the prepared materials are polycrystalline in their nature and the sizes ranged between 50 and 100 nm. The magnetic measurement demonstrated that the generated nanostructure has been found to exhibit ferromagnetism at room temperature with an optimum saturation magnetization value (0.2944 emu/g).

**Keywords:** Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> nanoparticles (NPs); X-ray diffraction (XRD); Fourier-transform infrared (FTIR); scanning electron microscope (SEM); energy-dispersive spectroscopy (EDS); transmittance electron micrograph (TEM); vibrating sample magnetometer (VSM)

## 1. Introduction

In several important applications such as electronics, optics, magnetism, catalysis to energy storage and conversion, spinel type materials have long attracted scientific and technological consideration [1]. Versatile applications for manganese-based spinels (MMn<sub>2</sub>O<sub>4</sub>) were determined in the case of lithium insertion electrodes, magnetic solids and catalysts [2–4]. For medical applications, including bio imaging, target drug development and hyperthermia, certain materials were being used [5,6]. The different benefits of manganese, such as low cost, easy implementation, low toxicity, multiple valence and a prominent Jahn–Teller effect, could be related to these behaviors [7].

Among the numerous varieties of manganese-based spinels, one of the most incredibly interesting composite oxides is hopcalite ( $CuMn_2O_4$  or  $Cu_{1.5}Mn_{1.5}O_4$ ) since it is very appropriate to several catalytic processes such as water-gas transfer, the reduction of nitrogen oxide with carbon monoxide, the direct decomposition of NO, selective ammonia oxidation to nitrogen gas and, more recently, in steam reforming and oxidative steam reforming of methanol, and the selective oxidation of carbon monoxide, benzyl alcohol



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and toluene [8–11]. Towards the production of copper-manganese mixed oxides, different preparation techniques have been employed. Co-precipitation, deposition-precipitation, impregnation, sol-gel, solvothermal and combustion methods include such techniques [12–15]. It is reported that due to Jahn–Teller distortion, the crystal structure of manganese-based spinels, such as spinel lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>), often has a tetragonal unit cell, but under certain preparation conditions it can become cubic [16].

The processing of single phase containing hopcalite nanoparticles is complicated, depending upon if the secondary phase of manganese and copper is more likely to be implemented during the synthesis process. In our previous work, the solid state reaction between both copper nitrate and manganese carbonate resulted in the production of a  $Cu_{1.5}Mn_{1.5}O_4$  spinel compound with the subsequent formation of both  $Mn_2O_3$  and CuO. In the same way, the use of copper chloride as a CuO source brought about the formation of both  $CuMn_2O_4$  and  $Mn_2O_3$  [15]. Researchers have focused on the synthesis of such a compound by the fusion of copper with manganese metals or by the coprecipitation technique of certain modifications to avoid such a challenge [15–18]. The high concentration of  $Cu^+$  and  $Mn^{4+}$  cations in  $Cu_{1.5}Mn_{1.5}O_4$  solid could activate  $O_2$  and  $NO_x$  in the diesel exhaust and convert these gases to  $NO_2$ , so this solid is expected to be quite favorable for diesel soot combustion [18]. Consequently, a few disadvantages, such as the complication of preparation methods, remain. The rapid and reasonable synthesis of crystalline spinels at room temperature and ambient atmosphere, however, represents a problem, despite continuous efforts.

In this research, to prepare copper maganite nanoparticles ( $Cu_{1.5}Mn_{1.5}O_4$  NPs) through egg white assisted green synthesis, a facial, scalable and environmentally friendly method was used. Here, we demonstrate the experimental method of preparing  $Cu_{1.5}Mn_{1.5}O_4$ nanoparticles through using egg white as an auxiliary bio material, which provides the dispersion of nanoscale oxides in one phase. The single-step process is straightforward, environmentally friendly, inexpensive and reproducible, generating high-quality nanoparticles of  $Cu_{1.5}Mn_{1.5}O_4$  that can be regulated in terms of structure, morphology and distribution of particle size. The characterization of the  $Cu_{1.5}Mn_{1.5}O_4$  NPs and magnetic properties developed has been determined.

#### 2. Materials and Methods

#### 2.1. Production of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> Nanoparticles

An egg white-based precursor containing copper nitrate trihydrate (2.41 g) and manganese nitrate tetrahydrate (2.51 g) was used to prepare the  $Cu_{1.5}Mn_{1.5}O_4$  nanocomposite. These reagents were dissolved in distilled water with an equimolar ratio of Cu and Mn until a clear solution was obtained; egg white (0, 2.5 and 5 mL) was added into the mixture. To evaporate water and increase the viscosity, the obtained mixture was first stirred at 60 °C, and then the solution was heated at 120 °C to create a gel. The resulting precursor gel was calcined for 15 min at 300 °C in a furnace. Several more foams were created; then, a spark appeared at one corner when a crucible temperature was achieved. The spreading of this spark through the mass led to the creation of a voluminous and fluffy substance in the container, with the subsequent production of black powder by grinding the end product. The produced solids prepared by using 0, 2.5 and 5 mL egg white are labeled as S1, S2 and S3, respectively. The chemicals used in the present work were of analytical grade delivered by Prolabo Company (Highlands North, South Africa). Figure 1 represents a clear schematic of the synthesis process.



**Figure 1.** Experimental flow chart for the synthesis of  $Cu_{1.5}Mn_{1.5}O_4$  nanoparticles (NPs).

#### 2.2. Characterization Techniques

The BRUKER D8 (Bruker, Karlsruhe, Germany) advance diffractometer was used for the X-ray study of various mixed solids. The patterns were run at 40 kV with Cu Karadiation and 40 mA with 2 theta  $2^{\circ}$  min<sup>-1</sup> scanning speeds. The average crystallite size (D), dislocation density ( $\delta$ ) and strain ( $\varepsilon$ ) of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> present in the solid investigated were determined using Equations (1)–(3) and based on X-ray diffraction line broadening as follows [19]:

$$D = 0.89 \lambda / \beta \cos\theta \tag{1}$$

$$\delta = 1/D^2 \tag{2}$$

$$\varepsilon = \beta \cos\theta/4 \tag{3}$$

Where D is the average crystallite size of the phase under examination, 0.89 is the Scherrer constant,  $\beta$  is the full width at half the height of the peaks in radians,  $\theta$  is the diffraction angle in radians, and  $\lambda$  is the wavelength of the X rays in nanometers.

The Fourier-transform infrared spectrum (FTIR) of the investigated solid was calculated using a PerkinElmer Spectrophotometer (type 1430, PerkinElmer, Unit a Llantrisant CF72 United Kingdom). The IR spectrum was collected at wavelengths from 4000 to  $400 \text{ cm}^{-1}$ . A total of 200 mg of potassium bromide (KBr) grade vacuum-dried IR was blended with 2 mg of solid samples. Dispersed for 3 min by grinding in a vibratory ball mill, the mixture was inserted as a disk with 13 mm diameter into a steel die and subjected to 12 ton pressure. In the double grating IR spectrometer holder, the sample disk was inserted.

Scanning electron microscope (SEM) and transmittance electron micrograph (TEM) were recorded with the help of JEOL JAX-840A and JEOL Model 1230 (JEOL, Tokyo, Japan), respectively, and in order to disperse individual particles over mount setup and Cupper grids, the samples were dispersed in ethanol and then treated ultrasonically for a few minutes.

Energy dispersive X-ray analysis (EDS with Mapping) was performed with a Delta kevex device attached to an electron microscope, JED- 2200 Series (JEOL, Tokyo, Japan). The following parameters were used: 20 kV accelerating voltage, 120 s accumulation time, and 6  $\mu$ m window width. Using the Asa procedure, Zaf-correction, and Gaussian approximation, the surface molar composition was calculated.

The vibrating sample magnetometer (VSM) (9600-1 LDJ, Weistron Co., Ltd., West Hollywood, CA, USA), was used to investigate the magnetic properties of the solids evaluated in a maximum field of 20 kOe. Loops of hysteresis, magnetization of saturation (Ms), magnetization of remanence (Mr) and coercivity (Hc) were established.

# 3. Results

### 3.1. XRD Investigation

The XRD patterns of the as-synthesized samples are shown in Figure 2. The XRD patterns showed an amorphous state for samples prepared without and with 2.5 mL egg white, while the sample treated with 5 mL egg white is a very good crystalline system with 10 peaks, two of which are very strong peaks at degree 2 theta equal to 37,634 and 43,862 degrees, encoding plane parameters (222) and (004), respectively. The miller planes, two observed theta, two calculated theta and the difference between them are listed in Table 1. These peaks are consistent with the values recorded for Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs Cubic Spinel (PDF file No. 35-1171) [20]. The Fulprof program is used to calculate the lattice parameters, unit cell dimensions, crystal system, space group, and other crystallographic parameters [21]. The mean crystallite size of the Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> particles was calculated depending upon Scherer's formula. The values of the crystallite size (D), X-ray density (Dx), unit cell volume (V), lattice constant (a), dislocation density ( $\delta$ ), micro-strain ( $\varepsilon$ ), the distance between the reacting ions (LA and LB) and bond lengths (A–O and B–O) on tetrahedral (A) sites and octahedral (B) sites in the spinel Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs are shown in Table 2 [22–25].



Figure 2. X-ray diffraction (XRD) pattern of the S1, S2 and S3 samples.

Table 1. Structural data of the as-	synthesized	$Cu_{1.5}Mn_{1.5}O_4$ NPs.
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Peak	20 Obs.	20 calc.	Difference	h	k	1
1	30.550	30.567	-0.017	0	2	2
2	35.955	36.009	-0.054	1	1	3
3	37.634	37.669	-0.035	2	2	2
4	43.862	43.774	0.088	0	0	4
5	47.990	47.936	0.054	3	1	3
6	54.312	54.330	-0.018	4	2	2
7	57.920	57.927	-0.007	1	1	5
8	63.620	63.631	-0.011	0	4	4
9	66.920	66.918	0.002	5	1	3
10	67.970	67.996	-0.026	2	4	4

Properties	Values
Crystal structure	Cubic spinel
Space group	FD3M (227)
Lattice constant (a), nm	0.82724
Unit cell volume (V), nm <sup>3</sup>	0.566101
Density (D <sub>x</sub> ), g/cm <sup>3</sup>	5.636
Crystallite size (D), nm	65
Dislocation density ( $\delta$ )	$2.44 imes 10^{-4}$
Micro-strain $(\varepsilon)$	$5.37 imes 10^{-4}$

Table 2. Some structural properties of the as-synthesized Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs.

### 3.2. FTIR Study

The chemical structural nature of the S3 sample containing a  $Cu_{1.5}Mn_{1.5}O_4$  lattice was identified by FTIR analysis. The FTIR spectrum measured in the range of 4000 to 400 cm<sup>-1</sup> is shown in Figure 3. (i) An extreme broad band detected in the 3650–3100 cm<sup>-1</sup> region and a small band of around 1677 cm<sup>-1</sup> may due to the stretching and bending vibrations of the adsorbed water molecules of the O-H surface hydroxyl groups [26]. Consequently, these bands validate which high humidity is absorbed by the nanocrystalline system with high surface-to-volume ratio [27]. (ii) The stretching vibration of O=C=O resulted in an IR band observed at 2352 cm<sup>-1</sup> [28]. During KBr palletization, the adsorption of CO<sub>2</sub> from the air on the surface of the as-synthesized material resulted in the presence of an IR band at 1411 cm<sup>-1</sup> [28]. Depending on the presence of carbon traces, the transmittance peak was observed due to C-OH stretching vibration at about 1147 cm<sup>-1</sup> [28]. (iii) It is possible to attribute the characteristic bands observed around 500 and 600 cm<sup>-1</sup> to the octahedral (B) and tetrahedral modes, respectively, in the spinel system [29]. Indeed, the 500 and 618 cm<sup>-1</sup> bands are related to the vibration of trivalent metal ions in A-sites of the spinel Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> lattice, respectively [30,31].



Figure 3. Fourier-transform infrared spectrum (FTIR) spectrum of the S3 sample.

## 3.3. Energy Dispersive X-ray (EDX) Analysis

Figure 4 shows the EDS pattern of the S3 sample. From the whole figure, the existence of the signal characteristic elements of copper (Cu), manganese (Mn) and oxygen (O) was recorded. In comparison, the percentage weights of Cu, Mn, and O measured from EDS were 49 percent, 29 percent, and 21 percent, respectively. The signal observed at 0.27 Kev in the spectrum is due to the presence of carbon (C, 1 percent) as an impurity, which is confirmed from the obtained FTIR analysis. However, EDS mapping findings indicate that copper, manganese, and oxygen atoms are very well distributed.



**Figure 4.** (a) EDS pattern and mapping of the S3 sample, (b) Cu, Mn, and O K, (c) SEM, (d) O K, (e) Mn K and (f) Cu K.

#### 3.4. Scanning Electron Microscopic (SEM) Analysis

The surface morphology based study of the S3 sample was determined using SEM analysis. The SEM images with different magnifications were collected in Figure 5. Figure 5a–f represents the SEM images of solid  $Cu_{1.5}Mn_{1.5}O_4$  obtained by using egg white assisted green synthesis. From the SEM images of this composite, it was observed that the particles have a spongy structure containing pores and voids. However, these particles have a tendency of agglomerations with a higher homogeneity. The synthesized nanoparticles had sizes ranging between 50 and 100 nm, indicating the formation of a polycrystalline solid. These observations are in agreement with the XRD measurement.



**Figure 5.** Scanning electron microscope (SEM) of the S3 sample with different magnifications. (a)  $500 \times$ , (b)  $1000 \times$ , (c)  $2700 \times$ , (d)  $5500 \times$ , (e)  $10,000 \times$  and (f)  $20,000 \times$ .

### 3.5. Transmission Electron Microscopic (TEM) Analysis

We used TEM analysis as an additional surface morphology of the S3 sample. The TEM images are shown in Figure 6 with different magnifications, 50 KX and 80 KX. From these figures, we can observe that there is an agglomeration of particles in the resulting Cu-Mn mixed oxides. Our method of preparing the studied mixed solids resulted in the creation of particles with homogeneous, uniform size and diameters varying from 50 nm to 100 nm. Indeed, the contrast observed in TEM images could be related to phase contrast. During the evaluation of the promoted sample, the distinct carbon particles were observed from the strong contrast in TEM images that would be predicted from the large difference in the atomic number and density of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> nanoparticles and that of carbon. This observation could be attributed to the sensitivity of the TEM technique to the atomic



number and density of the investigated material. However, the TEM morphology supports the results obtained from SEM and XRD measurements.

**Figure 6.** Transmittance electron micrograph (TEM) of the S3 sample with different magnifications. (**a**) is 50 k×, (**b**) is 80 k× and (**c**) particle distribution histogram.

#### 3.6. Magnetic Study

A vibrating sample magnetometer (VSM) measured the magnetic properties of the S3 sample at room temperature. Magnetization plots (M) as a function of the applied magnetic field (H) are shown in Figure 7. This figure shows the resulting cycle of hysteresis at 300 K. The values of saturation magnetization ( $M_s$ ), remenant magnetization ( $M_r$ ), squareness or the ratio of remenant magnetization to saturation magnetization ( $M_r$ ), coercive force or coercive force ( $H_c$ ) and anisotropic constant ( $K_a$ ) for the S3 sample containing Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs are reported in Table 3 [25].



Figure 7. M-H curve of the S3 sample.

Properties		Values	
Saturation magnet	ization ( $M_s$ ) emu/g	0.2986	
Remenant magnetization (M <sub>r</sub> ) emu/g		$5.573 \times 10^{-3}$	
Coercivity (H <sub>c</sub> ) Oe		215.16	
Squareness (M <sub>r</sub> /M <sub>s</sub> )		$18.663 \times 10^{-3}$	
Anisotropy constant (K <sub>a</sub> )		65.558	
Magnetic moment (µm)		0.0127	
Hoppling lengths, nm -	L <sub>A</sub>	0.3449	
	LB	0.2812	
Distance between the magnetic ions, nm	A-O	0.1821	
	В-О	0.1289	

Table 3. Magnetic properties of the S3 sample.

#### 4. Discussion

In this investigation, the egg white mediated green synthesis brought about the formation of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs as a single phase, and the mean average crystallite was approximately 75 nm. However, it can be seen from Table 1 that there is micro-strain and dislocation in the crystal lattice of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs. A dislocation inside a crystal structure is a crystallographic defect (slight misalignment), which greatly affects the properties of materials. The standard atomic array of the perfect crystals is skewed by this defect [22–25,32–34]. Within the crystal lattices, the strain confirms the existence of defects. In addition, the XRD and FTIR studies confirm that  $Cu_{15}Mn_{15}O_4$  NPs have a single-spinel structure. Furthermore, Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs can be prepared via a solid state reaction between Cu and Mn oxides via a ceramic path [15,17,18]. At the beginning of the solid state relation between unreacted Cu and Mn oxides, a thin layer of the copper manganite is formed to cover the unreacted oxides and prevent these oxides from interacting together. This thin layer acts as an energy barrier that must be overcome by the diffusion process to achieve the complete conversion of the unreacted oxides into  $Cu_{1.5}Mn_{1.5}O_4$  NPs. In other words, the counter-diffusion of copper and manganese ions through a relatively rigid manganite film about the surface of Cu and Mn oxides led to the formation of particles of  $Cu_{1.5}Mn_{1.5}O_4$ . Furthermore, by reacting with manganese ions, oxygen passes through the reacted region to be added to the CuO interface and form spinel. Indeed, techniques such as the route of preparation can be used to facilitate this diffusion [15,17]. Copper manganite  $(Cu_{1.5}Mn_{1.5}O_4)$  formation occurs according to the following stoichiometric reaction:

$$6CuO + 3Mn_2O_3 + 0.5O_2 \rightarrow 4Cu_{1.5}Mn_{1.5}O_4 \tag{4}$$

Copper manganite crystallizes in an inverse cubic spinel structure, where manganese ions are distributed among the tetrahedral and octahedral sites while copper ions are located at the octahedral sites [15]. In fact, the presence of the  $Mn^{n+1}/Mn^{n+}$  redox couple located in B-sites of the semiconductor spinel has been considered as the responsible factor of the controlled-valence conduction mechanism proposed by Verwey [35]. According to the preparation conditions, the copper manganite crystallizes in a random cubic spinel structure via the distribution of both Cu and Mn ions among the tetrahedral and octahedral sites. This structure could be attributed to the presence of Cu<sup>+</sup> ions at the sites [18]. Indeed, Cu<sup>+</sup> ions have a strong preference for tetrahedral interstices [36–38]. However, if Mn<sup>3+</sup> ions in octahedral sites are disproportionate to Mn<sup>2+</sup> and Mn<sup>4+</sup>, then Mn<sup>2+</sup> ions will move to tetrahedral sites [35]. In this regard, some researchers pointed out the stabilization of Cu<sup>+</sup> and Mn<sup>4+</sup> cations in the tetrahedral and octahedral sites, respectively, without the presence of a stabilizing agent [18,36–38]. These researchers confirmed abundant Cu<sup>+</sup> and Mn<sup>4+</sup> cations according to the following reaction:

$$Cu^{2+} + Mn^{3+} \rightarrow Cu^{+} + Mn^{4+}$$
 (5)

It was recently confirmed that it was not possible to prepare a pure cubic spinel  $Cu_{15}Mn_{15}O_4$  phase [39–43]. Many other authors mentioned that during the sintering phase of Cu-containing spinel materials, Cu<sup>+</sup> can be produced. Any oxidation of Cu<sup>+</sup> to  $Cu^{2+}$  on cooling in air does not allow the residual CuO to be incorporated into the spinel material [15,42]. This action led to the coexistence of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and CuO as a second phase. Similar results were observed in our previous works, which indicate the formation of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> with both CuO or Mn<sub>2</sub>O<sub>3</sub> by using the ceramic method with and without glycine via the thermal treatment of calculated amounts of copper nitrate and different manganese precursors [14,15]. The glycine assisted combustion route followed by heating treatment at 900 °C for a mixture of copper and manganese nitrates resulted in the formation of  $Cu_{1.5}Mn_{1.5}O_4$  with  $Mn_2O_3$  as a second phase [14]. Additionally, the heat treatment at 800 °C for a mixture of copper nitrate and manganese carbonate brought about the production of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> crystallites [15]. However, in this study, the presence of 5 mL egg white inhibited the oxidation of Cu<sup>+</sup> to Cu<sup>2+</sup>, yielding Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> without the appearance of any secondary phase. This does not negate the presence of Cu<sup>2+</sup> ions, especially at octahedral sites. The comparison between this investigation and our previous works confirms the role of the metal precursor and preparation method in the change of the crystallographic of the product. In other words, this study resulted in the preparation of cubic spinel  $Cu_{1.5}Mn_{1.5}O_4$  as a single phase.

The nano regime range of the synthesized  $Cu_{1.5}Mn_{1.5}O_4$  NPs with certain agglomerations has been verified by SEM results. Figure 5f indicates that the nanoparticles were clustered or very aggregated. The TEM results gave the same results that were obtained using the SEM technique.

From the EDS spectrum, it was evident that the  $Cu_{1.5}Mn_{1.5}O_4$  NPs were successfully synthesized in accordance with the main components of the sample prepared as Cu, Mn, and O elements with carbon traces. Nevertheless, the EDS mapping results were compatible with that of the XRD of the as-synthesized material.

The biosynthesized Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>NPs exhibit magnetic hysteresis loops with coercivity (215.16 Oe) and saturation magnetization (0.2986 emu/g). In order to understand the mechanism responsible for ferromagnetism in  $Cu_{1.5}Mn_{1.5}O_4$  NPs at room temperature, the origin of ferromagnetism is analyzed by different possibilities that can be present in this system. In other words,  $Cu_{1.5}Mn_{1.5}O_4$  NPs have a room temperature ferromagnetic-like state (RTFM) depending upon the competition between ferromagnetic and antiferromagnetic sublattices [44]. This competition could be attributed to the presence of a complex magnetic structure with the existence of several magnetic sublattices in the oxides. Some authors observed the Mn<sup>2+</sup>-Mn<sup>3+</sup> antiferromagnetic interactions at low temperatures [41]. These authors reported Mn<sup>3+</sup> and Mn<sup>4+</sup> ferromagnetic interactions at a higher temperature close to the magnetic transition. The interaction between  $Cu^{2+}$  and  $Mn^{3+}$  ions has been suggested to be ferromagnetic [45]. From this point, we can add that the ferromagnetic behavior of the prepared sample with 5 mL egg white is also due to the interaction between Cu<sup>+</sup> and  $Mn^{2+}$  ions at the tetrahedral site involved in the  $Cu_{1,5}Mn_{1,5}O_4$  lattice. It is reasonable to suspect that the indirect coupling between Mn ions mediated by O and Cu ions leads to the stabilization of ferromagnetism [46,47]. Additionally, Cu-O-Cu interactions may also play a role. In addition, the investigated system has superparamagnetism properties depending on its nano particle nature. Moreover, the squareness of the prepared Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs was below 0.5, indicating a decrease in anisotropy in the crystal lattice [27]. This behavior could be attributed to magnetostatic interaction between these particles [27]. Therefore, the prepared Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> system can be used in the manufacture of spintronic devices depending upon its room temperature ferromagnetic behavior.

## 5. Conclusions

Egg white assisted green synthesis resulted in spinel  $Cu_{1,5}Mn_{1,5}O_4$  NPs' formation in a few minutes, without the appearance of any second phase. This process has many advantages for the synthesis of  $Cu_{1.5}Mn_{1.5}O_4$  NPs with the presence of small carbon additives, such as no toxicity, economic feasibility, ease to scale up, being less time consuming and being an environmentally friendly approach. On the other side, in our previous work, both the ceramic method and glycine assisted combustion route followed by heating at 900 °C and 800 °C, respectively, led to the formation of Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs with both Mn<sub>2</sub>O<sub>3</sub> and CuO as second phases, respectively. The as-synthesized material consisted almost entirely of Cu<sub>15</sub>Mn<sub>15</sub>O<sub>4</sub> NPs, as approved with XRD and FTIR data. Using SEM, EDS mapping and TEM techniques, the elements and morphology of the prepared sample were characterized. Characterization techniques enabled us to calculate the crystallite size, X-ray density, unit cell volume, lattice constant, dislocation density, micro-strain, and the distance between the reacting ions and bond lengths on tetra-hedral (A) sites and octahedral (B) sites for the spinel Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> NPs. The morphological analysis of the prepared system displays a spongy, fragile structure containing pores and voids. The synthesized system has room temperature ferromagnetic behavior with an optimum value, 0.2986 emu/g, of saturation magnetism. This green process of synthesizing  $Cu_{1.5}Mn_{1.5}O_4$  NPs may also be applied in the future to the production of industrial single phases of inorganic functional materials.

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