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Investigation on hydrothermal synthesis of spinel ferrite $CuFe_2O_4$: morphology, crystallinity, chemical and magnetic properties

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In this study, a nanometer-size material $CuFe_2O_4$ was synthesized by a low-temperature hydrothermal reaction of $CuCl_2{\cdot}2H_2O$, $FeCl_2{\cdot}4H_2O$ and urea (CH_4N_2O) with various weight ratio between $CuCl_2$ and $FeCl_2$ namely 1:1, 1:2, 2:1 and 2:3, at 200°C for 6 h. The obtained powder was annealed at 300°C for 1 h. Various characterization methods, namely, Field-Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Vibrating Sample Magnetometer (VSM) analysis were used to investigate the properties of the $CuFe_2O_4$ nanomaterials. FESEM images revealed that the hydrothermal synthesis of $CuFe_2O_4$ resulted in a nanocubic structure with particle size of 45 nm; meanwhile XRD analysis indicated the crystalline nature of $CuFe_2O_4$ without any other impurities. In addition, FTIR and VSM allowed explaining the chemical and magnetic properties of nanocubic $CuFe_2O_4$.

Keywords: hydrothermal synthesis, nanocubic, magnetic properties.

Дослідження гідротермічного синтезу шпінелі фериту $CuFe_2O_4$: морфологія, кристалічність, хімічні та магнітні властивості. *Perdinan Sinuhaji, Awan Maghfirah, Marhaposan Situmorang, Johaidin Saragih, Muhammadin Hamid, Wina Miranti, Nurul Yaumilda Hasibuan, Martha Rianna*

Досліджено матеріал $CuFe_2O_4$ нанометрового розміру, синтезований методом низькотемпературної гідротермальної реакції $CuCl_2{\cdot}2H_2O$, $FeCl_2{\cdot}4H_2O$ і сечовини (CH_4N_2O) з різним масовим співвідношенням $CuCl_2$ і $FeCl_2$, а саме 1:1, 1:2, 2:1 і 2:3 при 200°C протягом 6 годин. Отриманий порошок відпалений при 300°C протягом 1 години. Досліджено морфологію, хімічні та магнітні властивості наноматеріалів $CuFe_2O_4$. Показано, що нанокристали $CuFe_2O_4$, отримані методом гідротермального синтезу мають нано-кубічну структуру з розміром частинок 45 нм, в той час як рентгеноструктурний аналіз вказує на кристалічну природу $CuFe_2O_4$ без будь-яких інших домішок.

Исследован материал $CuFe_2O_4$ нанометрового размера, синтезированный методом низкотемпературной гидротермальной реакции $CuCl_2{\cdot}2H_2O$, $FeCl_2{\cdot}4H_2O$ и мочевины (CH_4N_2O) с различным массовым соотношением $CuCl_2$ и $FeCl_2$, а именно 1:1, 1:2, 2:1 и 2:3 при 200°C в течение 6 ч. Полученный порошок отожжен при 300°C в течение 1 ч. Морфология, химические и магнитные свойства наноматериалов $CuFe_2O_4$ исследованы различными методами. Показано, что нанокристаллы $CuFe_2O_4$, полученные методом гидротермального синтеза, имеют нанокубическую структуру с размером частиц 45 нм, рентгеноструктурный анализ показывает кристаллическую природу $CuFe_2O_4$ без каких-либо других примесей.

1. Introduction

In general, spinels of a type $M^{2+}M_2^{3+}O_4$ attract the research interest due to their versatile practical applications [1]. In the case of M^{3+} = Fe, the resulting spinel ferrites having a general chemical composition of MFe_2O_4 (M = Mn, Mg, Zn, Ni, Co, Cd, etc.) are widely used as magnetic materials [2]. Currently, a large number of metal oxides, mixed oxides and ferrites have shown sensitivity to certain gas species. Spinel compounds, with a general formula of AB_2O_4, have also been proved as important oxides in gas sensors, and have been investigated for the detection of reducing gases. $NiFe_2O_4$, $CdFe_2O_4$ and $ZnFe_2O_4$ spinel ferrites have been extensively studied for various gas-sensing applications [3]. Copper ferrite ($CuFe_2O_4$) is one of the important ferrites [4]. The magnetic behavior of $CuFe_2O_4$ has been drawn much interest and has been a subject of intensive studies [5].

In fact, the diverse available methods or routes to prepare $CuFe_2O_4$ nanomaterials that have been published, such as ball-milling [6], sol-gel and co-precipitation [7] and combustion synthesis [8], are interesting and attract much research attention. However, these preparation methods are generally complicated and expensive especially when organo-metallic precursors and complex process control are involved. Sol-gel techniques involve the use of large amounts of organic solvents to the reaction medium. It is far from being environmentally friendly. Besides, in co-precipitation procedure, the pH of a metal salt solution was increased by adding a base in order to precipitate the hydroxides; this requires a strict control of the pH and the stirring rate. The ball-milling method and combustion synthesis are unfavorable to make $CuFe_2O_4$ at low cost, because of the problems such as the complex process and high-energy consumption. To apply $CuFe_2O_4$ to many nanoscale devices, an ideal process should be environmentally friendly and as simple as possible. Hydrothermal synthesis exhibited the remarkable merits of relatively short reaction time, good crystallinity, high purity, low energy consumption, low-cost and scalable synthesis [9].

With these inspirations in mind, in this work, we reported a hydrothermal strategy to prepare $CuFe_2O_4$ spinels, and further examined their infrared emissivity by using a SEM, XRD, FTIR and VSM. The effect of various $CuCl_2$ and $FeCl_2$ concentrations was systemically investigated.

2. Experimental

For synthesis of nanocubic $CuFe_2O_4$, $CuCl_2{\cdot}2H_2O$ (Merck, 99 %) and $FeCl_2{\cdot}4H_2O$ (Merck, 99 %) with various ratios (1:1, 1:2, 2:1 and 2:3) were mixed in 50 mL deionized water with stirring at 500 rpm for 1 h and ultrasonication (Powersonic 600) for 15 min. Then, the solution was transfer into a 100 mL hydrothermal Teflon-lining heated at 200°C for 6 h. After cooled down to room temperature, the solution was precipitated using centrifuge at 4000 rpm for 5 min, followed by washing with distilled water and ethanol. The obtained powder was dried at 60°C in hotplate and further annealed at 300°C for 1 h in furnace.

Field-Emission Scanning Electron Microscope (FESEM), Hitachi SU-3500, was used to determine the morphology of synthesized $CuFe_2O_4$. For microstructure analysis of $CuFe_2O_4$, X-Ray Diffraction (XRD), Rigaku Smartlab, was used in the diffraction angle range from 10 to 80 deg with CuKα (1.54 E) radiation. Fourier-Transform Infrared Spectrometer (FTIR) Thermo-Scientific Nicolet iS-10 using a KBr disk method and scanned in the range of 4000–450 cm^{-1} was used to determine the chemical composition of $CuFe_2O_4$. In order to investigate the magnetic properties of $CuFe_2O_4$, a vibrating sample magnetometer (VSM) VSM250 was used.

3. Results and discussion

The effect of various weight ratios between $CuCl_2$ and $FeCl_2$ on the particle morphology and crystal structure of the as-prepared samples was studied via FESEM analysis. Figures 1a–d indicate the FESEM images of $CuFe_2O_4$ samples synthesized after 6 h of hydrothermal reaction time at 200°C with following annealing at 300°C for 1 h. It can be seen that, at a 1:1 ratio, the $CuFe_2O_4$ sample consists of many spherical particles and has a loose porous structure. The formation of agglomerations was also observed. However, when ratio increases to 2:3, the cubic structure is clearly observed with particle size of 28 nm to 45 nm for 1:1 ratio. Figure 2 shows a diffraction pattern with 7 peaks at 2θ = 30.1, 35.4, 36.8, 43.1, 50.3, 53.2, and 62.6 degrees corresponding to the (220), (311), (222), (440), (442), (511) and (440) planes, respectively, of nanocubic spinel ferrite $CuFe_2O_4$. The cube-like and disk-like samples consisted of a pure cubic $CuFe_2O_4$ crystalline phase, and no other phase was observed. The crystallite size of $CuFe_2O_4$ can be calculated based on the Scherrer equation:

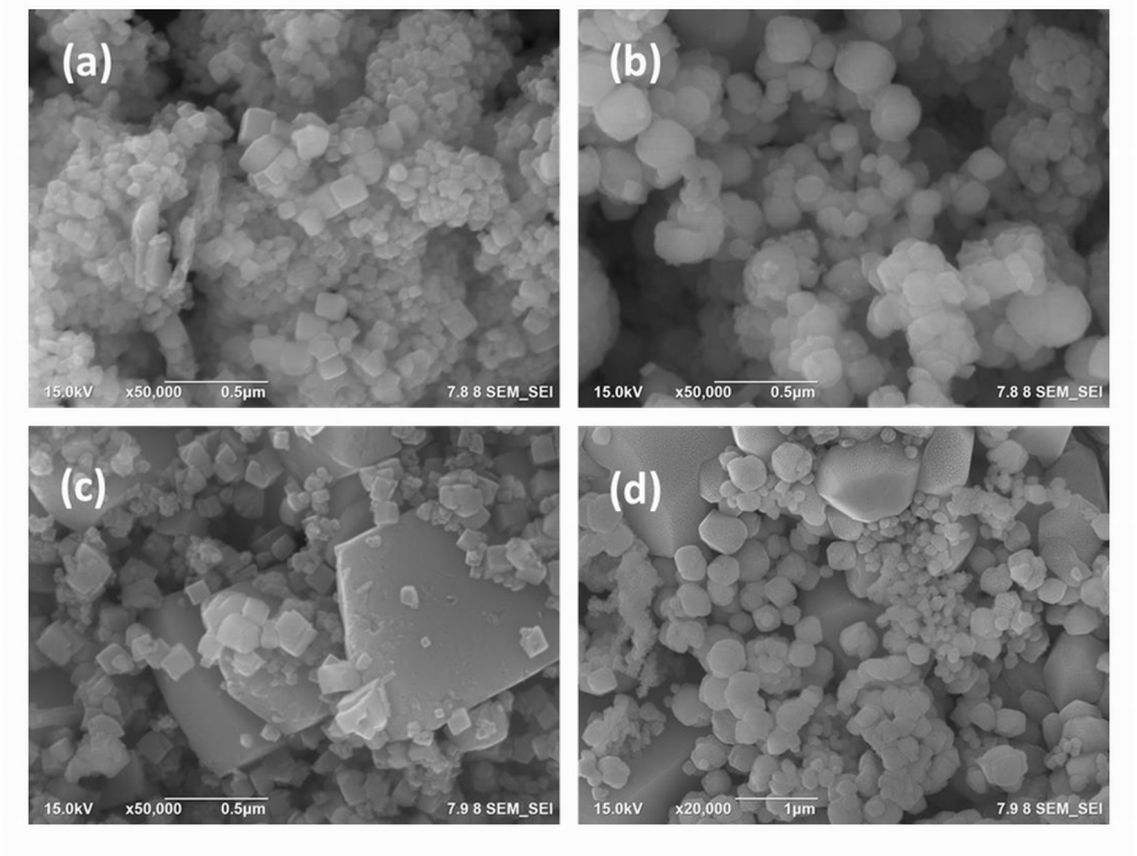

Fig. 1. FESEM images of $CuFe_2O_4$ with a ratio between $CuCl_2$ and $FeCl_2$ (a) 1:1, (b) 1:2, (c) 2:1 and (d) 2:3.

$$D = 0.9\lambda/\beta\cos\theta, \qquad (1)$$

where β is the broadening of the diffraction line measured at half maximum intensity (radians) and $\lambda = 1.5406$ E, the wavelength of CuKα. The average crystallite sizes of each sample with the ratios of $CuCl_2$ to $FeCl_2$ 1:1, 1:2, 2:1 and 2:3 are 11, 12, 15 and 18 nm, respectively.

The oxygen-strong two-metal band is in the range 400–1000 cm^{-1} which can be clearly observed by FTIR of all ferrite compounds. The first bands usually appearing in the range 380–450 cm^{-1} are associated to strain vibrations of metal cations located at octahedral sites. The second band usually appears in the range 550–600 cm^{-1} due to the metal strain vibrations at the tetrahedral sites. Figure 3 shows that the peaks of the $CuFe_2O_4$ octahedral (Cu–O) and tetrahedral (Fe–O) vibrations appear at 457 cm^{-1} and 573 cm^{-1}, respectively. The absorption bands appearing in both spectrums are at 1396, 1419, 1558 and 1651 cm^{-1} for O–H, CH vibrations, CH stretching, and C=C vibrations; this confirms the attachment of urea to the surface of Cu nanoparticles. In addition, a

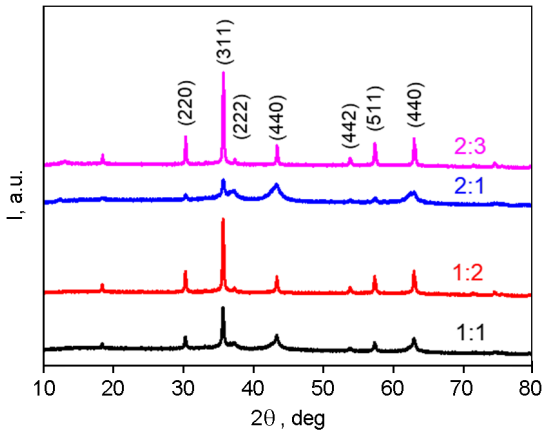

Fig. 2. XRD profiles of $CuFe_2O_4$ samples with various ratios of $CuCl_2$ to $FeCl_2$: (a) 1:1, (b) 1:2, (c) 2:1 and (d) 2:3.

wide band at about 3748 cm^{-1} was associated with the O–H strain in the H_2O molecule.

The VSM analysis is a tool to investigate the magnetic properties of the prepared spinel ferrite samples. The room temperature VSM analysis was performed on nanocubic $CuFe_2O_4$; the obtained magnetic hysteresis loops are shown in Fig. 4. The

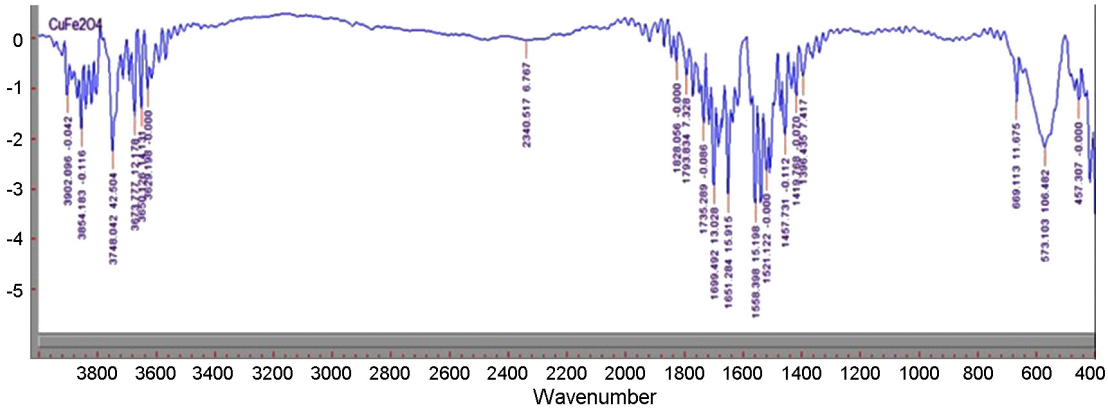

Fig. 3. FTIR analysis of hydrothermally synthesized nanocubic $CuFe_2O_4$.

saturation magnetization (M_s), residual magnetization (M_r), and coercivity (H_c) are 0.41 emu/g, 0.07 emu/g and 475.24 Oe, respectively for the $CuCl_2$:$FeCl_2$ (1:1) ratio; meanwhile for the ratio 2:1, M_s, M_r and H_c are 0.36 emu/g, 0.03 emu/g and 644.99 Oe, respectively. The difference between the saturation magnetization values for nanocubic $CuFe_2O_4$ at different Cu concentrations can be attributed to the surface effect of nanomaterials. This finding is also in good agreement with the previous report on magnetic properties of $CuFe_2O_4$ nanorods [9].

4. Conclusions

The obtained results demonstrate that nanocubic $CuFe_2O_4$ was successfully synthesized via facile hydrothermal methods with $CuCl_2$ and $FeCl_2$ as main precursors. According to FESEM images, the $CuFe_2O_4$ nanomaterials have a nanocubic structure, and an increase in the Fe concentration leads to an increase in the cubic size to 45 nm. The XRD analysis revealed the crystalline structure of $CuFe_2O_4$ at various $CuCl_2$ to $FeCl_2$ ratios with an average crystallite size of less than 20 nm; no other impurity peaks were observed. FTIR results indicate the chemical structure of the ferrite spinel $CuFe_2O_4$. VSM analysis shows that the saturation magnetization of $CuFe_2O_4$ decreases with an increase in the Cu concentration, however the coercivity increases.

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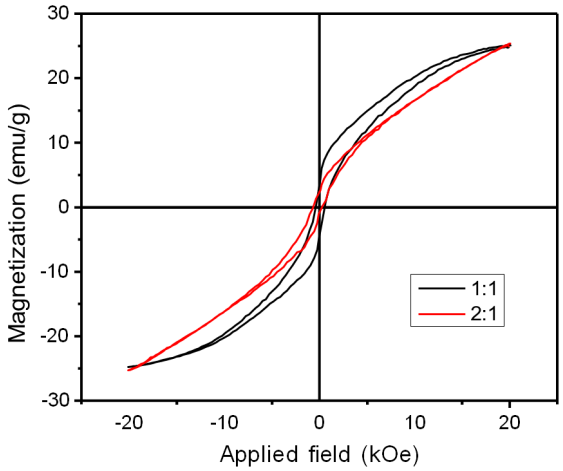

Fig. 4. Hysteresis loop for nanocubic $CuFe_2O_4$: (a) $CuCl_2$:$FeCl_2$ (1:1) and (b) $CuCl_2$:$FeCl_2$ (2:1) of at room temperature.

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