Effect of reaction condition on microstructure and properties of (NiCuZn) Fe₂O₄ nanoparticles synthesized via co-precipitation with ultrasonic irradiation

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ABSTRACT

Nano-spinel ferrites synthesized via chemical co-precipitation method are small in size and have serious agglomeration phenomenon, which makes separation difficult in the subsequent process. Ni₀.₃Cu₀.₇Zn₀.₄Fe₂O₄ ferrites nanoparticles were synthesized via co-precipitation assisted with ultrasonic irradiation produced by ultrasonic cleaner with 20 kHz frequency using chlorinated salts and KOH as initial materials. The effects of ultrasonic power (0, 40 W, 60 W, 80 W) and reaction temperature on the microstructure and magnetic properties of ferrite nanoparticles were investigated. The structure analyses via XRD revealed the successful formation of pure (NiCuZn)Fe₂O₄ ferrites nanoparticle without any impurity. The crystallites sizes were less than 40 nm and the lattice constant was near 8.39 Å. The TEM showed ferrite particle polygonal. M–H analyses performed the saturation magnetization and coercivity of ferrite nanoparticles obtained at the reaction temperature of 25°C were higher than at 50°C with same power. The samples exhibited the highest values of Ms 55.67 emu/g at 25°C and 47.77 emu/g at 50°C for 60 W and the lowest values of Hc 71.23 Oe at 25°C for 40 W and 52.85 Oe at 50°C for 60 W. The squareness ratio (SQR) were found to be lower than 0.5, which revealed the single magnetic domain nature (NiCuZn)Fe₂O₄ nanoparticles. All the outcomes show the ultrasonic irradiation has positive effects on improving the microstructure and increasing magnetic properties.

1. Introduction

In recent years, developments of magnetic nanoparticles have been receiving significant attention due to a wide range of potential applications and high absorption in the superparamagnetic characteristics, high surface-to-volume ratio, etc[1]. Spinel ferrites are the most attractive ferrite because of the presence of magnetic and electrical properties such as high saturation magnetization (Ms) as well as high dielectric properties and initial permeability, low eddy current loss [2–4]. they are used in broad applications such as biomedical imaging as MRI contrast agents[2,5], drug delivery[2,5,6], diagnostic of COVID-19 [7], wastewater treatment[8], nanofluids[9], visible light-enabled active photodegradation[10], gas sensing[5], energy storage[5], high-frequency antennas[5], electromagnetic interference (EMI) shielding [5], multilayer chip inductors (MLCs)[4], etc.

(NiCuZn)Fe₂O₄ spinel ferrite, developed on the basis of (NiZn)Fe₂O₄ ferrite ceramics is a great promising candidate material for core, switching, multilayer chip inductors (MLCIs) applications because of its high resistivity, excellent magnetic properties and low sintering temperature[11–13]. Better magnetic properties of nanoferrites are essential for modern MLCIs to reduce the number of ferrite layer in the chip [14]. Therefore, with the development of miniaturization of components, the preparation of (NiCuZn)Fe₂O₄ powder with excellent properties has attracted extensive attention[15,16]. Researchers have reported many methods about the synthesis of (NiCuZn)Fe₂O₄ nanoparticles such as solid-state reaction method[17,18], co-precipitation [19,20], egg-white method[21], hydrothermal synthesis[22], microwave synthesis[13] and sol–gel auto-combustion method[23–25].

Compared with other methods, chemical co-precipitation has the advantages of lower cost, faster reaction speed, lower requirements on reaction equipment, better performance of the prepared powder, high activity and purity, and is a common method for preparing nano-sized powder[19,20]. (NiCuZn)Fe₂O₄ ferrite prepared by co-precipitation method can reach nano particles level, which is beneficial to the subsequent sintering process[26]. However, in the reaction process, products with uniform performance cannot be obtained due to the
nonuniformity of the reaction. At the same time, ions prepared by co-precipitation method are small in size and have serious agglomeration phenomenon, which makes separation difficult in the subsequent process [27].

Ultrasonic wave is a high frequency wave with a frequency higher than 2000 Hz and has the advantages of good directivity, strong penetrating power, etc [28,29]. It is envisaged that ultrasonic-assisted co-precipitation reaction is adopted to find a method for preparing nano \((\text{NiCuZn})\text{Fe}_2\text{O}_4\) ferrite with uniform particle size distribution and excellent performance at lower temperature by Y. Slimani et al [30,31] using nitrated salts and NaOH as initial materials and by Hassen Harzali et al [32,33] using sulfated salts as raw materials. The experimental results shown that co-precipitation method coupled with ultrasound irradiation was favor in getting a single spinel phase, the uniformity of co-precipitation particles was significantly improved [28,34]. Therefore, it can be seen that the introduction of ultrasound-assisted technology into the co-precipitation reaction can achieve excellent results.

Despite such exploration, the effect of reaction condition including to ultrasound power and reaction temperature via using the chlorided salts and KOH as raw materials on microstructure and properties of \((\text{NiCuZn})\text{Fe}_2\text{O}_4\) powder remain unclear. There is also a lack of study on the evolution process of the nano ferrite particles under ultrasound. In the present work, it is aimed at carrying out a systematic study of nano-sized \(\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4\) ferrites synthesized by co-precipitation method with the aid of ultrasound irradiation using the chlorided salts and KOH as raw materials. These microstructure and properties were examined using X-ray diffraction (XRD), Fourier transform spectroscopy (FTIR), scanning and transmission electron microscopy (SEM and TEM), and vibrating sample magnetometry (VSM). The effects of reaction condition including to ultrasound power and reaction temperature on microstructure and properties of \((\text{NiCuZn})\text{Fe}_2\text{O}_4\) powder were investigated.

2. Experimental

2.1. Raw materials

The initial materials used in the experiment were commercial potassium hydroxide (KOH) and chlorinated salts including nickel chloride (NiCl\(_2\)⋅6H\(_2\)O), copper chloride (CuCl\(_2\)⋅6H\(_2\)O), zinc chloride (ZnCl\(_2\)) and ferric chloride (FeCl\(_3\)⋅6H\(_2\)O) with analytical reagent grade purchased from Sinopharm Chemical Reagent Co., Ltd.. The weight ratios of various chlorinated salts were calculated according to the stoichiometry of \(\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4\). The precipitator of KOH was matched according to the reaction exceeding 20% in order to the salt completely precipitated.

2.2. Preparation of ferrite powder

Four kinds of chlorinated salts were weighed based on the molar ratio dictated by the chemical formula \(\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4\). The reactants were dissolved in proper deionized water to obtain Solution A with the concentration of 0.25 mol/L. Meanwhile, KOH was dissolved in proper deionized water to obtain Solution B with the concentration of 1 mol/L.

A water bath was used to maintain the reaction temperature and ultrasonic wave by ultrasonic cleaner (KQ2200DE, frequency: 20 kHz). Solutions A and B were then added dropwise into a three-necked flask placed into the water bath together and followed by indirect ultrasonic wave irradiation with a input power (0, 40 W, 60 W or 80 W) and mechanical stirring (300r/min) for 25 min at the set temperature (room temperature or 50°C). The flow rate of metal salt and KOH were controlled to be 10 ml/min and 8 ml/min, respectively. The reaction was continued for 1 h after the dropwise addition was completed. During dropping and subsequent reaction, the pH of the solution was detected with a pH meter every 10 min, controlled within the range of 10.5 ± 0.1, and the pH was adjusted with ammonia solution.

After the precipitation reaction was completed, sample left for 48 h.
The precipitation was left to separate into layers, the upper clear liquid was poured out, and the lower suspension was poured into a 15 ml centrifuge tube. Then the tube was placed in a high-speed centrifuge (L500) for centrifugation at a speed of 3900 r/min for 5 min repeated for three times. Further washed with deionized water for the third time, a muddy product was obtained. The centrifuge tube was placed in a vacuum drying oven with temperature at 70°C for 16 h, and the required precursor powder was obtained by taking out the dried product. The ferrite powder particles was obtained via the precursor powder calcined at 800°C for 2 h and cooled with the furnace in an air atmosphere by a muffle furnace. The schematic representation of main synthesizing process shows in Fig. 1.

2.3. Characterization

The phase structure of ferrite powders were analyzed by DX-2700B XRD diffractometer, and the crystal grain size, cell parameters and other structural information of the particles were calculated. The morphology of ferrite particles were observed by SEM (Quanta-200 FEI) and TEM (Tecnai G2 20 FEI). Fourier transform infrared spectra (FTIR; Nicolet 6700) recorded in the range of 400–4000 cm⁻¹ at room temperature were used to investigate the chemical structure. The hysteresis loops of powder samples in the range of ±1.5 T were measured by a Quantum Design vibrating sample magnetometer (QD-VSM; VLM468P).

3. Results and discussion

3.1. Structural analysis (XRD)

Fig. 2 is the XRD diffraction pattern of samples synthesized at room temperature (25°C) and 50°C under different ultrasonic powers (0, 40 W, 60 W, 80 W). It can be seen from the figure that the reaction products have obvious diffraction peaks (111), (220), (311), (222), (400), (422), (511) and (440) regardless of whether there is ultrasonic assistance or not. Compared with the standard PDF card (JCPDS card No. 08-0234), it is a typical cubic spinel ferrite phase diffraction peak. And no obvious impurity peak is found in the x-ray diffraction pattern, indicating that the obtained spinel ferrite is relatively pure. A simplified chemical pathway that leads to the formation of (NiCuZn)Fe₂O₄ cubic spinel ferrite particles might be summarized as follows[35]:

Ni²⁺ + 2OH⁻ → Ni(OH)₂  
(1)

Cu²⁺ + 2OH⁻ → Cu(OH)₂  
(2)

Zn²⁺ + 2OH⁻ → Zn(OH)₂  
(3)

Fe³⁺ + 3H₂O → Fe(OH)₃ + 3H⁺  
(4)

Fe(OH)₃ → FeOOH + H₂O  
(5)

when calcined at 800°C,

0.4Ni(OH)₂ + 0.2Cu(OH)₂ + 0.4Zn(OH)₂ + 2FeOOH → Niₐ₄Cuₐ₂Znₐ₂Fe₂O₄  
(6)

In this case, the chemical formula of co-precipitation and calcined method is as follows:

2NiO₂CuO₂ZnO₄Fe₂O₄ + 10FeO + 20H₂O = 5Niₐ₄Cuₐ₂Znₐ₂Fe₂O₄ + 20H₂O  
(7)

The chemical reactions described by Eqs. (1), (2) and (3) are actuated immediately once Solution A and Solution B are mixed, whereas the first KOH solution contains precursor cations. The reactions shown by Eqs. (4) and (5) describe the processing that lead to the formation of ferric ions and their precipitation. The reaction described by Eq.(6) is a final form of well-crystallized ferrite has a formula Niₐ₄Cuₐ₂Znₐ₂Fe₂O₄ which has a spinel structure.

According to the obtained XRD diffraction pattern, the grain sizes and lattice parameters under different input powers were calculated. The grain sizes (D) of individual ferrite phase were evaluated based on their XRD patterns according to the Scherrer formula[6,12,36]:

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  
(8)

Where D is the crystallite size, λ is X-ray radiation wavelength (1.5418 Å for the Cu Kα radiation), θ is the Bragg angle and β is the full width at half maximum (FWHM) of all diffraction peaks. k is a constant related to crystallite shape, normally taken as 0.9. The grain sizes of (NiCuZn)Fe₂O₄ ferrites calculated according to (311) reflections are shown in Table 1.

Table 1

| Temperature (°C) | Ultrasonic power(W) | Crystallite sizes (nm) | Lattice parameters (Å) | X-ray density (g/cm³) |
|-----------------|---------------------|-----------------------|------------------------|----------------------|
| 25              | 0                   | 35.3                  | 8.388                  | 5.3805               |
| 40              | 40                  | 40.1                  | 8.392                  | 5.3728               |
| 60              | 39.7                | 8.396                  | 5.3652                 |                      |
| 80              | 38.4                | 8.394                  | 5.3690                 |                      |
| 50              | 0                   | 34.9                  | 8.388                  | 5.3805               |
| 40              | 36.5                | 8.389                  | 5.3786                 |                      |
| 60              | 36.6                | 8.387                  | 5.3824                 |                      |
| 80              | 33.5                | 8.391                  | 5.3748                 |                      |

Whereas the lattice parameter was investigated using the equation [6,32]:

\[ a = d_{hkl} \sqrt{h^2+k^2+l^2} = \frac{\lambda}{2 \sin \theta} \sqrt{h^2+k^2+l^2} \]  
(9)

Where a is the lattice parameter, and d is the inter-planar distance and hkl are Miller indices. The calculated values are listed in Table 1.

The X-ray density (ρ_x-ray) of synthesized (NiCuZn)Fe₂O₄ spinel ferrite nanoparticles at different sonication powers was determined by utilizing the following relation[37,38]:

\[ \rho_{x-ray} = \frac{ZM}{Na^2} \]  
(10)

Where, Z is the number of molecules per unit cell, Z is 8 for (NiCuZn)Fe₂O₄ ferrite. M is the molecular weight of Niₐ₄Cuₐ₂Znₐ₂Fe₂O₄ ferrite (238), Nₐ is the Avogadro’s number (6.02 × 10²³ mol⁻¹) and a is the lattice parameter of (NiCuZn)Fe₂O₄ ferrite nanoparticles prepared at different sonication power. The evaluated values of X-ray density of the prepared (NiCuZn)Fe₂O₄ spinel ferrite nanoparticles at different ultrasonic powers are tabulated in Table 1.

It can be seen that the grain size of ferrite powder with ultrasonic assistance at 25°C is significantly increased compared with that without ultrasonic assistance. The results of 40 W and 60 W are similar. The grain size of ferrite powder with ultrasonic assistance is decreased at 80 W, but it is still higher than that of samples without ultrasonic assistance. Lattice parameters also increase with the increase of input power, and reach the largest value 8.392 Å of lattice constant at 60 W. The change law of x-ray density is opposite to that of lattice constant.

Further, the structural parameters such as the tetrahedral and octahedral site radii (rₐ and rₖ), hopping length in tetrahedral and octahedral site (dₐ and dₖ), tetrahedral and octahedral bond lengths (dₐ₋ₖ), tetrahedral edge, shared and unshared octahedral edges (dₐ₋ₖₑ, dₖₑₑₑ) for sonechemically prepared (NiCuZn)Fe₂O₄ nanoparticles can be determined by using following equation[37,39,40]:

\[ r_a = \left( \frac{a - \frac{1}{3}}{\frac{a}{\sqrt{3}} - R_0} \right) \]  
(11)
Table 4
The values of interionic distances (p, q, r, s, b, c, d, e and f) for (NiCuZn)Fe\(_2\)O\(_4\) nanoparticles.

| Temperature(℃) | Ultrasonic power(W) | Ionic Radii | Hopping Length | Tet. Bond | Oct. Bond | Tet. Edge | Oct. Edge | Oct. Edge (Shared & Unshared) |
|----------------|----------------------|-------------|---------------|-----------|-----------|-----------|-----------|-----------------------------|
| 25             | 0                    | 0.6260      | 0.7015        | 3.6320    | 2.9660    | 1.9460    | 2.0248    | 3.1791                      |
|                | 40                   | 0.6269      | 0.7025        | 3.6337    | 2.9674    | 1.9469    | 2.0258    | 3.1806                      |
|                | 60                   | 0.6279      | 0.7034        | 3.6355    | 2.9688    | 1.9479    | 2.0268    | 3.1821                      |
| 50             | 0                    | 0.6260      | 0.7015        | 3.6320    | 2.9660    | 1.9460    | 2.0249    | 3.1791                      |
|                | 40                   | 0.6262      | 0.7017        | 3.6324    | 2.9664    | 1.9462    | 2.0251    | 3.1794                      |
|                | 60                   | 0.6258      | 0.7013        | 3.6316    | 2.9656    | 1.9458    | 2.0246    | 3.1787                      |
|                | 80                   | 0.6267      | 0.7022        | 3.6333    | 2.9670    | 1.9467    | 2.0256    | 3.1802                      |

The values of interionic distances (p, q, r, s, b, c, d, e and f) for (NiCuZn)Fe\(_2\)O\(_4\) nanoparticles.

| Temperature(℃) | Ultrasonic power(W) | Ionic Radii | Hopping Length | Tet. Bond | Oct. Bond | Tet. Edge | Oct. Edge | Oct. Edge (Shared & Unshared) |
|----------------|----------------------|-------------|---------------|-----------|-----------|-----------|-----------|-----------------------------|
| 25             | 0                    | 2.0215      | 1.9469        | 3.7276    | 3.6756    | 2.9660    | 3.4777    | 3.6320                      |
|                | 40                   | 2.0225      | 1.9478        | 3.7294    | 3.6774    | 2.9674    | 3.4793    | 3.6337                      |
|                | 60                   | 2.0234      | 1.9487        | 3.7312    | 3.6791    | 2.9688    | 3.4810    | 3.6355                      |
| 50             | 0                    | 2.0230      | 1.9482        | 3.7303    | 3.6782    | 2.9681    | 3.4802    | 3.6346                      |
|                | 40                   | 2.0215      | 1.9469        | 3.7276    | 3.6756    | 2.9660    | 3.4777    | 3.6320                      |
|                | 60                   | 2.0213      | 1.9466        | 3.7272    | 3.6752    | 2.9656    | 3.4772    | 3.6316                      |
|                | 80                   | 2.0222      | 1.9476        | 3.7290    | 3.6769    | 2.9670    | 3.4789    | 3.6333                      |

at room temperature is higher than at 50℃ react temperature. The variation law of other structural parameters is the same, because these parameters are dependent on the lattice constant. It implies that the distance between the magnetic ions in (NiCuZn)Fe\(_2\)O\(_4\) nanoparticles prepared assisted with ultrasonic is related with the amplitude of input power and react temperature. The observed change in structural characteristics triggered by input power and react temperature can lead the change in properties characteristics of (NiCuZn)Fe\(_2\)O\(_4\) nanoparticles prepared via sonochemistry.

The inter-ionic distances including to [cations (metal ions)-anions (oxygen ions)] (p, q, r, s) and [cations (metal ions)-cations (metal ions)] (b, c, d, e, f) were calculated according to the below relations and the values are tabulated in Table 3.

$$r_\theta = \left(\frac{5}{8} - u\right) a - R_0$$ \hspace{1cm} (12)

$$d_\alpha = \frac{1}{4} a \sqrt[3]{3}$$ \hspace{1cm} (13)

$$d_\beta = \frac{1}{4} a \sqrt[2]{2}$$ \hspace{1cm} (14)

$$d_\gamma = a \sqrt[3]{(u - \frac{1}{4})}$$ \hspace{1cm} (15)

$$d_{\alpha \beta} = a \left[3a^2 - \frac{11}{4} a + \frac{43}{64}\right]^{1/2}$$ \hspace{1cm} (16)

$$d_{\alpha \gamma} = a \sqrt[2]{2 \left(4a - \frac{1}{2}\right)}$$ \hspace{1cm} (17)

$$d_{\beta \gamma} = a \sqrt[2]{(1 - 2a)}$$ \hspace{1cm} (18)

$$d_{\alpha \beta \gamma} = a \left[4a^2 - 3a + \frac{11}{16}\right]^{1/2}$$ \hspace{1cm} (19)

where, a is the lattice parameter of spinel ferrite, u (=0.384 Å) is the oxygen positional parameter, and Ro (=1.32 Å) is the radius of oxygen.

These calculated values of structural parameters for (NiCuZn)Fe\(_2\)O\(_4\) nanoparticles prepared are listed in Table 2. The hopping length increases with the increase of input ultrasonic power, and reaches the largest value at 60 W power under room temperature. And the value of

Table 4
The values of bond angles (θ\(_1\), θ\(_2\), θ\(_3\), θ\(_4\) and θ\(_5\)) for (NiCuZn)Fe\(_2\)O\(_4\) nanoparticles.

| Temperature(℃) | Ultrasonic power(W) | θ\(_1\) (degrees) | θ\(_2\) (degrees) | θ\(_3\) (degrees) | θ\(_4\) (degrees) | θ\(_5\) (degrees) |
|----------------|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 25             | 0                    | 122.399           | 149.922           | 94.381            | 66.722            | 71.964            |
|                | 40                   | 122.395           | 149.919           | 94.378            | 66.720            | 71.962            |
|                | 60                   | 122.403           | 149.921           | 94.381            | 66.721            | 71.964            |
| 50             | 0                    | 122.402           | 149.917           | 94.376            | 66.721            | 71.963            |
|                | 40                   | 122.402           | 149.924           | 94.385            | 66.720            | 71.961            |
|                | 60                   | 122.394           | 149.920           | 94.376            | 66.721            | 71.964            |
|                | 80                   | 122.397           | 149.923           | 94.379            | 66.722            | 71.962            |
It is evidenced from Table 3, it is obvious of the variation of inter-ionic distances is consistent with that of the lattice constant a, because all these inter-ionic distances directly depend on the lattice constant values.

Apart from this, the inter-ionic angles such as bond angles (including to \( \theta_1, \theta_2, \theta_3, \theta_4, \theta_5 \)) were estimated by using the following formulas and the calculation results are summarized in Table 4.

\[
\theta_1 = \cos^{-1} \left( \frac{p^2 + q^2 - c^2}{2pq} \right) \\
\theta_2 = \cos^{-1} \left( \frac{p^2 + r^2 - c^2}{2pr} \right) \\
\theta_3 = \cos^{-1} \left( \frac{2p^2 - b^2}{2p^2} \right) \\
\theta_4 = \cos^{-1} \left( \frac{p^2 + s^2 - f^2}{2ps} \right) \\
\theta_5 = \cos^{-1} \left( \frac{r^2 + q^2 - d^2}{2rq} \right)
\]

As seen from Table 4, the inter-ionic angles are affected by the ultrasonic input power and the reaction temperature. This changing nature of the 'inter-ionic angles' can be attributed to the intensification and weakening of the cationic interaction with anion i.e. \((\text{A}) \leftrightarrow \text{B}\) and cationic interaction with cations i.e. \([\text{B}] \leftrightarrow [\text{B}]\) respectively. But the effect of ultrasonic and reaction temperature on the ionic interaction is much less than that of ion doping in ferrite [39-41].

The size control of materials is of great importance because the materials with different sizes have different physical properties and applications. Ultrasonic wave specific function is to provide reaction energy to reduce reaction temperature and disperse particles [28,30,34]. Previous study have shown that the dispersion rate of the produced particles increased with the increasing electric power for the ultrasonic irradiation [42]. A.L.Nikolaev, et al [43] researched results shown high power ultrasound regime provided smaller nucleation sites and smaller resulting particles, compared to vortices and particles obtained without ultrasound. Therefore, with the increase of ultrasonic power, the grain size of \((\text{NiCuZn})_2\text{Fe}_2\text{O}_4\) ferrite nanoparticle decreases. This conclusion was also confirmed by Huang [44] in the preparation of \(\text{Y}_2\text{BaCuO}_5\) nanoparticles by a co-precipitation process with the aid of ultrasonic irradiation.

As can be seen from Table 1, with the increase of ultrasonic power, the grain sizes first increase and then decrease at 50°C reaction temperature. When the input power is 60 W, the grain size is significantly larger than that of ferrite without ultrasonic assistance. When the power is increased to 80 W, the ferrite grain size is smaller than that without ultrasonic assistance. However, the lattice parameters of 60 W is the largest (8.391 Å) and of 80 W is the largest (8.387 Å). On the contrary, when the input power is 60 W, the grain size is significantly larger than that of ferrite without ultrasonic assistance. When the power is increased to 80 W, the ferrite grain size is smaller than that without ultrasonic assistance.

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than at higher temperature. Therefore, the grain size of ferrite samples prepared at low temperature was larger than that at high temperature. This phenomenon has also been confirmed in the other research [33].

Supersaturation was also affected by ultrasonic power. The main function of ultrasonic applied in chemical reaction was that when interacting with liquid, the solubility of liquid was reduced due to the negative pressure generated locally in the liquid, so that gas escaped to form small bubbles [28]. At the same time, cavitation also promoted the generation of many small bubbles in the liquid, which made the particle size of reaction product more uniform. It might also explain why the grain size under ultrasonic wave was larger than that without ultrasonic wave.

3.2. Infrared spectroscopic analysis

Fig. 3 is the infrared spectrum of the sample synthesized with different input powers at 50°C. Each sample has an obvious absorption peak in 581–584 cm⁻¹, which is related to the vibration of octahedral metal ion oxygen complex [33,46]. All samples presented FTIR stretching bands at about 410 cm⁻¹ (also due to Me-O stretching) [47]. The absorption peak with a wave number of 1630 cm⁻¹ comes from H-O vibration in water, which is due to the small amount of crystal water in the sample. An absorption peak appears at 3430 cm⁻¹, which comes from hydroxyl stretching vibration on ferrite surface [32]. Comparing the peaks of four samples prepared at different input powers, it can be seen that the absorption peak of octahedral metal ion oxygen complex slightly shifts with the increase of ultrasonic power, and the peak shift to the left is the most obvious at 60 W.

The absorption peak of infrared spectrum reflects the absorption of infrared light by the sample, which is not only related to the structure of the ferrite sample, but also affected by the other factor. The shift of position is related to the change of particle size [32]. According to XRD results, the grain size of the sample increases with the increase of ultrasonic power, but the increase of grain size is inhibited when the power exceeds a certain value.

As can be seen from Fig. 4, under the same power condition and different preparation temperatures, the infrared spectrum peaks of ferrite samples also shift to a certain extent. Similar to the previous analysis, this shift is mainly caused by changes in grain size.

3.3. Morphological analysis

The powder samples prepared under the power of 40 W at the reaction temperature of 50°C were selected for morphological characterization. Fig. 5 is the SEM obtained under a scanning electron microscope. As can be seen from the figure, because of the low magnification, the sample appears to be somewhat accumulated, and the formed particles have smaller particle sizes. The accumulated particles are roughly regular in shape, and the size distribution of the particles is relatively uniform. It is preliminarily judged that the particle size is below 100 nm, and the specific morphological characteristics and size information need to be further observed by high power electron microscopy.

The above sample was further observed under the transmission electron microscope. Fig. 6 shows the morphology characteristics of the ferrite powder particles under different multiples. As can be seen from Fig. 6, (NiCuZn)Fe₂O₄ ferrite particle is polygonal, with a size of less than 40 nm, but there are also a few particles with larger size. It is considered that some particles grow abnormally due to incomplete drying process and small amount of water remaining, but most of the particles are normal in size, proving that the prepared ferrite powder is nanoparticle and nanocrystalline. Compared with the calculated grain size, it can be found that the obtained small particles are of single crystal structure, i.e. each small particle contains only one crystal. According to the sample preparation process, spinel phase formation mainly occurs during the calcination process of particles. The calcination temperature selected in this experiment was 800°C, at which the easy growth direction of crystal preferentially grew to obtain polyhedral crystal grains.
3.4. Magnetic properties of ferrite particles

Fig. 7 shows the hysteresis loops of (NiCuZn)Fe$_2$O$_4$ nanoparticles synthesized under different reaction conditions. As can be seen from the graph, the measured hysteresis loops are all s-shaped, indicating that the sample has good soft magnetic properties.

The saturation magnetization (Ms), remanent magnetization (Mr) and coercivity (Hc) of (NiCuZn)Fe$_2$O$_4$ nanoparticles synthesized at different powers were evaluated from the magnetic hysteresis curves and mentioned in Table 5. It can be seen from the Table 5 that the saturation magnetization increases first and then decreases with the increase of power, and the saturation magnetization of the sample is the largest 47.77 emu/g under the preparation condition of 60 W. It is obvious that under the condition of ultrasonic assistance, the saturation magnetization is greater than that without ultrasonic assistance.

Compared saturation magnetization and coercive force under different reaction conditions, it can be seen from the Table 5, the saturation magnetization generated at reaction temperatures of 25℃ is higher than that of ferrite samples at 50℃. Considering the factors affecting the saturation magnetization, the grain size information obtained by combining the previous XRD results is mainly due to the larger grain size of ferrite particles formed at 25℃, so its saturation magnetization is larger.

Some main factors including the size of crystal grains, crystal lattice and distribution of various metal elements in the crystal structure affect saturation magnetization. From XRD results, it can be seen that the lattice constant of ferrite samples obtained with ultrasonic assistance of different powers has not changed much, but has a certain influence on the grain size. The grain size of ferrite powder at 60 W is the largest, and the corresponding saturation magnetization is also the largest. However, the saturation magnetization of ferrite powder particles prepared at 80 W is also higher than that without ultrasonic assistance, which indicates that ultrasonic wave not only has the influence on grain size, but also on the crystal structure. According to the change rule of saturation magnetization, it can be considered that this effect is beneficial and promotes the integrity of ferrite structure to some extent.

As can be seen from Table 5, with the increase of ultrasonic power, the coercivity of the prepared ferrite samples first decrease and then increase. The coercivity of sample prepared at 60 W reached the smallest 52.85Oe. One reason is that its grain size is large and grain boundary is thin, on the other hand, its crystal structure is complete and its internal stress is small. It is obvious that the coercivity of samples prepared under ultrasonic assistance is smaller than that without ultrasonic assistance. Under the assistance of certain ultrasonic waves, the ferrite sample has a more uniform particle size distribution, a certain increase in grain size, more complete crystallization, fewer defects in the crystal structure, and easier movement of magnetic domain walls. So the magnetization process and demagnetization process are easier to carry out, and the coercivity is smaller.

As can be seen from Table 5, the coercivity of ferrite powder produced at 50℃ is lower than that produced at 25℃. Coercive force is affected by many factors, not only crystal size but also crystal structure. The reason may be that the crystal structure of the sample at 50℃ is more complete and the coercivity is smaller.

It is well-known that the Hc and Ms are related by the following expression[30]:

$$H_c = \frac{2K}{\mu_0 M_s}$$  \hspace{1cm} (36)

Where, K is magneto-crystalline anisotropy constant, and $\mu_0$ is
Table 5
Magnetic properties of ferrite particles synthesized under different ultrasonic power and reaction temperature.

| Temperature (°C) | Ultrasonic power (W) | Ms (emu/g) | Mr (emu/g) | SQR | Hc (Oe) | nθ(μB) |
|-----------------|----------------------|------------|------------|------|---------|---------|
| 25              | 0                    | 45.89      | 0.72       | 0.0157 | 79.53   | 1.96    |
|                 | 40                   | 47.89      | 0.74       | 0.0154 | 71.23   | 2.04    |
|                 | 60                   | 55.67      | 0.80       | 0.0144 | 71.82   | 2.37    |
|                 | 80                   | 50.66      | 0.78       | 0.0154 | 82.56   | 2.16    |
| 50              | 0                    | 40.45      | 0.66       | 0.0163 | 66.78   | 1.72    |
|                 | 40                   | 42.34      | 0.67       | 0.0158 | 54.87   | 1.80    |
|                 | 60                   | 47.77      | 0.73       | 0.0153 | 52.85   | 2.04    |
|                 | 80                   | 45.50      | 0.71       | 0.0156 | 64.25   | 1.94    |

4. Conclusions

The (Ni₀.₄Cu₀.₂Zn₀.₄)Fe₂O₄ ferrite nanoparticles with cubic spinel structure were synthesized by ultrasonic assisted chemical coprecipitation method using salts chloride and KOH as raw materials. The effects of ultrasonic power and reaction temperature on the microstructure and magnetic properties of ferrite nanoparticles were investigated. The crystallites sizes were less than 40 nm and the lattice constant was near 8.39 Å. The properties of ferrite nanoparticles were the best for ultrasonic sound 60 W power at the reaction temperature of no matter room temperature or 50°C, with Ms 55.67 emu/g and Hc 71.82 Oe, and Ms 47.77 emu/g and Hc 52.85 Oe respectively. M–H analyses performed at RT and 50°C showed soft ferromagnetic behaviors. The saturation magnetization and coercivity of ferrite nanoparticles obtained at the reaction temperature of room temperature were higher than at 50°C with same power. The results showed that ultrasound had a positive effect on improving the magnetic properties. The ultrasonic irradiation method had a potential of industrial application for the controlled synthesis of nano-spinel ferrites.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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