The synthesis and microstructure of CuFeO$_2$ powders via microwave hydrothermal reaction

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The CuFeO$_2$ powders have been synthesized by the microwave hydrothermal reaction at different reaction temperatures. The pure rhombohedral phase for CuFeO$_2$ has been formed and confirmed by the X-ray diffraction (XRD). The microstructure and morphology for all CuFeO$_2$ samples have been scanned by the Transmission Electronic Microscope (TEM). Various scales of grains for powders have been found spanning from several nanometers to hundreds of nanometers, and even few scales are over 1 $\mu$m for some grains. The average grain sizes for all powders have been calculated basing on the XRD patterns to show the changing of grain sizes with the temperature. The distributions of the grain size have also been studied by counting grain numbers from the TEM images. Based on the above results, the mechanism of grain growth has been analyzed and found to be the classical Ostwald ripening.

Key-words : CuFeO$_2$ powders, Microwave hydrothermal reaction, Pure rhombohedral phase, Morphology, Grain size

1. Introduction

Delafossites with a chemical formula of $\text{A}^+\text{B}^{3+}\text{O}_2$ were firstly reported by Friedel in 1873 and named after the French mineralogist and crystallographer, Gabriel Delafosse. Their structure is formed by alternative stacking layers of O–A–O dumb-bell and BO$_2$ edge-shared octahedron along with the c-axis. Delafossites can be crystalized in either a rhombohedral 3R or hexagonal 2H type depending on the stacking of the alternating layers.\textsuperscript{1} By stacking the double layers with alternating A layers oriented 180° relative to each other, the hexagonal 2H type is formed.\textsuperscript{2} This layered structure is similar to NaCo$_2$O$_4$\textsuperscript{3} and BiCuSeO\textsuperscript{4} which show excellent thermoelectric performance. So it is difficult to obtain the intrinsic thermoelectric performance for the pure CuFeO$_2$ sample. So synthesizing pure phase of CuFeO$_2$ by new methods is very significant.

The hydrothermal reaction method is well known due to its environmental safety and simplicity. It does not require any organic solvent or other additional process, such as calcination. Additionally, the production in nanoscale can be easily formed by the hydrothermal reaction method. In the previous report, the CuFeO$_2$ samples have been prepared by the hydrothermal reaction method under high temperatures (500–700°C) and high pressure (3000 atm)
for about 24 h in thin walled platinum and gold tubes.\textsuperscript{9) \textit{}} Besides, CuFeO\textsubscript{2} powders have been synthesized via a facile one step hydrothermal method at 180°C for 24–64 h.\textsuperscript{10) \textit{}} It has also been successfully formed by using hydrazine hydrate as a reducing agent. The reaction temperatures are 150–280°C, and reaction time is 24–96 h.\textsuperscript{11) \textit{}} From the reports above, although the CuFeO\textsubscript{2} has been synthesized by the hydrothermal reaction, the high temperature, high pressure or long reaction time are also needed. While, the microwave hydrothermal reaction method can combine the advantages of hydrothermal reaction and microwave heating, which can promote the reaction going at relative low temperature in a very short duration. Therefore, the microwave hydrothermal reaction may be one of the suitable ways to synthesize the pure CuFeO\textsubscript{2} powders rapidly.

In this work, we deliver a facile one-step ultra-fast microwave hydrothermal reaction method to obtain the pure CuFeO\textsubscript{2} powders. The reaction time has been shorten to 30 min. The microstructure and morphology have been studied and then the grain size distributions have been analyzed. The relationship between the crystal phase of CuFeO\textsubscript{2} powders and reaction temperatures has been studied. The grain growth mechanism has been explained and is consist with the classical Ostwald ripening (OR) theory.

2. Experimental procedures

CuFeO\textsubscript{2} powders have been synthesized through the microwave hydrothermal reaction method. In a typical synthesis process, 0.022 mol FeCl\textsubscript{3}·6H\textsubscript{2}O (\(>\)97%, Aladdin) and CuCl\textsubscript{2}·2H\textsubscript{2}O (\(>\)99%, Aladdin) were weighted in stoichiometric proportion and then dissolved in 50 mL deionized water to form a clear solution. After that, 6g of NaOH (\(>\)96%, Aladdin) crystals were added into the solution with stirring to get a colloidal suspension. Following that, 1.5 mL of propionaldehyde (\(>\)97%, Aladdin) were added into the solution with stirring to get a colloidal suspension. This suspension was transferred to an 80 mL Teflon autoclave, and then put into the microwave hydrothermal synthesis system (XH-800S, Beijing XiangHu Science and Technology Development, China). The reaction temperatures and time were accurately regulated by the microcomputer program in the microwave hydrothermal synthesis system. The setting reaction temperatures were from 130°C to 210°C in every 10°C. The setting reaction time is 30 min. After the microwave hydrothermal reaction, the obtained products were washed for several times with dilute HNO\textsubscript{3} and deionized water in this order. After that, the obtained products were separated with a centrifugal machine. At last, the wet powders were dried in the oven.

Crystal structure of all CuFeO\textsubscript{2} powders was characterized by powder XRD with Cu K\textalpha\textsubscript{λ} radiation at room temperature using a diffractometer (Bruker AXS D8 ADVANCE, Bruker, Germany). The microstructure and morphology of powders were scanned using a Transmission Electron Microscope (TEM) system (JEM-1200EX, JEOL Ltd., Japan). Based on the above information, the crystal phase, distribution of grain size and grain growth mechanism have been discussed below.

3. Results and discussion

The room temperature XRD patterns for CuFeO\textsubscript{2} powders are shown in Fig. 1, which have been prepared at different reaction temperatures and only washed by distilled water. The major peaks have been indexed by the standard phase of CuFeO\textsubscript{2} with a rhombohedral structure (ICSD-PDF\#85-0605). Besides, the peaks of CuO are also found which have been marked with a rhombic symbol in Fig. 1. What’s more, the relative intensities of CuO peaks can be found getting stronger for samples synthesized at low temperatures. In general, the Cu\textsuperscript{2+} in the solution will be reduced to Cu\textsuperscript{+} by propionaldehyde and then reacts with ferric anionic complexes to form CuFeO\textsubscript{2}. However, the unreacted Cu\textsuperscript{+} is easy to be oxidized and precipitated as CuO.\textsuperscript{12) \textit{}} To remove the impure phase of CuO, HNO\textsubscript{3} solution has been used to wash the obtained CuFeO\textsubscript{2} powders. After washing and cleaning, the CuFeO\textsubscript{2} powders are characterized by XRD and the patterns at room temper-

![Fig. 1. The XRD pattern at room temperature for CuFeO\textsubscript{2} powders synthesized at different reaction temperatures.](image1)

![Fig. 2. The XRD pattern at room temperature for CuFeO\textsubscript{2} powders after HNO\textsubscript{3} washing.](image2)
ature are presented in Fig. 2. It is confirmed that the CuO phase has been removed for all products. This result indicates that the pure CuFeO₂ powders have been successfully achieved. Additionally, intensities of all peaks for CuFeO₂ powders also show increasing trend with the increase of reaction temperatures. Particularly, it is seen that the crystallinities for most of the CuFeO₂ samples get better when the synthesized temperatures are over 160°C. However, the peaks are relatively weak when the synthesizing temperature is 130°C–160°C. So for the present reaction time, the high temperature is significant for the crystallinity of CuFeO₂.

The TEM images for CuFeO₂ powders with pure rhombohedral phase have been presented in Figs. 3 and 4. In Fig. 3, all images are shown in the scale of 1μm for all CuFeO₂ samples while the Fig. 4 is under the scale of 200 nm. From the TEM images, it is easily seen that various sizes of grains exist for the obtained CuFeO₂ powders. The grain sizes can span from several nanometers to hundreds of nanometers, and even sizes of few grains are over 1μm. In Figs. 3 and 4, it can be found that the grain sizes are generally becoming larger for all CuFeO₂ powders with the increasing of the reaction temperature. Moreover, the grain morphology is more regular with the increasing of the reaction temperature. For example, it can be seen from Fig. 4 that the rhombohedral-like grains (marked by red arrows) become legible when the temperatures are over 160°C. These results are agreed with the peak intensity of the XRD patterns.

To quantize the changing tendency of the grain size as above descriptions, the average grain sizes of all powders will be presented. As shown in TEM images, the grains with size less than tens of nanometers are difficult to be distinguished. In this case, the average grain size will be not so accurate by counting grains in TEM images shown in Figs. 3 and 4. As we know, the XRD data can also be used to evaluate the peak broadening with crystallite size. Thus, the more accurate average grain sizes will be calculated for all CuFeO₂ powders. The calculated average grain sizes of all samples are shown in Fig. 5. The data were calculated basing on the Williamson-Hall method which is described by the formula below:

\[
\beta_{\text{hkl}} \cos \theta = \left( \frac{k \lambda}{D} \right) + 4 \varepsilon \sin \theta,
\]

where \( \beta_{\text{hkl}} \) is the full width at half maximum (FWHM).
intensity of the diffraction peak (deducted the instrumental width), \( k \) is a constant equal to 1, \( \lambda \) is the wavelength of the radiation (1.54056 Å for Cu K\( \alpha \) radiation), \( D \) is the crystallite diameter, \( \varepsilon \) is the lattice strain and \( \theta \) is the peak position. The average gain sizes are obtained by fitting with all orientation peaks of the rhombohedral CuFeO\(_2\). The calculation progress is carried out by the software of MDI Jade 5 as the previous report. The similar calculation process of the average grain size is also reported in the previous work.\(^{15,16}\) According to the Fig. 5, the average sizes are only a little fluctuant when the reaction temperatures are below 180°C. With the reaction temperature further increasing, the average grain sizes increase rapidly from about 60 nm to nearly 500 nm. So the enhanced reaction temperatures can suddenly increase the average grain size at a critical point and this must be related to the grain growth mechanism.

In order to analyze the mechanism of the grain growth generally, the grain size distributions are figured out for CuFeO\(_2\) powders synthesized at 140°C, 180°C and 210°C. Herein, the grain size distributions are measured basing on the TEM images of Figs. 3 and 4. The size for each grain has been measured at random directions for 4 times and then the obtained size values are averaged. The final obtained average value is considered as the grain size of this grain. Following the above process, all grains in Figs. 3 and 4 have been measured. In this case, all the grain sizes are counted. This statistical result is the grain size distribution. However, to get the accurate statistics, the too small grains with size below tens of nanometers are not considered as they are difficult to be clearly distinguished.

Fig. 4. TEM images of 200 nm scale for all CuFeO\(_2\) powders synthesized at (a) 130°C, (b) 140°C, (c) 150°C, (d) 160°C, (e) 170°C, (f) 180°C, (g) 190°C, (h) 200°C, (i) 210°C.

Fig. 5. The average grain sizes for all CuFeO\(_2\) powders, which are calculated by the Williamson-Hall method.
and we only focus on the change tendency of the grain size distribution. The obtained results are shown in Fig. 6. From the statistical figures, it can be seen that the fractions of small grain size areas decreased gradually with the increasing of the reaction temperature, especially for the percentage of the grain size less than 200 nm. While, the fractions of large grain size areas show increasing trend with the reaction temperature increasing. For example, the fraction of the grain size over 800 nm are very low for CuFeO₂ powders synthesized at 140°C while this fraction are enlarged to over 10% for CuFeO₂ powders synthesized at 210°C. This variation proves the decrease of the small grain number and the increase of the large grain number with the enhancement of the reaction temperature. In solid solutions or liquid sols, OR has been found to describe the change of inhomogeneous compositions over time. In this process, small crystals dissolve gradually and redeposit on larger crystals. The corresponding schematic diagram is shown in Fig. 7. The formation of the OR phenomenon is due to the higher solubility for the relative small grains (Gibbs-Thomson or Kelvin effect) and the molecular diffusion through the continuous phase. The high temperature will accelerate this progress according to the increased molecular diffusion rate. Basing on the analysis above, the mechanism of grain growth for CuFeO₂ powders is seen to be consistent with the classical OR. The phenomenon of the grain size can be explained by the OR. In TEM images, there are many fine nano-grains as shown in Figs. 3 and 4. Although they are not considered in the statistical process of the grain size distribution shown in Fig. 6, these fine nano-grains are much useful for the formation and growth of grains. These fine nano-grains will dissolve and redeposit on the large grains according to the OR. At high temperatures, the rate of the molecular diffusion will be accelerated. So when the ripening leads to the obvious decrease of the grain numbers, the average grain size will increase rapidly. What’s more, the rhombohedral-like grains will be more regular and larger as more and more small grains transfer to the larger ones. So the higher temperature will lead to the larger average grain size and better grain morphology. These results can be seen from the Fig. 5 and the temperature of 180°C may be the critical reaction condition that small grains begin to decrease rapidly.

To our knowledge, expect for the reaction temperature, the OR process can be also modified by the reaction time, concentration of the starting materials, addition of surfactants and so on. These reaction conditions can be adjusted on the basis of our work and the OR mechanism to regulate the grain morphology and grain size for CuFeO₂ powders synthesized by microwave hydrothermal reaction. This work will provide an improving direction to meet the required physical properties.

4. Conclusions

CuFeO₂ powders have been synthesized by the microwave hydrothermal reaction method at different reaction temperatures. The pure rhombohedral phase of CuFeO₂ powders has been successfully formed. The rhombohedral-like grains have been found to be more regular and larger with the temperature increasing. The grain sizes of
CuFeO$_2$ powders span from several nanometers to hundreds of nanometers, and even the sizes of few grains are over 1 $\mu$m. The average grain sizes are found increasing with the increase of reaction temperatures. From the grain size distributions, it can be found that the proportions of the small grains decreases with increasing the reaction temperature. These phenomena are considered that the small grains dissolve and redeposit on larger crystals. The grain growth mechanism is analyzed and found to be consist with the OR theory. Based on the OR mechanism, the grain size and morphology of CuFeO$_2$ powders can be further improved to meet the physical properties.

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