

Effect of Milling Time on $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ Microstructure and Particles Size Evolution via the Mechanical Alloying Method

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Abstract

Nanocrystalline CoZn-ferrite was fabricated by a high-energy milling method by mixing $\text{Fe}_3\text{O}_4 + \text{CoO} + \text{ZnO}$. The structural properties of the milled powder at different milling times were analysed so as to ascertain the diffusion of CoO and ZnO into the tetrahedral and octahedral sites using mechanical alloying method. The effect of mechanical alloying towards particle size was also investigated. The XRD spectra indicated the precursors reacted during milling with the diffusion of ZnO and followed by CoO into their respective crystallographic sites. SEM micrographs showed the agglomeration of powders due to high energy milling and TEM images confirmed that the particles of the materials were of nanosize dimension. In addition, the results show that the grain possesses a single-phase CoZn-ferrite structure in a typical size of ~16 - 30 nm. The experiment reveals that nanosize CoZn-ferrite can be obtained after the powder is milled for about 8 hours at room temperature. The mechanism and efficiency of the synthesis of the technique are also discussed in this paper.

Keywords

Mechanical Alloying, CoZn-Ferrite, Nanocrystalline, XRD Profile

1. Introduction

Nanocrystalline materials have attracted considerable interest in recent years because of the possibility of im-

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proved macroscopic properties of materials by varying the crystallite sizes. Development in the electronic sectors has put a pressure on the manufacturers to develop smaller and lighter products. A reduction in size and weight can be achieved by focusing on the development of nanosized particles by various techniques.

The useful properties of CoZn-ferrites in low- and high-frequency equipment and their roles in microwave devices, power transformers, rod antennas and read/write heads for high speed digital tapes has attracted much interest of researches in recent years [1]. The interesting properties of CoZn ferrites are having small eddy current at higher frequencies, high resistivity, chemical stability and low dielectric losses [2].

Common methods for preparation of nanocrystalline materials include the inert gas condensation (IGC), hydrothermal method, chemical vapor position (CVD), solid state technique, sol gel method and high energy ball milling [3]. In order to study grain size effects, the average grain size has to be varied over a large range; this can be readily achieved by varying the milling times used during alloying. In order to avoid impurities in the samples during milling, appropriate milling parameters have to be chosen (e.g., material of the milling vial, ball-to-powder weight ratio and optimum milling time) [4]. The advantage of ball milling is easy handling, the possibility to produce large quantities and the applicability to a wide range of different classes of materials. Mechanical alloying via high-energy ball milling has now become one of the conventional methods for producing nano/non-crystalline materials. In mechanical alloying, materials in powder form undergo multiple collisions with balls and vial wall of the grinding media through the process of high energy collision. Various attempts have been made to improve the structural, dielectric and magnetic properties of materials using this milling process. In this study, a compound comprising of three constituent elements was milled to study the effect of milling time on the compound, morphology and particle size of the nanopowder produced.

2. Materials and Methods

A nominal composition of powder for $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was prepared by mechanical alloying of a mixture of metallic oxides. The materials used were Fe_2O_3 (Sigma Aldrich) (99.95%), CoO (Sigma Aldrich) (99.99%) and ZnO (Sigma Aldrich) (99.99%) weighed according to the composition formula. The chemicals were mixed with chosen molar ratio of 1:0.5:0.5. High energy milling was carried out in a SPEX 8000D shaker mill in ambient atmosphere for 1, 4, 8, 12, and 17 hours. The ball-to-powder mass-charge ratio (BPR) was approximately 10:1. All the samples were examined with X-ray diffraction (Phillips Expert Pro PW3040) using $\text{CuK}\alpha$. Three samples were selected which are of 1, 4 and 12 h of milling and sent for Scanning Electron Microscope (SEM) images (JEOL 6400) and were further examined under a Transmission Electron Microscope (TEM) (LEO 912AB).

3. Results and Discussion

FTIR spectrum of as-made ferrite nanoparticles is presented in **Figure 1**. The spectrum showed that the as prepared nanoparticle has a transmittance of about 97.0%. In spinels and ferrites, there are two main broad metal-oxygen bands which are seen in the FTIR spectra. The bands consist of the highest and lowest bands.

The highest wave number (ν_1) is generally observed in the range $600 - 550 \text{ cm}^{-1}$ which corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site, $\text{M}_{\text{tetra}} \leftrightarrow \text{O}$, whereas the lowest wavenumber (ν_2) is usually observed in the range $430 - 385 \text{ cm}^{-1}$, and is assigned to octahedral metal stretching, $\text{M}_{\text{octa}} \leftrightarrow \text{O}$ [5] [6]. The absorption bands observed at ~ 3490 and $\sim 1610 \text{ cm}^{-1}$ confirms the presence of adsorbed water on the surface of the ferrite nanoparticles.

In the $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocrystals, Zinc ion occupies the tetrahedral site while cobalt and iron have two valences; hence they partially occupy both the tetrahedral and octahedral sites [6]. It is thus concluded that the vibrational mode of tetrahedral clusters is higher than the octahedral clusters, which is attributed to the shorter bond length of tetrahedral clusters.

XRD serves to identify phase transitions or chemical reactions by indicating the presence of new crystalline phases. The average grain size D of the samples was determined by the line broadening of XRD profiles. The ball-milled samples show increasing peak widths with longer milling times (**Figure 2**). As standard procedure we used the Scherrer Equation [7]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where k is a constant equal to 0.9, λ is the wavelength of the X-ray radiation (all diffraction patterns shown in

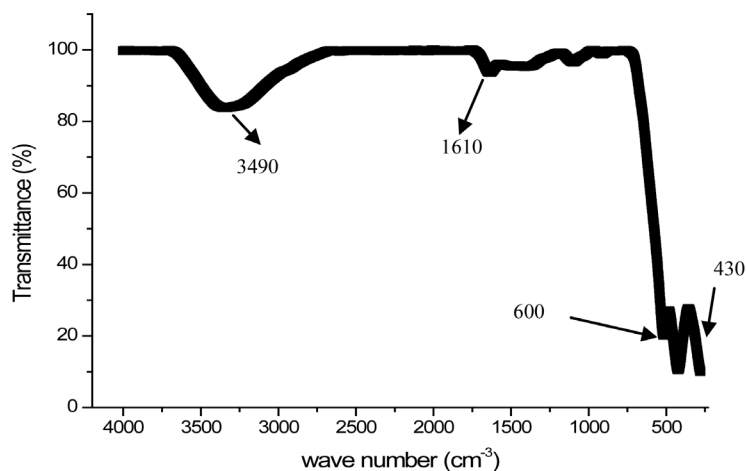


Figure 1. FTIR spectrum of prepared CoZn-ferrite nanoparticles.

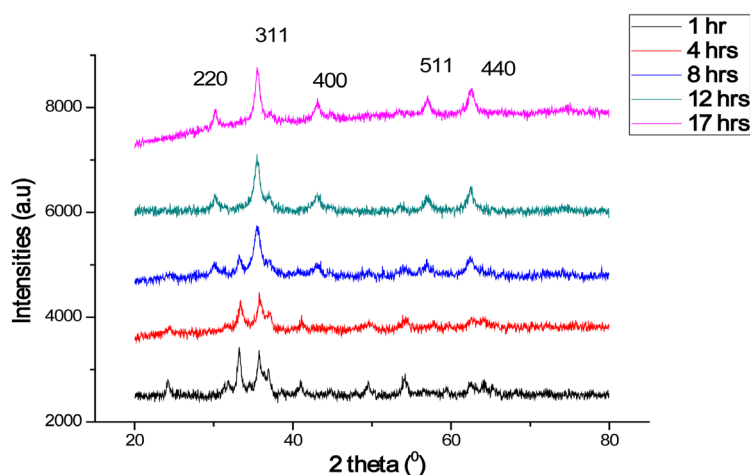


Figure 2. Variation in XRD spectra of CoZn-ferrites powder prepared by mechanical alloying.

this paper were performed with CuK α radiation), θ is the diffraction angle, and β is the full width half maximum (FWHM).

The XRD profile in **Figure 2** shows powder patterns recorded from unmilled and mechanically alloyed (BPR = 10:1) homogeneous powder mixtures at different milling times. The result in **Figure 2** is further used to calculate the crystallite sizes of samples at different milling hours. Careful observations on the figure showed that there are individual reflections of CoO-, ZnO- and Fe₂O₃-phases for the powder milled at 1 hour. Further milling up to 8 hours resulted in the disappearance of starting materials phases completely and the CoZn-ferrite phase began to appear.

It is evident from the spectra shown in **Figure 2** that in the course of milling of these three individual powders, the CoZn-ferrite phase was formed and its amount increased gradually with increasing milling time. There is a significant reduction of the ZnO phase to a large extent compared to the CoO and Fe₂O₃ phases after 1 hour of milling which subsequently vanished after 4 hours of milling. It shows that the ZnO phase is much more prone to deformation fault as all the reflections are sufficiently broadened in comparison to the other two phases [8]. Conclusion can be drawn that the rate of solid-state diffusion of ZnO into Fe₂O₃ lattice is higher than that of CoO. From the spectra, it suggests that ZnO diffused into Fe₂O₃ and the Zn-Fe₂O₃ phase is formed. This reaction was then followed by CoO diffusion which phase diffused slowly into the ZnFe₂O₃ as the milling process continues, finally forming the CoZn-ferrite phase. Careful observation in **Figure 2** shows that ZnO diffusion into Fe₂O₃ is very prominent compared to CoO diffusion. This could be explained by looking at the preferences of

Zn²⁺ ions into the tetrahedral site. It is also possible that longer hour of milling may not affect the crystal size of the materials under test. [9] stated that constant crystallite size from the longer milling time is a reflection of the lattice strain which no longer increases and remains almost constant till the end of milling. This shows that high-energy impact produces enormous amount of lattice imperfections to the sample.

Based on the result shown in **Table 1** for the crystallite sizes, it shows two stages of crystallite size attainment from the milling of samples. The first stage of the mechanical alloyed samples from 1 - 4 hours showed variation of sizes from 15.9 - 36.5 nm. The second stage started from 12 hours and up to 17 hours which showed the crystallite size ranges from 16.12 - 24.4 nm.

For the analysis using SEM and TEM, three samples were selected which were from 1, 4, and 12 hours of milling. **Figure 3** shows SEM images of CoZn-ferrite after being milled for 1, 4, and 12 hours. The size for the 12 hour milling ranges from 19.5 - 24 nm with an average grain size of 21.8 nm. The powders obtained after the milling showed high agglomeration of the materials as seen in the SEM micrograph.

Table 1. Crystallite size of CoZn-ferrite powder mechanically alloyed at various milling times.

Milling time (hour)	Crystal size (nm)
1	36.5
4	25.7
8	15.9
12	16.1
17	24.4

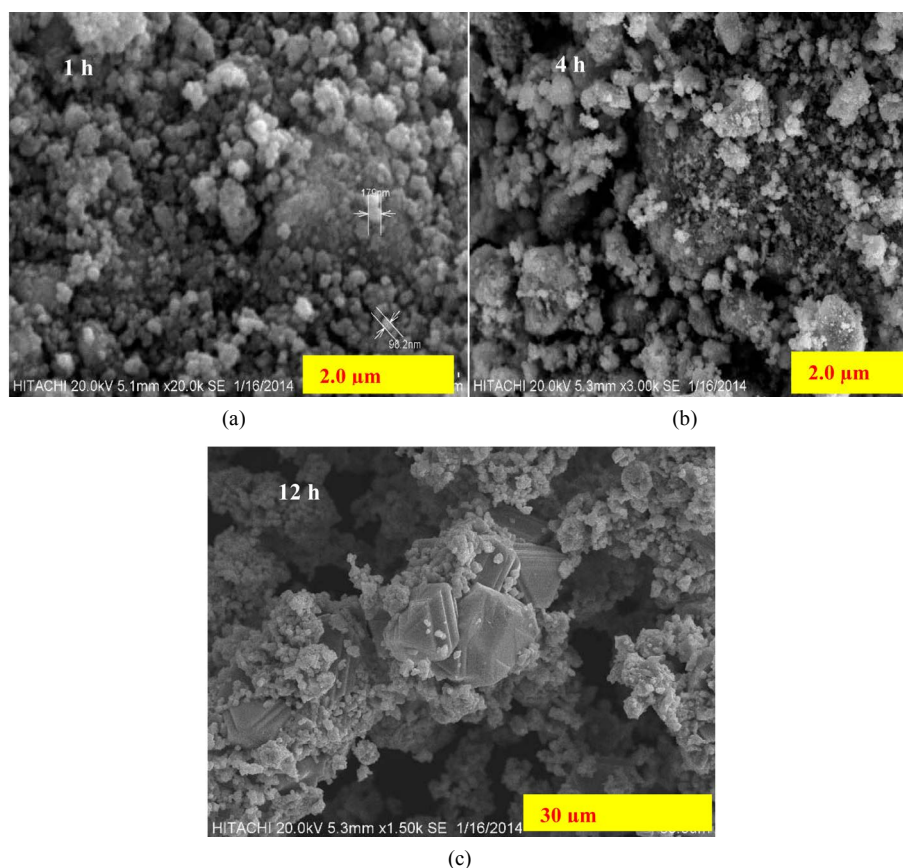


Figure 3. SEM micrograph of milled powders after (a) 1 h, (b) 4 h and (c) 12 h.

The particle size obtained using TEM (**Figure 4**) for 1, 4 and 12 hours of milling are 30 nm, 20.5 nm, and 13.8 nm which are smaller than the crystallite size obtained from the XRD pattern which implies that the particles exist as nonporous aggregates, due to their high surface energy [10]. From the crystallite size shown in **Table 1**, it is evidently clear that the result are not in close agreement with the particle size result gathered from the micrograph shown in **Figure 4**. The Scherer equation used in deducing the crystallite size may also contribute some error to the calculations.

Additional effects such as crystal strain or defects can make significant contributions to line broadening of the FWHM values [11]. It is known that if the particle size of a powder material is as big as its crystallite size, it shows that the material is a single crystal. However in this study, the TEM results for the mechanically alloyed materials showed a smaller crystallite size than that calculated from the Scherer equation. It is thus speculated that this might be due to an instrumental error of the XRD machine. In [12], they reported that instrumental factors governed the line broadening of the FWHM for particle size above 0.1 μm .

4. Conclusion

The mechanical alloying method was employed to prepare CoZn-ferrite nanoparticles at milling time as low as 1 hour at room temperature which was successfully used to study grain size effects and make reasonable comparison. FT-IR spectra indicate that successive esterification reaction and formation of metal-oxygen bands are attributed to the spinel phase. XRD patterns reveal that the mechanical alloying method can produce cobalt zinc ferrite at relatively low milling time while the spectra from XRD indicates the diffusion of ZnO into the tetrahedral sites followed by CoO into the octahedral sites. The diffusion occurs during the early stage of the milling process. The crystal size calculated exhibits the nanosized regime of powder due to high energy ball milling and it shows 2 crystal-size attainment stages of the materials. SEM images show that the samples at different milling hours have nearly homogeneous grain distribution. The 12-hour-milled sample has an average particle size of about 19 - 24 nm as analysed by the SEM. Despite the procedure used, agglomeration is observed as the milling time increased above 12 hours. The study confirms that the technique used is able to produce materials in nanosize dimension as evident in TEM analysis.

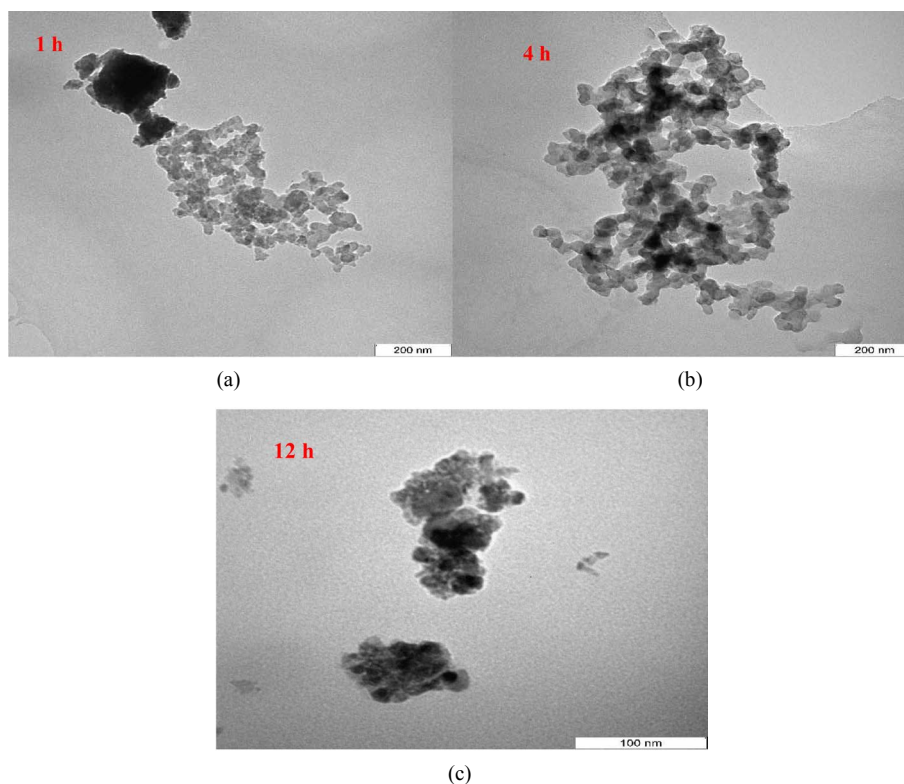


Figure 4. TEM micrograph of milled powders after (a) 1 h, (b) 4 h and (c) 12 h.

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