

## The Effect of Milling Time on Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> Compositional Evolution and Particle Size Distribution

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**Abstract: Problem statement:** This study involved an investigation to ascertain the diffusion of NiO and ZnO into the tetrahedral and octahedral sites using mechanical alloying method. The effect of mechanical alloying towards particle size was also reported. **Approach:** NiO, ZnO and Fe<sub>2</sub>O<sub>3</sub> precursors were mechanically alloyed to synthesis ultrafine powders of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. Various milling times were employed to study the effect of milling time on the materials. The ultrafine powder was sampled after each milling time and further characterized using XRD to investigate the phases of the powder and the crystallite size, SEM for the morphology and TEM for particle size investigation. **Results:** The XRD spectra indicated the precursors reacted during milling with the diffusion of ZnO and followed by NiO into their respective crystallographic sites. SEM micrographs showed the agglomeration of powders due to high energy milling and TEM images proved the particles of the materials were of nanosize. **Conclusion:** It was concluded that samples prepared using mechanical alloying technique appear to be a potential method for large production due to the possible reduction of cost and also reduction of particle size against milling time.

**Key words:** Mechanical alloying, NiZn ferrites, milling

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### INTRODUCTION

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. Recent interest in the study of soft ferrites has helped to ease this burden. Among the different soft ferrites is NiZn ferrite which is the most versatile magnetic materials and has been used for many years. The useful properties of NiZn ferrites in low and high-frequency equipment and their roles in microwave devices, power transformers, rod antennas, read/write heads for high speed digital tapes has attracted much interest for the researchers. Among the interesting properties of NiZn ferrites are having small eddy current loss even operating at higher frequencies (10-500 MHz), high resistivity, chemical stability, low dielectric losses, moderate mechanical hardness and high Curie temperature. This mixed spinal formula AB<sub>2</sub>O<sub>4</sub> has tetrahedral (A) sites which are

occupied by Zn<sup>2+</sup> and Fe<sup>3+</sup> ions whereas octahedral (B) sites are occupied by Ni<sup>2+</sup> and Fe<sup>3+</sup> ions.

Magnetic properties of NiZn ferrites rely heavily on the chemical composition and are also sensitive to their microstructure<sup>[1,2]</sup>. There are a few factors that determine the microstructure of ferrites such as the quality of raw materials, the calcinations temperature, the milling procedure and the sintering regime<sup>[3]</sup>. Generally, the parameters of microstructure are the grain size, the pore size, the porosity and the density, intra-granular and inter-granular distribution of pores and grains. The quantity, size, shape and distribution of both crystal grains and pore of a ferrite will vary with different preparation conditions and techniques<sup>[4]</sup>. One of the various techniques for synthesizing magnetic materials is mechanical alloying which is used to reduce grain size, mix powder uniformly and make non-equilibrium structure materials, including nanocrystals, quasicrystals and amorphous alloys. Mechanical alloying via high-energy ball milling has now become one of the conventional methods for

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producing nano/non-crystalline materials. During mechanical alloying, materials in powder form will undergo severe collisions between balls and ball and vial wall of the grinding media by the process of high-energy collision. In the course of milling, various attempts have been made to improve the structural, magnetic and frequency properties.

In this study, a ternary system material was milled to study the effect of milling time on the composition and particle size of the samples.

### MATERIALS AND METHODS

A nominal composition of powder for Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> was prepared by mechanical alloying of a mixture of metallic oxides. The materials used were Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar) (99.95%), NiO (Alfa Aesar) (99.99%) and ZnO (Alfa Aesar) (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, 16, 20, 24, 30, 36, 42 and 48 h. The ball-to-powder mass-charge ratio (BPR) was approximately 10:1. Another sample, Fe<sub>3</sub>O<sub>4</sub> (magnetite), was prepared via the conventional ceramic processing method as a micro-structural reference sample (Sample B), which was prepared in a pellet form and sintered at 1200°C for 4 h. All the samples were examined with X-ray diffraction (Phillips Expert Pro PW3040) using CuKα. Three samples were selected which are of 12 and 24 h of milling and Sample B were sent for Scanning Electron Microscope (SEM) images (JEOL 6400). The former two samples were examined under a Transmission Electron Microscope (TEM) (LEO 912AB).

### RESULTS

Figure 1 shows the XRD powder patterns recorded from unmilled and mechanically alloyed (BPR = 10:1) homogeneous powder mixtures. From the spectra shown above, the unmilled powder mixture shows only individual reflections of NiO, ZnO and Fe<sub>2</sub>O<sub>3</sub> phases. Further milling up to 48 h resulted in the disappearance of starting materials phases completely and the Ni-Zn-ferrite phase began to appear.

The crystallite sizes in the mechanically alloyed samples are shown in Fig. 2 and Table 1. The Scherrer equation, shown below, was used to give the crystallite size of these samples:

$$B = \frac{0.9\lambda}{t \cos \theta} \quad (1)$$

Where:

B = FWHM (Full width at half maximum) of the broadened diffraction line on the 2θ scale (radians)  
t = Diameter of the crystallites

By scrutinizing the graph, we could see 3 stages of crystallite size attainment from the milling of these samples. Mechanical alloying of these samples from 1-4 h shows the variation of sizes from 33.33-44.44 nm. 12 h and up to 30 h shows second stage of crystallite size ranges from 11.12-22.22nm. Above 30 h of milling shows no changes in crystal size. The crystallite size of Fe<sub>3</sub>O<sub>4</sub> pellet (Sample B) using Eq. 1 is 53.62 nm.

Further studies were carried out on the particle size of the samples using SEM and TEM. Two samples were selected which were from 12 and 24 h of milling.

Figure 3 shows SEM images of NiZn ferrite after being milled for 12 and 24 h. The size ranges from ~82-~101 nm with an average grain size of ~87 nm for 12 h of milling. The powders obtained after the milling showed high agglomeration of the materials as seen in the SEM micrograph. Further milling up to 24 h shows smaller region of size distribution of the materials, which is due to the high impact of the milling. The size ranges from ~62-~104 nm.

Table 1: List of crystallite size of NiO, ZnO and Fe<sub>2</sub>O<sub>3</sub> mechanically alloyed with various milling times

Milling time (h)	Crystal size (nm)
1	44.44
4	33.33
8	33.33
12	44.44
16	22.22
20	26.68
24	16.67
30	11.13
36	13.44
42	13.44

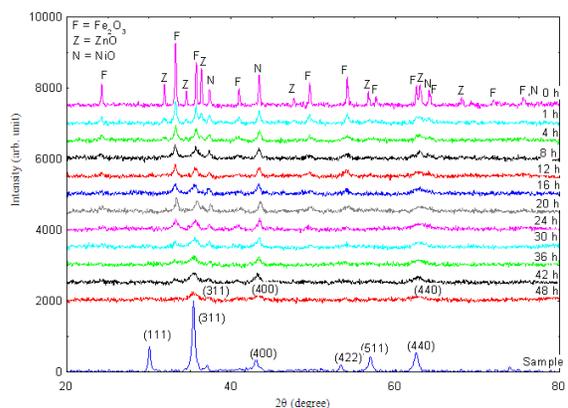


Fig. 1: XRD spectra of Ni-Zn-ferrites powder prepared by mechanical alloying and Fe<sub>3</sub>O<sub>4</sub> pellet (Sample B) prepared by conventional method

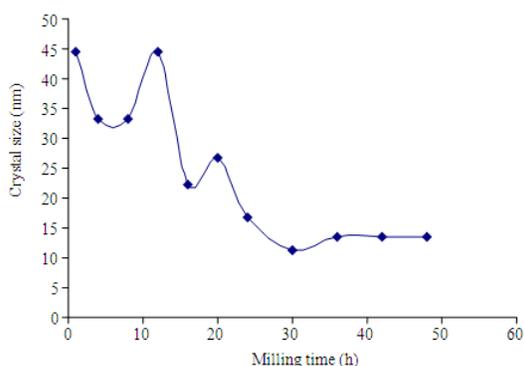


Fig. 2: Graph showing the crystal size of NiO, ZnO and Fe<sub>2</sub>O<sub>3</sub> mechanically alloyed with various milling times

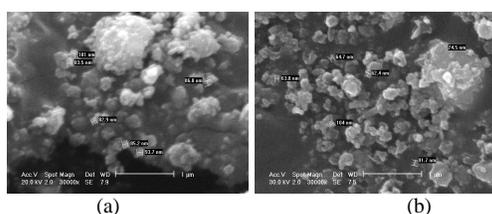


Fig. 3: SEM micrograph of milled powders after; (a): 12 h and (b): 24 h

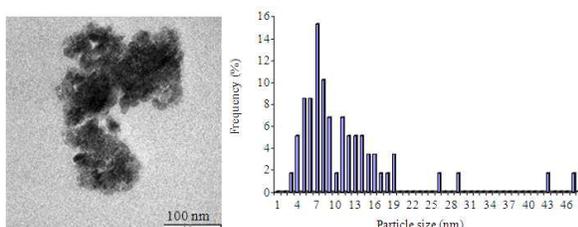


Fig. 4: TEM picture of nanosized NiZn ferrite powder milled for 12 h and the corresponding particle size histogram

Figure 4 and 5 show the TEM picture of the ferrite powder obtained from the milling processes for 12 and 24 h respectively. After being sonicated in acetone the materials were dispersed uniformly on the copper grid and showed a significant difference in size distribution. The particle size distribution obtained from TEM micrographs (Fig. 4 and 5) shows that the size distribution is not too narrow as various particles were obtained. For 12 h of milling, the particle size ranges from ~3~47 nm meanwhile after 24 h of milling the distribution becomes smaller which ranges from ~5~21 nm. Further milling up to 24 h has contributed elimination of bigger particles and narrow size distribution. Comparing the histogram of Fig. 4 and 5,

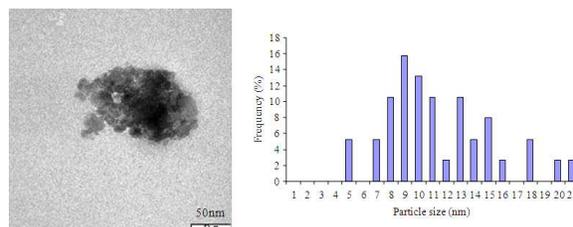


Fig. 5: TEM picture of nanosized NiZn ferrite powder milled for 24 h and the corresponding particle size histogram

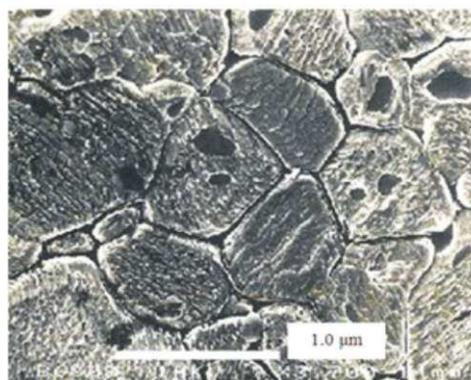


Fig. 6: SEM micrograph of Fe<sub>3</sub>O<sub>4</sub> pellet (Sample B) showing the grain boundary of the sample after sintering at 1200°C

shows the particle size of 24 h of milling becomes bigger than 12 h of milling implying that the particles started to agglomerate after 12 h of milling due to prolonged milling. The micrograph of Fe<sub>3</sub>O<sub>4</sub> pellet (Sample B) in Fig. 6 shows clearly the size of the grain boundary at about 0.5-1.0 µm after being sintered at 1200°C for 4 h.

## DISCUSSION

It is evident from the spectra shown in Fig. 1 that in the course of milling of these three individual powders, the Ni-Zn-ferrite phase was formed and its amount increased gradually with increasing milling time. A significant change after 1 h of milling is the reduction of the ZnO phase to a large extent compared to the NiO and Fe<sub>2</sub>O<sub>3</sub> phases which vanished after 4 h 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. It could be deduced that the rate of solid-state diffusion of ZnO into Fe<sub>2</sub>O<sub>3</sub> lattice is higher than that of NiO. From the spectra, it suggests that ZnO diffused

into  $\text{Fe}_2\text{O}_3$  and the  $\text{Zn-Fe}_2\text{O}_3$  phase is formed. This reaction was then followed by NiO diffusion as NiO phase diffused slowly into the  $\text{ZnFe}_2\text{O}_3$  in the course of milling and little Ni-Zn-ferrite is formed. A study by Bid *et al.*<sup>[5]</sup> showed the formation of  $\text{ZnFe}_2\text{O}_4$  could occur within only 30 minutes of ball milling with homogeneous stoichiometric (1:1 mol%) powder mixture of ZnO and  $\text{Fe}_2\text{O}_3$  phases. The reduction of intensities of the starting materials in the course of milling shows the contents of starting phases were reduced considerably within the time of milling. The broadening effect due to mechanical alloying indicates nanocrystallite particles contained a huge amount of lattice strain arising from the high-energy milling. It could also be attributed to very small particle size produced by this mechanical alloying. A closer look at the XRD spectra of 48 h milling reveals 3 peaks of Ni-Zn-ferrite which are (311), (400) and (440) at 35.53, 43.32 and 62.58° respectively. Since 3 strong peak of the NiZn ferrite phase were detected, it can be concluded that the phase can be formed by pure mechanical alloying.

By scrutinizing Fig. 2, we can see 3 stages of crystallite size. The first stage of crystallite size which ranges from 11.33-44.44nm due to mechanical alloying shows ZnO diffusion into  $\text{Fe}_2\text{O}_3$  is very significant compared to NiO. This could be explained by looking at the preferences of  $\text{Zn}^{2+}$  ions into the tetrahedral site. An intermediate phase of the second stage (crystallite size ranges from 11.12nm-22.22nm) showing that the powder is evolving towards a complete phase. 30 h of milling and above reveals no changes in crystal size and it remains constant till the end of the milling. The 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. From the graph plotted (Fig. 2), further milling above 30 h did not reduce the crystallite size anymore.

The particle size obtained using TEM for both 12 and 24 h (Fig. 4 and 5) of milling are smaller than the crystallite size obtained from the XRD pattern implies that the particles exist as nonporous aggregates, due to their high surface energy<sup>[6]</sup>. From the XRD spectra in Fig. 1, Sample B was deduced to have an average crystallite size of about 53.62 nm which is not in a good agreement with the micrograph shown in Fig. 6. The Scherrer 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<sup>[7]</sup>. 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 our case, the TEM results for the mechanically alloyed materials showed a smaller crystallite size than that calculated from the Scherrer equation. We speculate this is due to an instrumental error of the XRD machine. O'Connor *et al.*<sup>[7]</sup> reported the instrumental factors that governed the line broadening of the FWHM for particle size above 0.1  $\mu\text{m}$ . Their result shows that the FWHM contribution due to particle size is dominated by instrumental factors for the size range considered, 5.0  $\mu\text{m}$  down to 0.1  $\mu\text{m}$ . The particle size should not cause troublesome smearing of the X-ray powder diffraction lines if the particles are formed from component single crystal domains of size substantially below 0.1  $\mu\text{m}$ <sup>[7]</sup>. All diffraction lines have a measurable breadth, even when the crystallite size exceeds 1000 Å, due to such causes as divergence of the incident beam and size of the sample and width of the x-ray source (in diffractometers)<sup>[8]</sup>. The breadth B in Scherrer equation refers, however, to the extra breadth, or broadening, due to the crystallite-size effect alone<sup>[8]</sup>. In other words, B is essentially zero when the crystallite size exceeds about 1000 Å. The experimental difficulties involved in measuring crystallite size from line broadening increase with the size of the crystallite measured. Roughly speaking, relatively crude measurements suffice in the range 0-500 Å, but very good experimental technique is needed in the range 500-1000 Å<sup>[8]</sup>. With diffractometers, the upper range limit can approach 2000 Å<sup>[8]</sup>. Very careful work is required and back-reflection lines are employed, since such lines exhibit the largest crystallite-size broadening, as shown by using Scherrer equation. The reference sample,  $\text{Fe}_3\text{O}_4$  (Sample B), micrograph shows a large crystallite size which does not tally with that deduced from the XRD measurement. We attribute this to the limitation of Scherrer equation which is not suitable for materials with crystallite sizes above 1000 Å.

## CONCLUSION

Nanosized NiZn ferrite powders were synthesized using the mechanical alloying method with a molar ratio of 1:0.5:0.5. The XRD spectra indicate the diffusion of ZnO into the tetrahedral sites followed by NiO into the octahedral sites. The diffusion occurred during the early stage of the milling process. The crystal size calculated exhibits the nano sized regime of powder due to high energy of ball milling and shows 3 crystal-size attainment stages of the materials. The micrograph of SEM shows the synthesized powders were agglomerated with sizes ranging from ~82-~101

nm for 12 h of milling and ~62~104 nm for 24 h of milling. TEM pictures however proved that the powders are of nanosize after sonication and dispersion. Prolonged milling after 12 h caused powder to start agglomerating, though narrowing the particle size distribution.

#### ACKNOWLEDGEMENT

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