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# Effect of High-Energy Ball Milling on the Magnetic Properties of NiZn Ferrite Ceramics Synthesized by Spark Plasma Sintering

**Shang Gao, Shenhua Song*, Qingguo Song**

Shenzhen Key Laboratory of Advanced Materials, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen, China
Email: *shsong@hitsz.edu.cn, gaoshang@hitsz.edu.cn

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## Abstract

**High-density fine-grained $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite ceramics were synthesized by spark plasma sintering (SPS) in conjunction with high energy ball milling. The precursor powders were milled for 20 h, 40 h, and 60 h, respectively, and the milled powders were all sintered for 5 min at 900˚C. All the samples exhibit a single spinel phase. With increasing of the ball milling time, the relative density of the samples increases (up to 97.7%), however, the grain size decreases (down to ~200 nm). At room temperature, the sample from the 40 h-milled powder has the best combination of saturation magnetization and coercivity (83 emu/g and 15 Oe). These outstanding magnetic properties may be associated with high density and uniform microstructure created by SPS on the basis of fine precursor powders produced by high-energy ball milling.**

## Keywords

**Ferrites, Functional Materials, Magnetic Materials**

## 1. Introduction

Spinel ferrites constitute an important class of magnetic materials. Their applications always demand for high-density, low-porosity and controlled-microstructure. NiZn ferrite is one of them, which is commercially used in rod antennas, radio frequency circuits, transformer cores and read/write heads for high speed digital tape [1].

*Corresponding author.

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The extensive application of NiZn ferrite is due to its remarkable magnetic behavior.

Normally, conventional methods for preparation of ferrites involve high-temperatures and long-reaction times, which would result in coarse-grained microstructures and poor magnetic properties. Conventional sintering for NiZn ferrite preparation usually requires temperatures up to 1300˚C for several hours even though small-sized powers are used [2]. Recently, spark-plasma-sintering (SPS) is recognized as a novel sintering method of preparing ceramic materials because of even lower sintering temperature and shorter sintering time compared with microwave sintering and hot isostatic pressing [3]-[5]. Before SPS, the particle size of the powder is usually reduced by high-energy ball milling which can also increase the homogeneity and reactivity of the mixture [6]. High-energy ball milling is a simple, effective and productive way to produce various nano-crystal powders in high-energy planetary ball mills [7]. High reactivity and small particle size can facilitate the production of high-density ceramics at low sintering temperatures [8]. Therefore, the SPS along with high-energy ball milling has specific features of low sintering temperatures and short processing times. Until the present time, there have been limited reports on NiZn ferrite preparation by SPS [9]. The aim of the present work is to fabricate a high-density fine-grained $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite material by SPS in conjunction with high-energy ball milling, emphasizing the effect of ball milling on the magnetic properties of resulting ceramics.

## 2. Experimental Procedure

The raw materials were reagent-grade NiO (>99.9%), ZnO (>99.9%), and $Fe_2O_3$ (>99.9%). Weighed powders according to the composition of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (abbreviated as NZF) were simply mixed in an evaporating dish and then milled thoroughly using a high-energy planetary ball mill with tungsten carbide (WC) bowls and balls in alcohol at a speed of 400 rpm for 20 h, 40 h and 60 h, respectively. The powders were dried at 80˚C for 2 h and observed by scanning electron microscopy (Hitachi S-4700 SEM). These powders were used as the precursor ones for SPS. They were placed in a graphite die and sintered at 900˚C for 5 min under a vacuum of $10^{-2}$ Pa by SPS. During the SPS, a pressure of 48 MPa was maintained. After the SPS, the prepared pellets with the size of 10 mm in diameter and 3 mm in thickness were annealed for 2 h at 50˚C lower than the SPS temperature to remove possible carbon contamination.

The phase purity and structure of the samples were analyzed by X-ray diffraction (XRD) using a Rigaku diffractometer (D/max 2500) with Cu-K$\alpha$ radiation. Microstructures of the fracture surfaces were examined by SEM. Magnetic measurements were performed by a vibrating sample magnetometer (Lake Shore 7410 VSM).

## 3. Results and Discussion

The morphologies of the powders milled for different times are shown in **Figure 1**. As seen, the powder particles become finer and finer with increasing milling duration and their average size could be ~100 nm after 40 h milling. However, the 60 h-milled powder presents apparent agglomeration. It is anticipated that the 40 h-milled fine-sized powders are highly reactive and thereby can facilitate densification and homogenization of the sintered ceramics at a lower temperature.

The densities of the samples are represented in **Figure 2(a)**. Clearly, the sample from the 20 h-milled powder has a density of 4.70 g/cm$^3$, which is 89.4% of the theoretical density (5.26 g/cm$^3$ [2]). With increasing milling time, the density increases and reaches 5.10 g/cm$^3$ when the milling time is 40 h. This value is equivalent to 97.0% of the theoretical density. The density can further increase slightly to 5.14 g/cm$^3$ with longer milling time to 60 h although there is agglomeration of the powder particles. Consequently, the high-energy ball

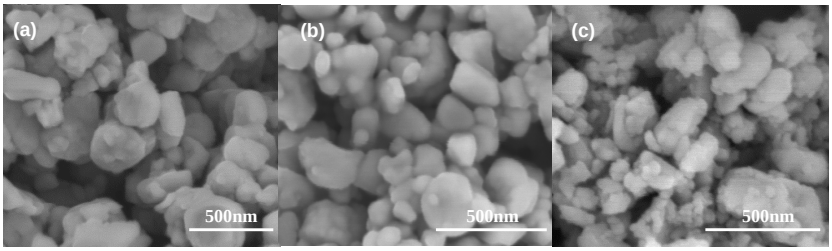


**Figure 1.** Morphologies of the powder particles after high energy ball milling for (a) 20 h; (b) 40 h; and (c) 60 h.

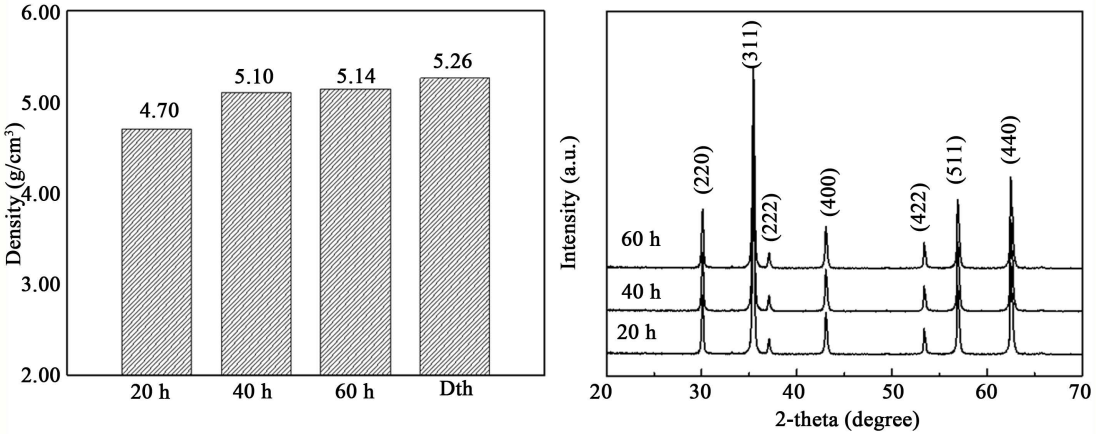


**Figure 2.** (a) The densities of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramic samples prepared by SPS after high-energy ball milling for 20 h, 40 h, and 60 h (Dth = theoretical value); (b) The corresponding XRD patterns.

milling is an effective method of preparing the precursor powders in order to produce high-density ceramics. The XRD patterns of the samples presented in **Figure 2(b)** show that all the samples possess a spinel structure and there are no any secondary phases introduced during sintering.

Typical SEM images of the fracture surfaces of the samples are represented in **Figure 3**. Obviously, the microstructure is quite uniform and increasingly dense with rising milling time. The grain size decreases gradually and linear intercept measurements indicate that the average values are approximately 300 nm, 250 nm and 200 nm for the milling times of 20 h, 40 h and 60 h, although there is some agglomeration in the 60 h-milled powder. This demonstrates that the sufficient high-energy ball milling may considerably promote densification and homogenization in the SPS process with a reduction in average grain size. Usually, the ultrafine-grained structure of the SPS-prepared ceramics cannot be achieved by conventional sintering. The conventional sintering usually leads to a grain size of ~2 μm [2], and even the microwave sintering usually results in a grain size of 1 - 2 μm [10].

Magnetic hysteresis loops of the samples are shown in **Figure 4(a)**. Clearly, these loops have typical characteristics of soft magnetic materials. The coercivity ($H_c$) is small and the saturation magnetization ($M_s$) is high. The narrow hysteresis loop indicates that the amount of dissipated energy in repeatedly reversing the magnetization is small, which is desirable for soft magnetic applications.

The values of $M_s$ and $H_c$ extracted from **Figure 4(a)** are shown in **Figure 4(b)** and **Figure 4(c)**. As seen, the $M_s$ increases with increasing milling time and may reach 83 and 86 emu/g for the samples prepared from the powders milled for 40 and 60 h, respectively. Nevertheless, the $H_c$ of the sample from the 40 h-milled powder has a minimum value of 15 Oe, which is much lower than those from the other powders (19 Oe and 23 Oe). It is widely recognized [11] that the high density of soft magnetic material is beneficial to its magnetic properties for a high magnetization and low coercivity. Also, as far as the grain size effect is concerned, the coupling effect of ferromagnetic exchange between the grains may considerably reduce the magnetocrystalline anisotropy of local regions within the grains when the grain size approaches the single-domain size (~50 nm [12]), leading to enhancement of the soft magnetic properties of the material [13]. Consequently, the smaller the grain size, the better the magnetic properties become. When the grain size is beyond the single-domain size, the coupling effect of ferromagnetic exchange between the grains cannot significantly reduce the magnetocrystalline anisotropy of local regions within the grains. In this case, the domains in the material have distinctly non-uniform states of magnetization. Since the spin magnetic moments in the grain boundary regions are randomly distributed, it is difficult to magnetize these regions. Moreover, the randomly distributed magnetic moments can be counteracted each other to some degree [14]. Accordingly, the magnetic properties may enhance with increasing grain size due to a reduction in total grain boundary area. In the present case, all the grain sizes are larger than the single-domain size and thus the magnetic properties should become better with a larger grain size. Based on the above discussion, the changes in $M_s$ and $H_c$ should originate from a combined effect of density increase and grain size decrease in. As shown in **Figure 4**, the sample from the 40 h-milled powder has the best combination of saturation magnetization and coercivity (83 emu/g and 15 Oe).

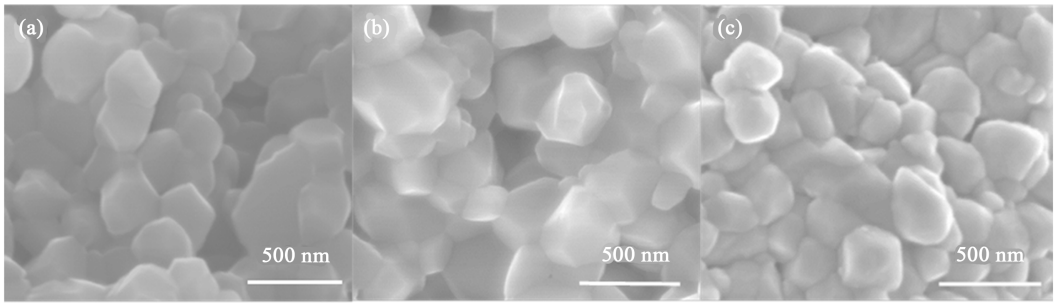


**Figure 3.** FE-SEM images of the fracture surfaces for the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramic samples prepared by SPS after high-energy ball milling for (a) 20 h, (b) 40 h, and (c) 60 h.

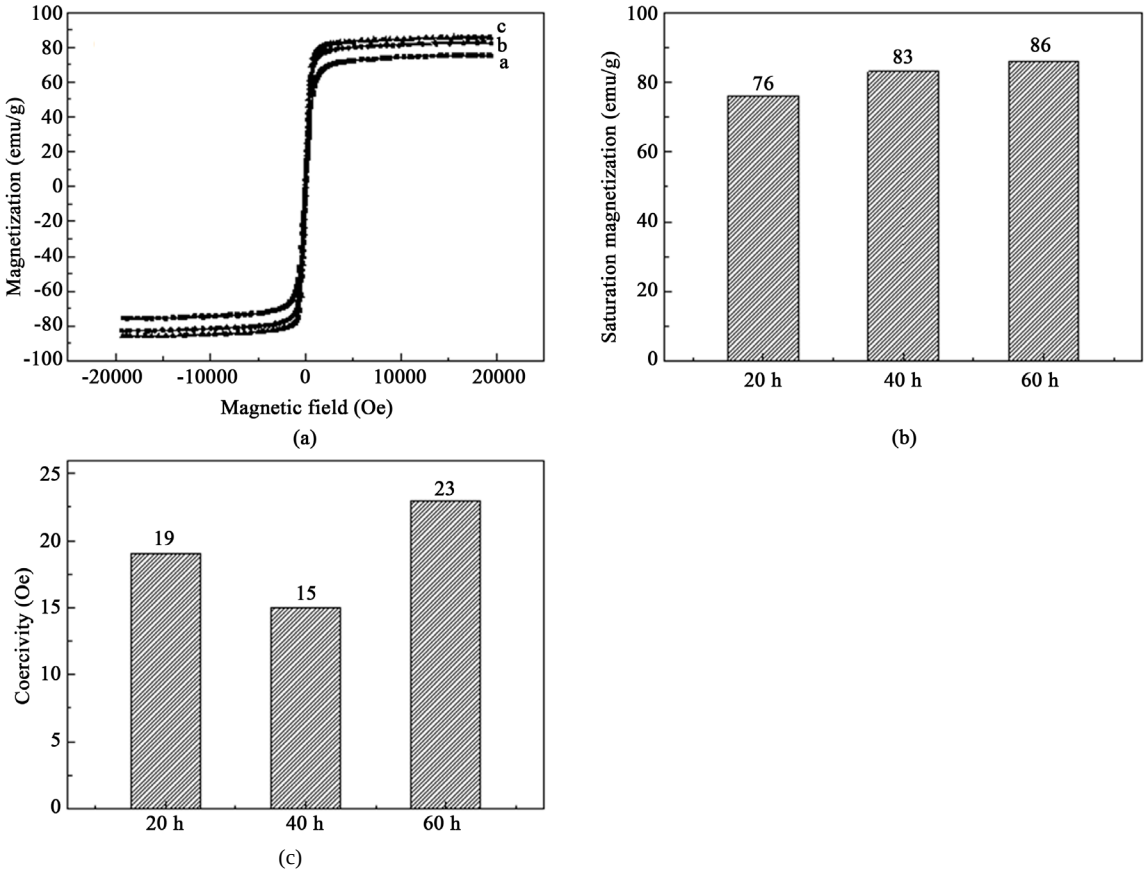


**Figure 4.** (a) Magnetic hysteresis loops of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ceramic samples prepared by SPS after high-energy ball milling for different times ((a) 20 h, (b) 40 h, and (c) 60 h), measured at room temperature; (b) The corresponding saturation magnetization values; and (c) The corresponding Coercivity values.

Narayanasamy and Sivakumar [15] fabricated $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite pellets through a conventional route. The sintering temperature and time were 1200˚C and 5 h. The pellets were re-ground into powders by milling and the resulting powders with an average particle size of 50 nm were used as the as-prepared sample. Then the as-prepared sample was milled for 25 h using a planetary high-energy ball mill, resulting in an average particle size of 14 nm. The saturation magnetizations were 73 emu/g and 61 emu/g, correspondingly. These two values are apparently lower than ours although their powder particle sizes are much smaller than the grain sizes of our bulk samples. The corresponding values of coercivity reported by Narayanasamy and Sivakumar were 88 Oe and 349 Oe, which are much higher than ours. Therefore, the bulk NZF prepared by SPS possesses a higher saturation magnetization and lower coercivity as compared with the powder NZF although the grain size in the

bulk is much larger than the particle size in the powder. Costa *et al.* [2] prepared $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders by combustion synthesis. The powders were uniaxially compacted and conventionally sintered for 2 h at 1200˚C and 1400˚C, respectively. The obtained ceramic samples had an average grain size of 2 μm with a density of 5.0 g/cm$^3$ for the 1200˚C-sintering, and 6.75 μm with a density of 4.71 g/cm$^3$ for the 1400˚C -sintering. The values of coercivity were obtained as 64 Oe and 110 Oe, respectively. Clearly, our values are much lower than theirs. The high density and uniform microstructure created by SPS on the basis of fine precursor powders created by high-energy ball milling could be mainly responsible for the difference.

## 4. Conclusion

High-density fine-grained $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite ceramics are successfully fabricated by SPS from fine precursor powders created by high-energy ball milling for 20 h, 40 h and 60 h, respectively. With increasing milling time, the relative density of the sample increases ranging from 89.4% to 97.7%, while the average grain size decreases, ranging from ~300 nm to ~200 nm. With increasing milling time, the saturation magnetization increases gradually being up to 86 emu/g, while the coercivity has a minimum value of 15 Oe for the 40 h-milling. The sample from the 40 h-milled powder has the best combination of saturation magnetization and coercivity (83 emu/g and 15 Oe). The variation of magnetic properties with milling time could result from a combination effect of density increase and grain size decrease.

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