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Characterization of submicrometer-sized NiZn ferrite prepared by spark plasma sintering

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Abstract

High-density submicrometer-sized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite ceramics were prepared by spark plasma sintering in conjunction with sufficient high energy ball milling. They were evaluated by different characterization techniques such as X-ray diffraction, scanning electron microscopy, and dielectric and magnetic measurements. All samples prepared at sintering temperatures ranging from 850 to 925 °C exhibit a single spinel phase and their relative densities and grain sizes range from 90% to 99% and ~100 nm to ~300 nm, respectively. The dielectric constant increases with decreasing grain size until ~250 nm, and then decreases dramatically with further decreasing grain size. The saturation magnetization increases continuously with increasing grain size/density but the magnetic coercivity decreases. The highest dielectric constant and saturation magnetization at room temperature are approximately 1.0×10^5 and 84.4 emu/g, respectively, while the lowest magnetic coercivity is only around 15 Oe. These outstanding properties may be associated with high density and uniform microstructure created by spark plasma sintering. Therefore, the spark plasma sintering is a promising technique for fabricating high-quality NiZn ferrites with high saturation magnetization and low coercivity.

Keywords: A. Sintering; C. Magnetic properties; D. Ferrites; D. Spinels

1. Introduction

Spinel ferrites constitute an important class of magnetic materials. Their technological applications always demands for high density, low porosity and controlled microstructure. In the spinel lattice AB_2O_4, the anions (O^{2-} ions) form cubic close packing in which the interstices are occupied by tetrahedral (A-sites) and octahedral (B-sites) coordinated cations [1–3]. If the soft magnetic platelet cores with few vacancies are developed, the application to the substrate of the perpendicular magnetic recording hard disks in combination with a single-pole-type head may be feasible. $NiFe_2O_4$ ferrite has a high Curie temperature (~560 °C) and low saturation magnetization (~25 emu/g) [4]. In order to lower its Curie temperature and increase its saturation magnetization, the $NiFe_2O_4$ ferrite is usually doped with Zn to form $Ni_{1-x}Zn_xFe_2O_4$. Saturation magnetization of the spinel depends upon the site of magnetic ion and the intensity of superexchange effect. Zinc ions normally occupy A-sites in the spinel structure, replacing Fe^{3+} at A-sites and increasing the number of Fe^{3+} at B-sites, and thus increasing the saturated magnetic induction intensity. Therefore, the saturation magnetization increases with an increase of zinc content [5]. Nevertheless, zinc ions are nonmagnetic and would reduce the superexchange effect. When zinc-replaced sites reach a certain value, these two effects will be kept in balance, producing the highest saturated magnetic induction intensity. In this case, $Ni_{0.5}Zn_{0.5}Fe_2O_4$ could be a proper NiZn ferrite material for soft magnetic applications. NiZn ferrite is currently being recognized as one of the most versatile magnetic materials for multilayer chip inductors (MLCI) applications due to its high electrical

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resistivity, high permeability as well as good magnetic properties [6,7].

Normally, conventional methods for preparation of ferrites involve high temperatures and long reaction times which would result in coarse-grained structures. Conventional sintering for NiZn ferrite preparation requires temperatures up to 1300 °C and several hours of soaking time even though a small size of power is used [8]. Techniques for producing dense ceramics at lower temperatures include hot isostatic pressing (HIP) [9] and microwave sintering (MW) [10]. Both MW and HIP techniques have characteristics of a rapid sintering rate, high density and fine-grained structure.

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 period as compared with MW and HIP [11–15]. In the SPS process, the precursor powders are pressed uniaxially in a graphite die and then an on–off pulsed dc voltage is simultaneously applied. The current passes through the die as well as the sample, enabling the sample to be heated from both outside and inside. Before SPS, the particle size of the powder is reduced by high energy ball milling which can also increase the homogeneity and reactivity of the mixture [16]. High-energy ball milling is a simple, effective and productive way to produce various nanocrystal powders in high-energy planetary, ball and vibratory mills. With other things being equal, the higher the grinding intensity and the longer the grinding duration, the smaller is the average size of resulting powder particles [17]. High reactivity and small particle size can facilitate to produce high density ceramics at low sintering temperatures [3]. Therefore, the SPS method along with high energy ball milling has specific features of low sintering temperatures and short processing times. Although its sintering mechanism is not yet well understood, the SPS has been employed to process many materials, such as metals and alloys [18], ceramics [19], dielectrics [20], thermoelectric materials [21], solid oxide fuel cells [22] and biomaterials [23].

For the time being, there are limited reports on NiZn ferrites preparation by SPS [24]. This investigation was involved in preparing a novel high-density fine-grained $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite material by SPS in conjunction with high energy ball milling. The prepared samples were characterized by different techniques to evaluate the effects of microstructural features on their dielectric and magnetic properties.

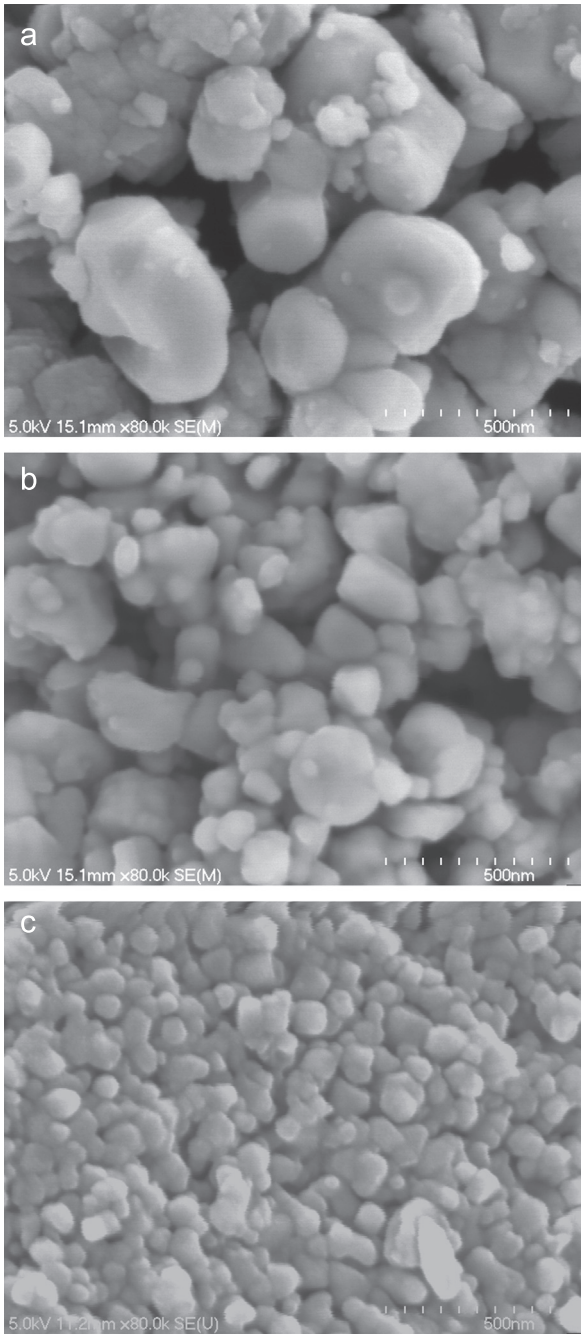

Fig. 1. Morphologies of the powder particles after high energy ball milling for (a) 10 h, (b) 20 h, and (c) 40 h.

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 a medium of alcohol at a speed of 400 rpm for 10, 20 and 40 h. After the powders were dried at 80 °C for 2 h, they were evaluated using field emission scanning electron microscopy (FE-SEM, Hitachi S-4700). As shown in Fig. 1, the powder particles became finer and finer with increasing milling duration and their average size could be well below 100 nm after 40 h milling. It could be anticipated that the 40 h-milled ultrafine-sized powders were highly reactive and thereby could facilitate densification at a lower sintering temperature. These powders were used as the precursor ones for SPS. They were placed in a graphite die and sintered at different temperatures (850, 875, 900 and 925 °C) for 5 min in a vacuum of 10^{-2} Pa by SPS. During heating and soaking of the SPS, a pressure of 48 MPa was constantly maintained to the samples. After the SPS, the prepared pellets with a size of 10 mm diameter and 3 mm thickness were