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Short communication

Comparison of different methods to produce dense zinc ferrite ceramics with high electrical resistance

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Abstract

Three different methods were used to produce dense $ZnFe_2O_4$ ceramics with high electrical resistance – spray pyrolysis (SP), conventional sintering (CS) and spark plasma sintering (SPS). The phase purity was determined by X-ray diffraction and the morphology/particle size investigated by scanning electron microscopy. It was found that SP is the most appropriate method to produce a dense $ZnFe_2O_4$ ceramics with high electrical resistivity. By using the SP method, about 500 nm thick $ZnFe_2O_4$ films were obtained possessing a resistivity with 7 orders of magnitude higher than resistivity of $ZnFe_2O_4$ pellet sintered by SPS. Both samples obtained by SP and SPS show density close to the theoretical value. The sample obtained by CS shows a low resistivity and relatively high porosity.

Keywords: C. Electrical properties; Spray pyrolysis; Spark plasma sintering; Zinc ferrite

1. Introduction

Spinel type ferrites are widely used in microwave devices due to its high resistivity and low eddy current losses at high frequencies [1]. For microwave applications not only high electrical resistivity is necessary but ferrite material also needs to be dense to provide high magnetic permeability, flux density and susceptibility [2].

Conventional sintering (CS) is a well-known method for ceramic powder densification which is still used in industry. Main drawbacks of this method are high processing time and energy consumption, as well as it is hard to obtain fully dense ceramic element by using CS [3].

Spark plasma sintering (SPS) is considered as an outstanding method to obtain dense ceramics in short time [4]. SPS also provides to obtain dense ceramics with nanosized grains [5]. Due to short sintering time, growth of raw powder nanoparticle size is relatively small. In the same time SPS process involves the sintering of powders under reducing conditions due to graphite die and vacuum atmosphere. Reduction can decrease electrical resistivity of the spinel ferrites due to formation of oxygen vacancies and reduction of Fe^{3+}–Fe^{2+}, thus increasing possibility for electron hopping conductivity: $Fe^{3+}+e^- \leftrightarrow Fe^{2+}$.

Spray pyrolysis (SP) has been applied to deposit a wide variety of thin and thick metal oxide films with high density close to theoretical [6]. Main advantages of this method are low cost, high deposition rate and low temperature, as well as this method is suitable for the preparation of stoichiometric compounds.

In the present work all these three methods have been used for preparation of the spinel zinc ferrite materials with high density. The phase purity, microstructure and electrical properties of the obtained materials are reported.

2. Experimental

Raw zinc ferrite ($ZnFe_2O_4$) nanopowders used for CS and SPS were synthesized by sol–gel auto combustion from a xerogel layer as described previous [7]. In CS method the

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ferrite sample in shape of pellet with 10 mm diameter and 1 mm thickness was prepared from as-burnt powders in a uniaxial press at 5 MPa and sintered at 1300 °C for 1 h in ambient atmosphere. After SPS process a pellet of 12 mm in diameter and thickness of 2 mm was obtained. The sintering was performed in a vacuum atmosphere at a sintering temperature of 900 °C during three minutes. During sintering a uniaxial pressure of 75 MPa was applied. The SP method has been used to produce $ZnFe_2O_4$ thin films on soda-lime glass slides (Thermo Scientific Menzel-Gläser, Germany) at 500 °C by using zinc and iron nitrate 0.1 M aqueous solution. Detailed deposition conditions are shown in our previous work [8].

The obtained powders were characterized with an Ultima +X-Ray diffractometer (Rigaku, Japan) with CuKα radiation. The lattice constant a was calculated from the position of the peaks using the Nelson-Riley function [9]. Microstructural features of the samples were detected by SEM using a Field Emission Gun SEM (Tescan Mira/Lmu, Czech Republic). The pore fraction P of the sintered samples was calculated by considering the theoretical sample density ρ_x and geometrical sizes of the pellets.

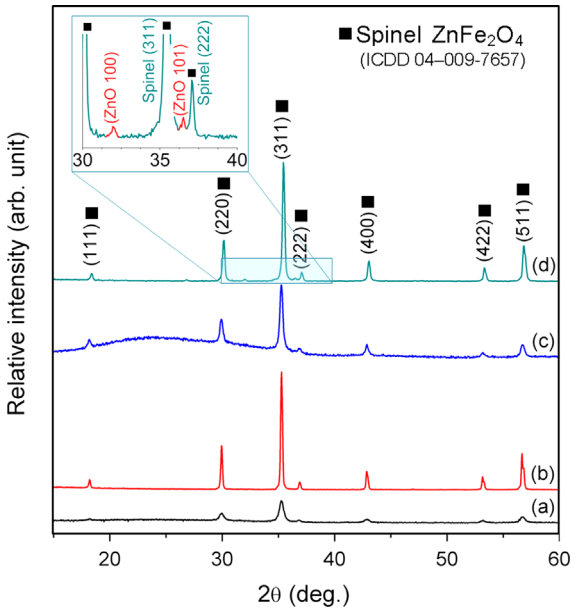

Fig. 1. X-ray diffraction patterns of (a) sol–gel combustion derived $ZnFe_2O_4$ raw powder; (b) conventionally sintered combustion derived $ZnFe_2O_4$ raw powder; (c) spray pyrolysis deposited $ZnFe_2O_4$ thin film on glass substrate; and (d) spark plasma sintered combustion derived $ZnFe_2O_4$ raw powder.

Two probe DC measurements were carried out to study electrical resistivity for pellet samples, but four probe DC measurements for thin films. Silver electrodes were painted on both pellet surfaces by using ISP (USA) high purity silver paint to achieve good ohmic contacts. An impedance spectrometer (HP 4194, USA) was used to measure the dielectric losses of the materials at room temperature.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of all three different $ZnFe_2O_4$ samples. Monophasic $ZnFe_2O_4$ (ICDD 00-022-1012) forms during combustion of the xerogel layer on a hot plate (Fig. 1(a)), as described in our previous work [7]. No additional peaks appear after CS of the combustion derived $ZnFe_2O_4$ raw powder at 1300 °C for 3 h (Fig. 1(b)). XRD pattern of thin film obtained by the SP method using aqueous solutions of metal nitrates (Fig. 1(c)) also confirmed formation of monophasic zinc ferrite. After SPS of the combustion derived $ZnFe_2O_4$ powder additional peaks (100) and (101) corresponding to the ZnO phase (ICDD 00-036-1451) was detected. This could be attributed to the reducing conditions during SPS, which causes a reduction of Fe^{3+}–Fe^{2+}. To maintain M^{2+}/M^{3+} cation ratio close to 1:2, some of the Zn^{2+} could travel out of spinel structure and form ZnO impurity phase. This is confirmed also by change of the lattice constant. Obtained lattice constant of the spinel phase for SPS sample is smaller than the lattice constant of CS and SP derived samples (Table 1). This could be attributed to the replacement of larger Zn^{2+} by smaller Fe^{3+} in the tetrahedral sites of spinel structure. The Fe^{3+} ions being smaller than Zn^{2+} narrow the tetrahedral sites leading to decrease of the lattice parameter. Divalent iron ion Fe^{2+} has a strong preference of the octahedral sites of spinel structure [10].

The initial synthesized nanopowder used for SPS and CS, as well as microstructures of different samples are shown in Fig. 2. As we can see in Fig. 2(a) after combustion reaction a nanopowder with particles size of ~20 nm is formed. During SP (Fig. 2(b)) and SPS (Fig. 2(c)) completely dense polycrystalline structures is obtained. Both samples consist of close packed grains without pores between them. During CS the sample does not show a completely dense microstructure (Fig. 2(d)). It is possible to see pores of different sizes between grains in CS samples. Porosities for all samples are shown in Table 1.

The smallest grains (~0.03 μm or 30 nm) are for SP derived $ZnFe_2O_4$ thin films, while for SPS and CS samples average

Table 1
Properties of various $ZnFe_2O_4$ samples obtained by spray pyrolysis (SP) using aqueous solution of metal nitrates, as well as conventional sintering (CS) or spark plasma sintering (SPS) of combustion derived $ZnFe_2O_4$ powders. T – processing/sintering temperature; a – lattice constant; ρ_x – theoretical (X-ray) density; ρ_x – measured density; D – average grain size (from SEM); ρ_{DC} – electrical resistivity; tanδ – dielectric loss.

	T, (°C)	a, (Å)	ρ_x, (g/cm^3)	ρ_m, (g/cm^3)	P, (%)	D, (μm)	ρ_{DC}, (Ω cm)	tanδ (100 kHz)
SP	500	8.431	5.34	–	–	~0.03	$1.8 \cdot 10^{10}$	0.024
SPS	900	8.423	5.36	5.22	~2.5	~0.50	$4.4 \cdot 10^{3}$	1.05
CS	1300	8.431	5.34	4.54	~15.0	~3.50	$1.0 \cdot 10^{4}$	4.110

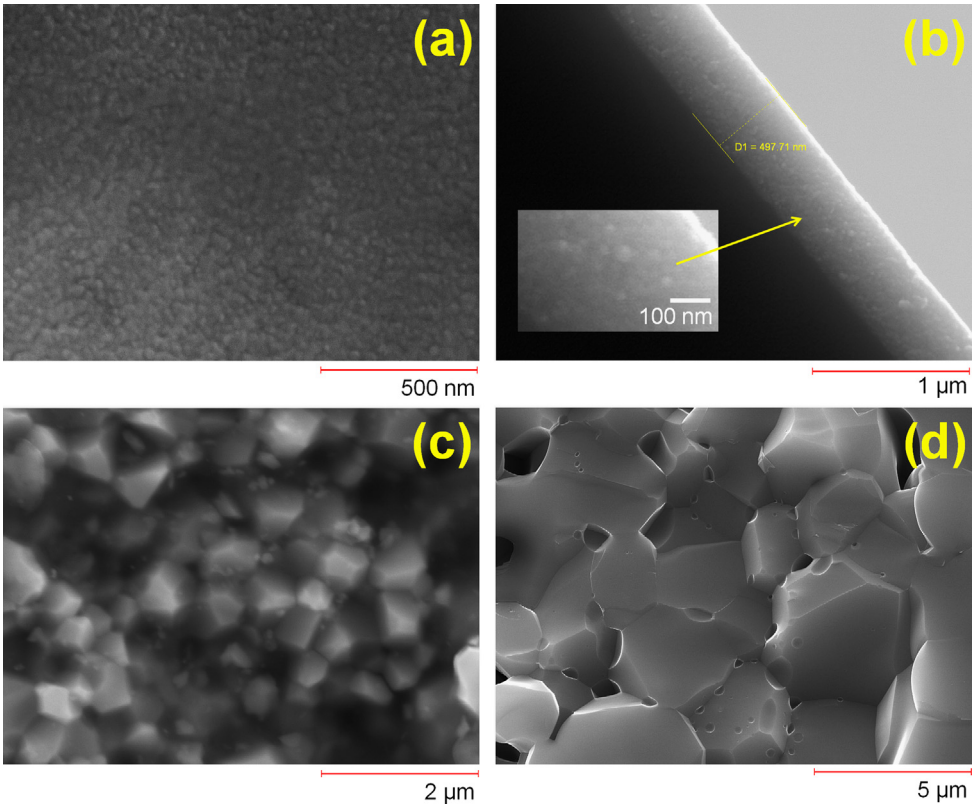

Fig. 2. (a) Synthesized $ZnFe_2O_4$ nanopowder for CS and SPS, (b) SP deposited $ZnFe_2O_4$ thin film, (c) and (d) fractured surfaces of $ZnFe_2O_4$ samples obtained by SPS and CS.

grain sizes are 0.3 μm and 3.5 μm, respectively. Larger grains in case of CS can be attributed to higher sintering temperature and longer time (1300 °C for 1 h).

Electrical resistivity (ρ_{DC}) of zinc ferrites obtained by different methods are compared in Table 1. As we can see, highest resistivity is obtained for $ZnFe_2O_4$ thin film, in spite to large density and grain interconnectivity of this sample. High resistivity can be attributed to high stoichiometry [11] and small grain sizes [12]. Volume of the grain boundaries increases with decreasing grain size. Grain boundaries are most resistive part in the n-type transition metal oxide semiconductors and can act as barriers for the electron flow, thus decreasing conductivity [12].

SPS sample shows the lowest resistivity although its grain size is 10 times smaller than $ZnFe_2O_4$ sample obtained by CS. SPS derived sample has almost 7 orders of magnitude lower resistivity than SP derived $ZnFe_2O_4$ thin film. The low resistivity of the SPS sample can be attributed to reducing environment during sintering. Reduction causes formation of oxygen vacancies and Fe^{2+} in octahedral sites, thus promoting charge hopping and increasing conductivity.

Zinc ferrite obtained by CS has higher resistivity than SPS produced $ZnFe_2O_4$, but much lower than that of the $ZnFe_2O_4$ thin film. During CS from $ZnFe_2O_4$ evaporates zinc ion [13], thus increasing Fe^{2+} content in octahedral site of spinel structure according to equation: $(Zn^{II}_{1-x}Fe^{III}_x)[Fe^{III}_{2-x}Fe^{II}_x]O_4$. This is the reason for lower resistivity in comparison with $ZnFe_2O_4$ thin film which was obtained at 500 °C not 1300 °C. The higher resistivity for CS sample in comparison with SPS sample can be attributed to higher porosity [14].

Table 1 shows the dielectric loss tangent (tanδ) at room temperature for different zinc ferrite samples. The tanδ was calculated from measured qualitative factor Q using equation $\tan\delta = 1/Q$. The dielectric loss arises from Maxwell–Wagner interfacial polarization, as well as due to local displacement of charge carriers through a mechanism similar to conduction process in ferrites. Observed tanδ values correlates with ρ_{DC} measurements. SP sample with highest resistivity possess smaller polarization and lower tanδ attributed to lower concentration of charge carriers.

4. Conclusions

Three different methods were used to produce dense $ZnFe_2O_4$ ceramics – spray pyrolysis, conventional sintering and spark plasma sintering. SP derived 500 nm thick films, but sintering pellet shaped samples. SP and SPS samples had highest density close to theoretical, but samples obtained by CS contained relatively large fraction of pores. Processing temperatures and conditions also differ greatly between these methods. For example, $ZnFe_2O_4$ were obtained at 500 °C by SP, but for SPS and CS optimal temperatures were 900 °C and 1300 °C, respectively. CS besides highest sintering temperature has also longest sintering time.

During SPS besides spinel formed ZnO impurity phase, attributed to strong reducing conditions. It was interesting to

observe, that SP sample has 6 and 7 orders of magnitude higher resistivity as samples obtained by CS and SPS. This is attributed to zinc loss during CS due to long sintering time and high sintering temperature, as well as to reducing conditions during SPS.

Overall, to produce materials for microwave applications it is better to choose SP between these three methods, because obtained materials characterizes with both – high density and resistivity. However, by using SP it is not possible to obtain large volume materials.

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