Journal of Magnetism and Magnetic Materials 349 (2014) 57–62

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

# Effect of heat treatment on microwave absorption properties of Ni–Zn–Mg–La ferrite nanoparticles

Yi Liu*, Shicheng Wei, Binshi Xu, Yujiang Wang, Haoliang Tian, Hui Tong

*National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, China*

ARTICLE INFO

*Article history:*
Received 9 November 2012
Received in revised form
13 April 2013
Available online 29 August 2013

*Keywords:*
Sol–gel growth
Magnetic materials
Heat treatment

ABSTRACT

Spinel structure Ni–Zn–Mg–La ferrites have been prepared by the sol–gel route and investigated as a radar absorbing material (RAM) in a frequency range of 1–18 GHz. The structure and morphological studies on the nanoparticles of the ferrites have been carried out using X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy. The complex permeability and complex permittivity are measured by a network analyzer. The electromagnetic wave loss and microwave absorbing property are studied as a function of frequency, annealing temperature and thickness of the absorber. The results indicate that electromagnetic wave loss of the ferrite only annealed at 850 °C shows two peaks. The reflection loss varies with the change of the annealing temperature. The absorber annealed at 850 °C exhibits the best microwave absorbing properties, which is suitable for microwave absorption materials.



## 1. Introduction

The production of electromagnetic wave absorbers has recently been increasing [1]. Among these absorbers, spinel ferrites, which can be used in 3–30 GHz band, are becoming one of the versatile magnetic materials for general use [2]. Spinel Ni–Zn ferrites have many applications in both low and high frequency devices and play an important role in many technological applications, due to their high resistivity, low dielectric loss, mechanical hardness, high Curie temperature and chemical stability [3]. Various methods have been proposed for the synthesis of sipnel Ni–Zn ferrite in the past several years, such as the sol–gel preparation [4,5], low temperature solid-state reaction [6,7], co-precipitation method [8] and high energy milling method [9]. Among these technologies, the sol–gel route is a method which can prepare pure ferrite at a relatively low temperature.

The magnetic and electrical properties of ferrites are sensitive to the preparation method and the distribution of cations [10]. Small amount of additives can be used to modify their microstructure and hence magnetic properties. Nowadays rare earth oxides are becoming promising additives to improve the magnetic properties of ferrite. Many investigations have been carried out to explore the effect of La substitution on the properties of Ni–Zn ferrites. However, in some literature conflict results are obtained [11,12]. Ahmed studied the substitution of rare earth $La^{3+}$ into the spinel structure of Ni–Zn ferrites. In his work, a secondary phase appeared due to the substitution of $La^{3+}$, and dielectric constant of the ferrite showed more than one peak [13]. However, in Gable's study of the structural and magnetic properties of La substituted NiCuZn ferrites, no secondary phase was detected in XRD patterns for the calcined samples even at higher La contents [14].

Heat treatment process is an important influencing factor for the magnetic property of ferrite. Ichiyanagi investigated Mg-ferrite nanoparticles and found a clear difference in the magnetization between the quenched samples and annealed samples [15]. Pozo López studied the magnetic properties of NiZn ferrite/$SiO_2$ nanocomposites synthesized by ball milling and found that complete transformation of the precursor oxides into NiZn ferrite was only achieved after the as-milled powders were annealed at 1273 K in air for 1 h. This heat treatment favored the formation of Ni–Zn ferrite in detriment of the precursor oxides [16]. Nevertheless, in some other literature Ni–Zn ferrite formed the spinel structure at around 350 °C when prepared by the sol–gel method [17]. Therefore, further studies on the effect of heat treatment and the substitution of $La^{3+}$ on the magnetic and microwave absorption property of the ferrite still need to be done. Although researchers have already synthesized Ni–Zn–La ferrite [18] and Ni–Zn–Mg ferrite [19], Ni–Zn–Mg–La ferrite is still not studied. In this paper, Ni–Zn–Mg–La ferrite is synthesized by the sol–gel methods. The aim of our work is to describe and evaluate the effect of heat treatment on magnetic and microwave absorbing properties of the ferrite.

* Corresponding author. Tel.: +86 10 667 185 41; fax: +86 10 667 171 44.
*E-mail address:* liuyi5556@sina.com (Y. Liu).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.08.054

## 2. Experimental

### 2.1. Synthesis of ferrite

Nanoparticles ferrites have been synthesized by the conventional sol–gel method. Analytical grade metal nitrates and citric acid are used as raw materials. The molar ratios of $Ni^{2+}$:$Zn^{2+}$:$Mg^{2+}$:$La^{3+}$:$Fe^{3+}$ are 0.5:0.4:0.1:0.01:1.99, which gives a composition of $Ni_{0.5}Zn_{0.4}Mg_{0.1}La_{0.01}Fe_{1.99}O_4$. The nitrates and citric acid are weighed in desired stoichiometric proportions and dissolved separately in the minimum amount of distilled water. The reactants are mixed together and ammonia solution is added to the solution drop by drop to adjust the pH value of the mixture to 6. The solution is slowly heated and stirred using a hot plate magnetic stirrer till it turns into a dark vicous liquid and then it is dried at 120 °C for 24 h. The dried gels are ignited in order to obtain loose powders. These as burnt ferrite powders are labeled as 1#. The heat treatment process is as follows: the powders are annealed at 650 °C, 750 °C and 850 °C for 2 h and labeled as 2#, 3# and 4#, respectively. Then these powders are cooled down to room temperature naturally.

### 2.2. Characterization

The crystal structure of the obtained particles is recorded by X-ray diffraction (XRD) using a Rigaku model D/max 2500 system with $\lambda$=0.154 nm (Cu-$K_\alpha$ radiation). The morphology is analyzed by a HITACHI S-5500 field emission scanning electron microscope (SEM). The composition analysis of the ferrites is performed by energy dispersive spectra (EDS, OXFORD Feature Max). The valence states of elements are analyzed by X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 220i-XL, USA). The complex permeability and complex permittivity are measured in the range of 1–18 GHz by an HP8722ES network analyzer. For this purpose, the Ni–Zn–Mg–La ferrite powders are homogeneously dispersed into the wax matrix and compacted into rings for the permeability and permittivity measurement. The size of the ring is 7 mm in outer diameter, 3 mm in inner diameter and 2 mm in thickness. The ferrite–wax composites contain 60% of ferrite (wt%). Static magnetic properties are studied using a Lake Shore 7410 vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 10 kOe.

## 3. Results and discussion

### 3.1. Structure and morphological study

The X-ray diffraction patterns of the powders are shown in Fig. 1. The existence of (311) peak around 35° confirms the formation of spinel structure in the prepared samples. It is found that all the peaks could be indexed to a spinel phase. Lima reported that Ni–Zn ferrite calcined in argon atmosphere at 1000 °C/3 h showed single spinel phase structure [20]. In this work, the Ni–Zn–Mg–La ferrite powders annealed at 650 °C/2 h already have single spinel phase. In some literature [21], secondary phase $LaFeO_3$ formed upon La substitution for Fe in the ferrite. However, in our research, the secondary phase is not found in all the samples. The sharp and strong diffraction peaks also confirm the good crystallization of the products. The average crystallite sizes of the samples are calculated using Scherer's relation for the strongest peak of the (311) plane [22]

$$D = 0.9\lambda/(\beta \cos \theta) \quad (1)$$

where $D$ is the crystallite size of the particle in nanometer, $\beta$ is the half-maximum line width and $\theta$ is Bragg angle of diffraction, $\lambda$ is the wavelength of radiation. The calculated crystallite size of the particles is exhibited in Table 1. It is observed that the average crystallite size increases with adding temperature. This result is in accordance with the study of Yousefi [23]. This is due to the grain growth of the ferrites.

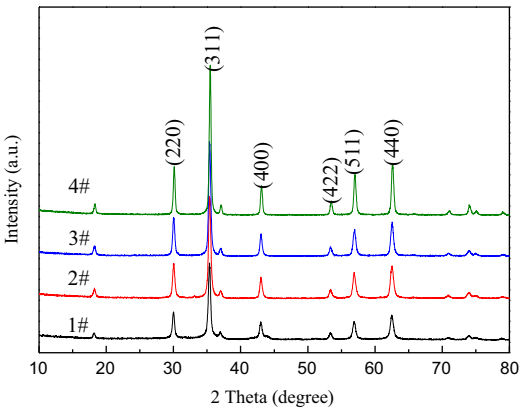


**Fig. 1.** X-ray diffraction of Ni–Zn–Mg–La ferrites.

**Table 1**
Calculated grain size of Ni–Zn–Mg–La ferrite.

| Sample | 1# | 2# | 3# | 4# |
|---|---|---|---|---|
| Crystallite size (nm) | 20 | 20 | 23 | 26 |

The microstructures of magnetic Ni–Zn–Mg–La ferrites annealed at different temperatures are displayed in Fig. 2(a–d). SEM observations show that nanocrystallites of the ferrites are spherical in morphology. The average particle sizes of the ferrites are in the range of 40–80 nm. The grain size is larger than data estimated by the Scherer formula because the instrument errors are not taken into account. Moreover, the difference is indicative of the fact that every particle is formed by the aggregation of a number of crystallites or grains [24]. The surface composition of Ni–Zn–Mg–La ferrite is distinctly determined with EDS. Fig. 2(e) shows the composition of the Ni–Zn–Mg–La ferrite. The predominant composition is made up of iron and oxygen. In order to determine the valence states of the elements, surface/near surface of the ferrite is analyzed by XPS within a range of binding energies of 0–1400 eV. Core levels of Ni 2p, Zn 2p, Mg 1s, and Fe 2p can be identified in Fig. 3(a). The fine spectra of the Fe 2p peaks are displayed in Fig. 3(b). The Fe 2p3/2 spectrum and Fe 2p1/2 spectrum obtained from the present study generally show two distinguishable main peaks of around 710.4 eV and 723.5 eV, respectively, which demonstrates the presence of $Fe^{3+}$ cation. Meanwhile, the presence of the peak around 713.9 eV indicates that $Fe^{3+}$ species exist in more than one chemical state. The two chemical states may be related to the different coordination environments of $Fe^{3+}$—the tetrahedral (A) environment and octahedral (B) environment of $Fe^{3+}$ cations in spinel structure: $Fe_A{}^{3+}$ at higher binding energy and $Fe_B{}^{3+}$ at lower binding energy [25]. In this ferrite, the number of $Fe_B{}^{3+}$ cations is much more than that of $Fe_A{}^{3+}$ cations. This result is in accordance with Priyadharsini's report [24], which used X-ray diffraction to detect the lattice constant and cation distribution of $Ni_xZn_{1-x}Fe_2O_4$. In his report the percentage of $Fe_A{}^{3+}$ is only 27% when $x$=0.6.

### 3.2. Microwave absorption properties of Ni–Zn–Mg–La ferrite

It is well known that the basic principle of microwave absorption property is to consume electromagnetic wave energy by increasing the energy conversion when the electromagnetic wave