Journal of Magnetism and Magnetic Materials 322 (2010) 2777–2781

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Effect of Nd^{3+} substitution on structural and electrical properties of nanocrystalline zinc ferrite

T.J. Shinde [a,*], A.B. Gadkari [b], P.N. Vasambekar [c]

[a] Department of Physics, KRP Kanya Mahavidyalaya, Islampur 415409, India
[b] Department of Physics, G.K.G College, Kolhapur 416012, India
[c] Department of Electronics, Shivaji University, Kolhapur 416004, India

ARTICLE INFO

Article history:
Received 3 December 2009
Received in revised form
11 April 2010
Available online 24 April 2010

Keywords:
Zn–Nd ferrites
Co-precipitation method
DC resistivity
Dielectric property

ABSTRACT

Polycrystalline soft ferrite samples with general formula $ZnNd_xFe_{2-x}O_4$ (where $x=0$, 0.01, 0.02 and 0.03) were synthesized by oxalate co-precipitation method. The samples were characterized by XRD and SEM techniques. The single phase cubic spinel structure of all the samples was confirmed by XRD. The lattice constant and grain size of the samples are found to decrease with increase in Nd^{3+} content. Room temperature DC resistivity of the Nd^{3+} substituted zinc ferrites is 10^2 times higher than that of zinc ferrite. The dielectric constant (ε') and dielectric loss ($\tan\delta$) of all the samples were measured in the frequency range 20 Hz–1 MHz. The dielectric behaviour is attributed to the Maxwell–Wagner type interfacial polarization. The dielectric loss of the samples is found to decrease with increase in Nd^{3+} content. High resistivity and low dielectric loss makes these ferrites particularly suitable for high frequency applications.

1. Introduction

Zinc ferrite is an important technological material with wide applications in photoinduced electron transfer, photo electrochemical cells, photochemical hydrogen production [1,2] and regenerable absorbent material for desulphurization of hot coal gases [3,4].This ferrite is also used in electronic devices, photoconductive materials, information storage and sensors [5–8]. Recently nanoparticles and films of $ZnFe_2O_4$ have been prepared to detect certain kinds of reducing gases, such as sulfureted hydrogen [9], carbon monoxide [10], chlorine [11] and ethanol [12]. Chu et al. [13] reported that $ZnFe_2O_4$ nanoparticles have great response to reducing gases. Zhang et al. [14] reported the use of $ZnFe_2O_4$ tubes as a gas sensor with high sensitivity and low-energy consumption. Niu et al. [11] prepared zinc ferrite by microemulsion method. They reported that $ZnFe_2O_4$ sensors have a high sensitivity, excellent selectivity and quick response behaviour to Cl_2 gas compared with $ZnCo_2O_4$ and $ZnCr_2O_4$ sensors. Zheng et al. [15] studied gas sensing properties of nanocrystalline zinc ferrite thin films. They reported that it is a promising sensor material.

Generally ferrites were prepared by conventional ceramic method. This method requires high sintering temperature which may cause evaporation of zinc in zinc substituted ferrites and changes the desired stiochiometry and also affects the electrical as well as magnetic properties [16,17].

In recent years, a number of chemical and physical methods have been attempted to produce nanosize ferrites. Various chemical methods such as co-precipitation [18], sol–gel [19], molten salt-route [20], ultrasonic radiation [21], tartrate precursor [22], electrodeposition [23], urea combustion [24], aerogel [25], mechanochemical [26], etc. have been developed to synthesize nanosized zinc ferrites.

The co-precipitation technique is a useful and attractive technique for the preparation of nanosized particles because of its advantages like good stoichiometric control and the production of ultrafine particles with low sintering temperature and smaller duration [27,28].

Several reports are available on the magnetic properties of nanocrystalline zinc ferrites [26,29–31]. However the structural and electrical properties of Nd^{3+} substituted nanocrystalline zinc ferrites prepared by co-precipitation technique have not been investigated in detail. In the present communication, the effect of Nd^{3+}substitution on structural and electrical properties of nanocrystalline zinc ferrite prepared by oxalate co-precipitation method is reported.

2. Experimental

Ferrite samples with chemical formula $ZnNd_xFe_{2-x}O_4$ ($x=0$, 0.01, 0.02 and 0.03) were prepared by oxalate

---

* Corresponding author. Mob.: 9860735543; fax: +91 2342 224094
E-mail address: pshindetj@yahoo.co.in (T.J. Shinde).

0304-8853/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2010.04.026

co-precipitation technique. Analytical grade zinc sulphate ($ZnSO_4\cdot 7H_2O$, 99.5% pure), ferrous sulphate ($FeSO_4\cdot 7H_2O$, 98.5% pure) and neodymium sulphate ($Nd_2(SO_4)_3\cdot 8H_2O$, 99.9% pure) were used as starting materials. These chemicals were weighed in desired stoichiometric proportion and dissolved in distilled water. The pH of the solution was adjusted to be 4.7 using conc. H_2SO_4. The solution was then heated at 80 °C for 2 h. After cooling the solution, ammonium oxalate solution was added with stirring until complete precipitation was obtained. The precipitation of the zinc ferrites occurred according to the following reactions:

$$ZnSO_4+2H_2O+C_2O_4^{2-}\rightarrow ZnC_2O_42H_2O+SO_4^{2-}$$

$$NdSO_4+2H_2O+C_2O_4^{2-}\rightarrow NdC_2O_42H_2O+SO_4^{2-}$$

$$2FeSO_4+2H_2O+C_2O_4^{2-}\rightarrow Fe_2C_2O_42H_2O+2SO_4^{2-}$$

The precipitate was filtered and washed several times with glass distilled water, in order to remove the sulphate ions. The removal of sulphate ions was confirmed by barium chloride test. The precipitate was dried and presintered at 600 °C for 1 h. The presintered powder was milled in agate mortar and sintered at 1000 °C for 4 h. The rate of heating and cooling was 80 °C/h. The sintered powder was again milled and mixed with an appropriate amount of 2 wt% polyvinyl alcohol as a binder and pressed into pellets of 1.3 cm diameter at a pressure of 5.27×10^{-7} MPa. The pellets were finally sintered at 1000 °C for 4 h.

The X-ray powder diffraction (XRD) patterns were obtained at room temperature by using a Philips PW-3710 X-ray powder diffractometer operated at 40 kV and 30 mA using CuKα radiation ($\lambda=1.5424$ Å). The diffraction patterns were recorded in angular range 20–80°.

The scanning electron microscope (JEOL-JSM-6360 model) was used to record microphotographs of all the samples. DC resistivity measurements of all the samples in the range 300–800 K were carried out by using two probe method. The dielectric constant (ε') and dielectric loss ($\tan\delta$) of all the samples in the pellet form were measured using a HP 4284 A impedance analyzer in the frequency range 20 Hz–1 MHz at room temperature.

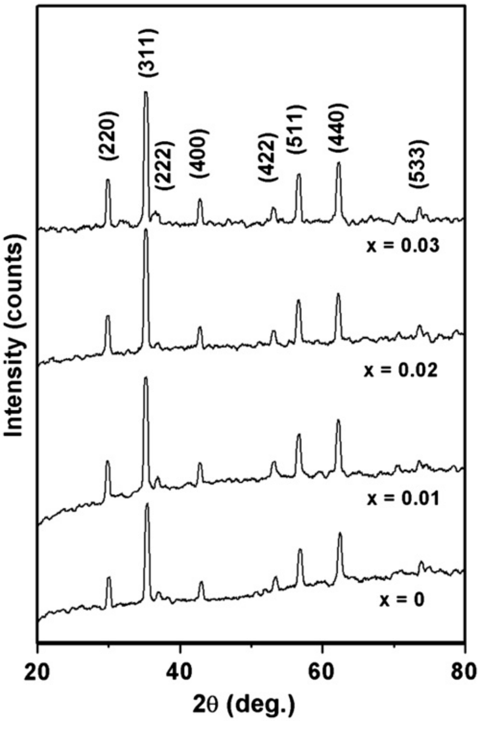

Fig. 1. X-ray diffraction patterns of $ZnNd_xFe_{1-x}O_4$ ($x=0$, 0.01, 0.02 and 0.03) system.

3. Results and discussion

3.1. Structural analysis by XRD and SEM

The X-ray diffraction patterns of powders of $ZnNd_xFe_{2-x}O_4$ ($x=0$, 0.01, 0.02 and 0.03) system are presented in Fig. 1. The patterns of all the samples indicate the formation of single spinel phase with cubic structure. The variation of lattice parameter (a) as a function of Nd^{3+} content is shown in Fig. 2. From this figure, it is observed that the lattice parameter decreases with increase in Nd^{3+} content. This is due to the formation of isolating ultra-thin layer around the grains by diffusion of some of the Nd^{3+} ions at the grain boundaries rather than entering into the lattice, during the sintering process [32]. Reduction in the lattice parameter of Nd^{3+} substituted Mg–Zn ferrites system was reported by Ladgaonkar et al. [33], suggesting the occupancy of Nd^{3+} ion on B-site. Zhao et al. [32] studied magnetic properties of Re-substituted Ni–Mn ferrite nanocrystallites. They reported that the lattice parameter decreases with rare earth (La^{3+}, Nd^{3+} and Gd^{3+}) substituted samples compared to un-substituted sample.

The X-ray density (ρ_x) of all the samples was calculated by using the formula [34],

$$\rho_x=\frac{8M}{Na^3} \tag{1}$$

where M is the molecular weight, N is Avogadro's constant.

Physical density (ρ_p) of all the samples was measured by using Archimedes principle. The percentage porosity (p) of all the samples was calculated by using the relation [34],

$$p=1-\frac{\rho_{\mathrm{p}}}{\rho_{\mathrm{x}}} \tag{2}$$

X- ray density, physical density and porosity of all the samples under investigation are presented in Table 1. From this table, it is revealed that the X-ray density increases with increase in Nd^{3+} content. This is attributed to increased mass overtaking the increased volume of the unit cell. Physical density of the samples

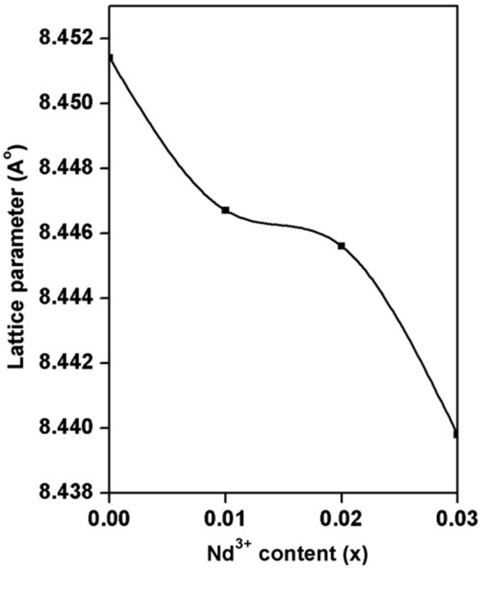

Fig. 2. Variation of lattice constant with Nd^{3+} content of $ZnNd_xFe_{1-x}O_4$ ($x=0$, 0.01, 0.02 and 0.03) system.