Journal of Magnetism and Magnetic Materials 434 (2017) 143–150

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Dielectric and impedance study of praseodymium substituted Mg-based spinel ferrites

Hafiz Muhammad Tahir Farid [a,*], Ishtiaq Ahmad [a], Irshad Ali [a], Shahid M. Ramay [b], Asif Mahmood [c], G. Murtaza [d]

[a] Department of Physics, Bahauddin Zakariya, University Multan, 60800, Pakistan
[b] College of Science, Physics and Astronomy Department, King Saud University, P.O. Box 2455, 11451 Riyadh, Saudi Arabia
[c] Chemical Engineering Department, College of Engineering, King Saud University, Riyadh, Saudi Arabia
[d] Centre for Advanced Studies in Physics, GC University, Lahore 5400, Pakistan

ARTICLE INFO

Article history:
Received 15 December 2016
Received in revised form 6 March 2017
Accepted 22 March 2017
Available online 24 March 2017

Keywords:
Spinel ferrites
Dielectric constant
Impedance
AC conductivity
Cole–Cole plots

ABSTRACT

Spinel ferrites with nominal composition $MgPr_yFe_{2-y}O_4$ (y = 0.00, 0.025, 0.05, 0.075, 0.10) were prepared by sol-gel method. Temperature dependent DC electrical conductivity and drift mobility were found in good agreement with each other, reflecting semiconducting behavior. The dielectric properties of all the samples as a function of frequency (1 MHz–3 GHz) were measured at room temperature. The dielectric constant and complex dielectric constant of these samples decreased with the increase of praseodymium concentration. In the present spinel ferrite, Cole–Cole plots were used to separate the grain and grain boundary's effects. The substitution of praseodymium ions in Mg-based spinel ferrites leads to a remarkable rise of grain boundary's resistance as compared to the grain's resistance. As both AC conductivity and Cole–Cole plots are the functions of concentration, they reveal the dominant contribution of grain boundaries in the conduction mechanism. AC activation energy was lower than dc activation energy. Temperature dependence normalized AC susceptibility of spinel ferrites reveals that $MgFe_2O_4$ exhibits multi domain (MD) structure with high Curie temperature while on substitution of praseodymium, MD to SD transitions occurs. The low values of conductivity and low dielectric loss make these materials best candidate for high frequency application.

1. Introduction

The extensive use of spinel ferrites is due to their low price, easy fabrication and abundant use in technological and industrial applications [1]. The technological and industrial applications of these magnetic materials is because of their excellent electrical and magnetic properties, which leads to their use in magnetic memory devices, transformers, high frequency applications and electronic devices like cellular phones, video cameras, notebook computers [2]. The high electrical resistivity and consequently low eddy currents and dielectric losses make them very important material for technological and industrial applications [3]. These materials have wide range of applications in microwave devices, computer memories, transformers, magnetic recordings and switches [4]. The electrical properties of these materials have been the subject of continuous investigation, which depend upon the preparation conditions, amount of doping element and preparation time etc. It is well known that impedance spectroscopy is an important method to study the electrical properties of ferrites, since impedance of the grains can be separated from other impedance sources, such as impedance of electrodes and grain boundaries [5]. One of the important factors, which influences the impedance properties of ferrites, is micro-structural effect. One semi-circle of Cole–Cole plots has been observed when the role of grain boundary is more dominant on the grains effect [6].

In the present work, the dielectric, electrical properties and AC susceptibility of praseodymium substituted $MgFe_2O_4$ spinel ferrites have been reported. The impedance spectroscopy or ac conductivity technique enables us to evaluate and separate out the contributions to overall electrical properties due to various components such as grain, and grain boundary or polarization phenomenon in a material, in the frequency domains. Here, the principle of analysis is based on the fact that ac response of a sample to sinusoidal electrical signal, and subsequent calculation of the resulting transfer (impedance) with respect to the frequency of the applied signal.

---

* Corresponding author.
E-mail address: tahirfaridbzu@gmail.com (H.M.T. Farid).

http://dx.doi.org/10.1016/j.jmmm.2017.03.039
0304-8853/© 2017 Elsevier B.V. All rights reserved.

The aim of this work is to study the bulk and interface phenomena over a wide range of frequencies. It is worth to note that various physical Parameters and characteristic properties that influence the performance of a ferrite material can be obtained from the analysis of complex impedance spectra.

2. Experimental procedure

2.1. Samples preparation

Spinel ferrites with composition $MgPr_yFe_{2-y}O_4$ (y = 0.0, 0.025, 0.05, 0.075, 0.10) were successfully synthesized by Sol–gel technique followed by auto-combustion. Initially, measured quantities of analytical grade $Mg\,(NO_3)_2$ and Fe_3Cl_2 were dissolved in 100 ml de-ionized water. The Pr_2O_3 (99.99% pure) was first dissolved in HCl in order to obtain praseodymium chloride and then mixed with the solution. Citric acid was employed as Chelating agent. The precursor's solution was put on stirring at ≈80 °C to obtain homogeneity. The pH of the solution, was set at 7 by drop wise addition of 1 M NH_3 solution and the stirring continued for 8 h till the solution turned into viscous gel. The product was then let to self-combustion at 370 °C for 3 h and the obtained fluffy product was grinded to obtain fine powder and sintered in a furnace at 700 °C for 5 h. Fine pellets of 0.13 cm diameters and 0.14–0.26 cm thickness were formed by using Paul–Otto Weber Hydraulic Press at a load of 30 kN by using binder polyvinyl alcohol (3–5 wt%). The binder of pellets was evaporated by annealing the pellets at 250 °C for 1 h followed by sintering at 950 °C for 7 h.

2.2. Characterization of the samples

The two-probe method was employed to measure the DC electrical conductivity of spinel ferrites in the temperature range 293–663 K. For this purpose, Keithly source meter model-197 was used. Following equation was used to measure the DC conductivity (σ_{Dc}) of each sample [7].

$$\sigma_{Dc} = \frac{d}{RA} \tag{1}$$

where "R" is resistance of the sample, "A" and "d" are the area and thickness of the sample pellet.

To calculate the Drift mobility (μ_d) of spinel ferrites from measure conductivity, we use the following relation [7].

$$\mu_d = \frac{\sigma_{Dc}}{ne} \tag{2}$$

Here "e" denotes the charge of the electron and "n" represents the concentration of charge carrier. The 'n' was calculated by the well-known equation: [7]

$$n = \frac{N_A d_b P_{Fe}}{M} \tag{3}$$

where 'N_A' is the constant quantity, called Avogadro's number while 'd_b' is the measured bulk density of the sample, 'P_{Fe}' is the number of iron atoms in the chemical formula of ferrites and 'M' is the molecular weight of the samples.

By using Wayne Kerr 6500B LCR Meter Bridge, dielectric properties were measured in the frequency range of 1 MHz–3 GHz.

The formula for permittivity is

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{4}$$

The real part of permittivity that is known as 'dielectric constant' can be measured by the formula,

$$\varepsilon' = \frac{cd}{\varepsilon_o} \tag{5}$$

Here 'c' represents the capacitance,'d' is the thickness, 'A' is the cross sectional area and 'ε_o' is the permittivity of free space.

The imaginary part of permittivity call 'dielectric loss' (ε') was calculated by using this relation.

$$\varepsilon'' = \varepsilon' \tan\delta \tag{6}$$

Here '$\tan\delta$' is the tan loss.

By using the values of applied field, dielectric constant and dielectric loss tangent (tan δ), AC conductivity was calculated by the formula

$$\sigma_{Ac} = 2\pi f \varepsilon_o \varepsilon' \tan\delta \tag{7}$$

Here "f" is the frequency of applied field.

Impedance was measured by using Agilent impedance analyzer model E4991ARF. All measurements were performed in the frequency range of 1 MHz–3 GHz at room temperature. The real (R) and imaginary (X) parts of impedance can be measured by using the absolute value of impedance |Z| with varying complex angle θ_Z

$$Z' = R = |Z|\cos\theta_Z \tag{8}$$

$$Z' = X = |Z| Sin\theta_Z \tag{9}$$

Real and imaginary parts of complex. Electric modulus are described as

$$M' = \frac{\varepsilon'^2}{(\varepsilon'^2 + \varepsilon'^2)} \tag{10}$$

$$M'' = \frac{\varepsilon''^2}{(\varepsilon'^2 + \varepsilon''^2)} \tag{11}$$

3. Results and discussions

3.1. Dielectric properties

Dielectric properties of spinel ferrites depend upon the dielectric polarization and localized electric charge carriers.The dielectric constant (ε') as a function of praseodymium concentration for $MgPr_yFe_{2-y}O_4$ (y = 0.00, 0.025, 0.075, 0.10) is listed in Table 1. The observed decrease in ε' with the substituted ions of praseodymium contents can be explained in same way as the conduction mechanism. The exchange of electrons between Fe^{2+} and Fe^{3+} ions arise the local displacements between charges, which helps to determine the polarization of charges in these ferrites. Thus the abundance of Fe^{2+} ions on octahedral sites plays an effective role in the dielectric polarization. Due to larger ionic radius, Pr^{3+} ions occupy the octahedral site. On substitution of praseodymium ions for iron ions (B-site), it empedes the conduction mechanism due to its stable valence. This suggests that electron transfer cannot take place between Pr^{3+} and Fe^{2+} ions. Hence dielectric polarization decreases.

Dielectric constant and dielectric loss as a function of frequency at 300 K are presented in Figs. 1 and 2 respectively. The Figs. 1 and 2 clearly demonstrate that with the increase in frequency, values for parameters like dielectric loss and dielectric constant go on decreasing. The decrease in polarization at high values of frequency governs the decline in dielectric constant and loss factor with frequency and eventually they become constant. The space charge polarization phenomenon illustrates this sort of trend in the dielectric materials [8–12]. The aforementioned phenomenon mandates that the dielectric materials have well conducting grains separated by highly resistive grain boundaries. The applied electric field causes space charge accumulation at grain boundaries and voltage drop takes place primarily at these boundaries [13,14]. According to Koops' theory, low frequencies direct a higher grain