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Structural and magnetic properties of Mg substituted NiCuZn Nano Ferrites

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ABSTRACT

The present paper examines the effect of magnesium substitution on structural and magnetic properties of NiCuZn nano ferrites synthesised by sol-gel method. The prepared samples were characterised by using X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Field Emission Scanning Electron Microscopy (FE-SEM) and Vibration sample magnetometer (VSM) techniques. The phase identification, unit cell parameter and crystallite size was determined using XRD analysis. The lattice constant reduced with increasing Mg content. Room temperature saturation magnetisation and coercivity showed reverse trend with increasing Mg content. Curie temperature (T_c) obtained from the thermo magnetic curves increases with Mg concentration. The initial permeability (μ_i) decreased with increasing Mg content. This is due to reduced magnetisation, grain size and increased magneto-crystalline anisotropy constant. Simultaneously, there is an upward shift of domain wall relaxation frequency with increasing Mg content. Also the permeability is observed to be constant up to 30 MHz frequency range showing compositional stability and quality of the material. The prepared samples were suitable for applications in Multilayer Chip Inductors due to their invariable permeability up to 30 MHz frequency and high thermal stability along with low sintering temperature.

1. Introduction

Magnetic nanoparticles of mixed spinel ferrites have been the subject of current interest because of their interesting magnetic, electric, dielectric and optical properties, which are considerably different from that of their bulk counterparts [1]. These properties can be tailored for a specific device applications by choosing the proper type of cations and their distribution among tetrahedral (A) and octahedral (B) sites of the spinel lattice. In addition, the preparation conditions such as sintering temperature, sintering time and the method of preparation are the other important parameters in this regard [2]. Recently there is a growing interest on Mg based ferrites to use in microwave devices because of their high electrical resistivity and low dielectric losses [3]. Besides that they possess high Curie temperature, environmental stability, hard mechanical properties and they are available at low cost [4]. Moreover, MgO is a very stable oxide and avoids the formation of divalent iron and thereby increasing its resistivity [5].

Varalakshmi et al. [6] examined NiMgCuZn system for stress insensitive multilayer chip inductor applications (MLCIs). Roy et al. [7] investigated electromagnetic properties of Mg substituted NiCuZn ferrites suitable for MLCIs. Gabal et al. [5] studied the magnetic properties of $Ni_{0.5-x}Mg_xCu_{0.2}Zn_{0.3}Fe_2O_4$ ferrites prepared using egg white as binder cum gelling for applications in miniaturised multilayer chip inductors. Bharati et al. [8] reported that $Mg_{0.8-x}Cu_{0.2}Zn_xFe_2O_4$ ferrites prepared through sol-gel auto combustion method exhibiting improved electromagnetic properties with increasing Zn substitution.

There are reports on the compositions of the type $Mg_xZn_{1-x}Fe_2O_4$ present in the literature demonstrating good dielectric properties [9–11]. A. Hossain et al. studied $Ni_{0.50}Zn_{0.50-x}Mg_xFe_2O_4$ system and found that though both Mg and Zn are non magnetic, there is a great effect on magnetic properties of ferrites due to the substitution of Zn by Mg [3]. Murbe et al. [12] investigated $Mg_{0.201+x-y}Cu_yZn_{0.62-x}Fe_{1.98}O_{3.99}$ ferrite with $0 \le x \le 0.2$ and $0 \le y \le 0.3$ for obtaining low sintering temperature, high permeability and high thermal stability and to use them as Multilayer chip inductor materials as an alternate to the NiCuZn ferrite system. Thus, substitution of Mg in place of Zn has got some advantages namely improved thermal stability, enhanced operating frequency and increased electrical resistivity [3,11].

Very few literature related to the effect of magnesium substitution in place of Zn on electromagnetic properties of NiMgCuZn nano ferrites exists [3,6]. In this context the present paper deals with systematic study of effects of Mg substitution in place of Zn, particularly, on structural and magnetic properties of $Ni_{0.5}Cu_{0.05}Zn_{0.45-x}Mg_xFe_2O_4$ ferrites which are prepared through sol-gel method. Since both Mg and Zn are non magnetic ions thus

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there is no complexity in magnetic ordering. Here we focussed, our attention, mainly to observe how the change in the dimension of the cation and their distributions, over the two sub lattices, of a spinel will influence the structural and magnetic properties of ferrites.

2. Experimental

$Ni_{0.5}Cu_{0.05}Mg_xZn_{0.45-x}Fe_2O_4$ (x=0.09, 0.18, 0.27, 0.36 and 0.45) nano ferrites have been processed through sol-gel method. Analytical grade nickel, zinc, copper, magnesium and ferric nitrates were weighed in stoichiometric proportions and made dissolved separately in deionised water. Thus obtained cationic solutions were mixed one into another and stirred continuously for one hour in order to improve homogeneity. To the resulting solution, precursor, polyvinyl alcohol (PVA) solution was added drop by drop under constant stirring and heating. The gelation continued step by step till a red gel type product was formed with the release of reddish brown gases at about 100 °C, leaving the fluffy mass in the reaction vessel which was annealed at 500 °C for 3 h to remove PVA. This powder was compacted in the shape of disc shaped pellets and toroids which were sintered at 950 °C for 1 hour with a heating rate of 5 °C/min using temperature controlled muffle furnace.

The phase identification, lattice constant and crystallite size of the sintered samples were characterised by X-ray diffraction using Inel X-ray diffractometer (XRG 3000) with Co-Kα radiation (1.78897 Å). Formation of pure spinel phase was also confirmed using Fourier Transform Infrared spectra (BRUKER OPTICS TENSOR 27) recorded in the wave number region 4000-400 cm^{-1} using KBr pellet method. The morphology and grain size distribution of nanoparticles having gold with palladium coated surfaces were investigated by field emission scanning electron microscope(FE-SEM) of make Carl Zeiss Ultra 55, operating at an accelerating high tension voltage of 17 kV with a working distance (WD) of 8.5 mm;while the elemental analysis was carried out using Energy Dispersive X-ray spectroscopy (EDAX).Room temperature magnetic parameters were determined using vibration sample magnetometer (EV-7 VSM) in an applied magnetic field of 20 kOe. Temperature variation of magnetisation, in an applied magnetic field of 100 Oe is obtained up to a temperature range of 520 °C using the same instrument. Permeability spectra in the frequency range 20 Hz–50 MHz was obtained using High frequency LCR metre (WAYNKERR 6500 P).

3. Results and discussion

The X-Ray Diffraction patterns of the sintered $Ni_{0.5}Cu_{0.05}Mg_xZn_{0.45-x}Fe_2O_4$ (x=0.09, 0.18, 0.27, 0.36, 0.45) ferrites are as shown in Fig. 1. The existence of (3 1 1) peak, centre around $2\theta \approx 41^\circ$ confirms the formation of cubic spinel structure. The highest intensity (3 1 1) peak position with Cu-Kα radiation for spinel ferrites were observed conventionally around 35° but it is shifted towards higher angle side due to Co-Kα radiation. The well resolved peaks in the XRD pattern clearly indicate polycrystalline nature of the ferrites.

It is observed that there is nominal change in peak positions for all the compositions studied, indicating that, all the samples are crystallised in the same spinel phase with space group Fd3m [13]. The mean crystallite size is calculated from X-ray line broadening of the high intensity (3 1 1) diffraction peak using Debye Scherrer's equation

$$D_{xrd} = \frac{0.9*\lambda}{\beta \cos\theta}$$

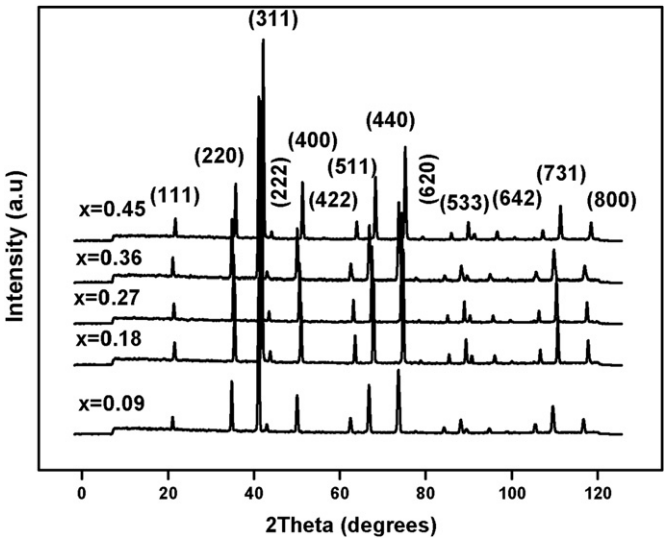

Fig. 1. XRD patterns of sintered $Ni_{0.5}Cu_{0.05}Mg_xZn_{0.45-x}Fe_2O_4$ ferrites for x=0.09, 0.18, 0.27, 0.36 and 0.45.

where λ is the wavelength of the X-rays (1.78897 Å), β is the full width at half maximum (in radians) and θ is the Bragg's angle.

Accurate estimation of lattice constant has been done using Nelson–Riley (NR) extrapolation method by minimising both systematic and random error. The values of the lattice parameter obtained from each reflected plane were plotted against the NR function $F(\theta)$ [14] and straight lines were obtained.

$$F(\theta) = \frac{1}{2}\left[\frac{cos^2\theta}{sin\theta} + \frac{cos^2\theta}{\theta}\right]$$

The extrapolation of these straight lines to $F(\theta)$=0 or θ=90° gives the accurate lattice constant. The lattice constant obtained from NR function showed decreasing trend with increasing magnesium content. This can be attributed to the smaller ionic size of Mg^{+2} (0.78 Å) substituted for Zn^{+2} (0.82 Å) [8].

The bulk density of the disc shaped pellet is calculated by considering mass and dimensions of the sample

$$d = \frac{mass}{volume}$$

$$d = \frac{m}{\prod r^2 * t}$$

where m is the mass and r, t are the radius and thickness of the pellet. The density decreased with magnesium substitution for zinc. This is due to magnesium having low atomic weight and density (24.305 amu, 1.738 g/cm^3) compared to zinc (65.39 amu, 7.14 g/cm^3). The lattice constant, crystallite size, density along with grain size and tetrahedral, octahedral frequency bands are as shown in Table 1.

IR spectroscopy is one of the useful tools to know the completion of the solid-state reaction; the cationic distribution; deformation in the spinel structure due to the entry of foreign ions [15]. The FTIR spectra (Fig. 2) showed only two prominent frequency bands around 400 and 600 cm^{-1} in the measured wave number range indicating that the samples are in pure spinel phase. In ferrite, the metal cations are situated according to the geometric configuration of the oxygen ion nearest neighbours, in two different sub lattices such as tetrahedral(A-sites) and octahedral sites (B-sites) [5]. The FT-IR spectra of the investigated ferrites showed two strong absorption bands in the wave number range 586–595 and 423–432 cm^{-1}. These bands (ν_1 and ν_2) are assigned to the vibrations of the metal-oxygen ion complexes in the tetrahedral and octahedral sites, respectively. This