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Effect on the structural, DC resistivity and magnetic properties of Zr and Cu co-Substituted$Ni_{0.5}Zn_{0.5}Fe_2O_4$using sol-gel auto-combustion method

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ABSTRACT

The Zr and Cu co-substituted $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite nanoparticles have been synthesized by the sol-gel auto combustion method. The XRD patterns confirmed single phase cubic spinel structure for present ferrite systems. The substitution of co-dopants in the spinel structure initially decreases the lattice parameter from $x = 0.00$ to 0.08 and thereafter increases and the same tendency reflecting in cell volume. The DC resistivity was initially increased later followed the decreasing trend; however the drift mobility of all ferrite samples appears to be in opposite phenomenon to DC resistivity. The saturation magnetization and net magnetic moments of all ferrite samples are decreasing with increasing dopant concentration. The coercive field and Y–K angles are increased with dopant concentration. The initial permeability of all samples is decreased with increasing dopant concentration. The Q-Factor for all samples shows the narrow frequency band with increasing frequency.

1. Introduction

The magnetic materials such as iron metallic alloys most probably have low DC Electrical resistivity. They are useless at high frequencies, due to their low electrical resistivity induces currents (called eddy currents) which produces heat. The materials become inefficient as their waste of energy and this is increases at higher frequencies. However, ferrites can perform much better at high frequencies because of their high electrical resistivity. The another important characteristic of ferrites is high temperature stability which is enhance the use of ferrites at high frequency as well as at higher temperature, wide-band transformers, quality filter circuits, adjustable inductors, delay lines and other high-frequency electronic circuits. The ferrites can perform better relative to that of other circuit components at high frequencies. The easily tailoring methods and cheap cost made them important than other magnetic materials and alloys. Ferrites are the best core material choice for frequencies from 10 kHz to a few MHz. Ni-Zn ferrites are good candidates for the sake of many technological applications like high frequency circuits, core materials, microchip inductor application because of their high resistivity and low permeability. The resistivity and permeability of Ni-Zn ferrites are varied in between 10^5 Ω-cm to 10^6 Ω-cm and 120–150 respectively. The structural electrical and magnetic properties of Ni-Zn ferrites are sensitive to their preparation technique and sintering conditions. The substitution of Zr and Cu as co-dopants in spinel lattice will bulge the respective lattice site, as things go to the miss match between the ionic radius of substitute ions and lattice site radius. Therefore the lattice parameter increases with increasing dopant concentration. The formation of Fe^{2+} ions in the ferrite material during the sintering process of ferrite materials increases the resistivity of ferrite material. The electron hopping between the Fe^{2+}/Fe^{3+} ions increases the conductivity in the ferrite material thus, the increase in drift mobility caused by the increase in conductivity. The activation energy is associated with induced porosity of material. The saturation magnetization and net magnetic moments are depending on the Fe^{3+} ions present in the material. The low permeability of Ni-Zn ferrites compel in the material by cause of high resistivity accompanied by the low magnetic losses. The permeability of Ni-Zn ferrites are affected by pores aroused by the non-growth of grains. Most probably the permeability affected by the sewages present in the spinal lattice as well as preparation technique. The inherent technique for preparation of ferrites is the solid state reaction method in which reactants reacted at higher temperature. During the sintering of the material the exaggerated grain size compels by non-stoichiometric and non-homogeneity of material, this exaggerated grain size contributes the high permeability [1]. To moderate higher permeability the grain size must be controlled by preparation technique, we adopt the solution technique known as the sol-gel auto-combustion

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method in the course of material preparation. In sol-gel auto-combustion method reactants are mixed in solution form at atomic scale level and reacted at lower temperature as a results precursor material becomes stoichiometric with homogeneity and have controlled of grain size.

2. Synthesis and experimental details

The poly crystalline Ni-Zn ferrites with chemical formula $Ni_{0.5}Zn_{0.5}Zr_xCu_x\ Fe_{2\text{-}2x}O_4$ where x values varies from the 0.0 to 0.4 in steps of 0.08 wt% have been prepared by sol-gel auto combustion method using metal nitrates, the starting materials $Ni(No_3).H_2O$, $Zn(NO_3).H_2O$, $Cu(No_3).H_2O$, (Zro) $(NO_3).H_2O$ and ferric citrate are took with appropriate weights, in de ionized water, the citric acid added to solution as per the oxygen balance in chemical formula, then 50 ml ethylene glycol was added to the solution as extra fuel agent for combustion, finally the ammonia solution added to the solution drop wise to adjust the PH value for 7. Then the solution was heated with continuous stirring at 60–70 °C for 8–10 Hrs. The combustion leads to the formation of ferrite nano powders. The obtained powders were grinded fined and calcinate at 800 °c for 3 hrs [2]. The 5% PVA added to these calcinate powders then pelletized in require size and shape with 5 min pressure of 5 tons and the pellets were sintered at 1200 °C for 2 h. The X-ray diffraction measurements were taken by using the X-ray diffractometer. The pellets were coated both sides with silver past to provide the electrode for good electrical contact in measuring the electrical properties. The inductance and corresponding loss factor Tanδ of torroids were taken in frequency range 10 Hz-120 MHz with impedance analyzer (HP-4192-A).

3. Results and discussions

3.1. XRD, SEM and TEM

The Fig. 1 shows X-ray diffraction patterns of all prepared samples of $Ni_{0.5}Zn_{0.5}Zr_xCu_xFe_{2\text{-}2x}O_4$ confirms the single phase cubic spinel with no extra peaks. The XRD peaks of prepared samples are shown in Fig. 1. The lattice parameter was calculated using the following formula.

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where h, k, l, are the miller indices.

The calculated lattice parameter and cell volumes were initially decreased with increasing dopant concentration from 8.3995 Å to 8.3911 Å and 592 to 590 for x = 0.00 to 0.08 respectively. Thereafter found to increase from 8.3911 Å to 8.4125 Å and 592 cm^3 to 595 $cm^3$for x = 0.16 to x = 0.4 respectively with an increasing dopant concentration of Zr and Cu. The increase in lattice parameter expands the cell volume elastically [3,4]. The error bar given to lattice parameter and cell volume the occurred errors in lattice parameter and cell volumes are ±0.0007 and ± 0.16 respectively and they are shown in Fig. 2(a) and (b). The X-ray density increased from 5.3292 g/cm^3 to 5.6890 g/cm^3as things go to the increased mass of chemical formula by Zr and Cu substitution. Since the lattice parameter and Dx values are inversely related in following general formula

$$D_x = \frac{8M}{N_a a^3}$$

where M is molecular moss Na is Avagadro number “a” is the lattice parameter. Therefore increase in the lattice parameter decreases Dx value, but the reported value increases with increasing dopant concentration this may be as a result of lattice parameter is dominated by the chemical mass in the general formula. The porosity of prepared samples is measured by comparing the sintered density with X-ray density and it is calculated from the following equation.

$$P = 1 - \frac{d_s}{d_x}$$

where *ds* and *dx* are the sintered density and X-ray density respectively. The porosity increased from 10.57% to 20.11% due to decreases in grain size, attributed by the dragging of sintering rate with the formation of Fe^{2+}ions by substituting ions of Zr and Cu, this is in shown SEM micro graphs of present prepared samples with clear pores in Fig. 3. The consequence of this increase in the porosity decreases the sintered density from 4.7657 g/cm^3 to 4.6064 g/cm^3 [5]. The particle size was measured using TEM pictures of present prepared samples are shown in Fig. 4. The crystallite size was measured using following equation.

$$D = \frac{0.94 * \lambda}{\beta \cos \theta}$$

where λ and θ are constants β is FWHM of (311) peak it is varied with dopant concentration. The crystallite size and FWHM are inversely related hence increase in the FWHM is decreases the crystallite size [6,7]. The measured particle size and crystallite sizes are in comparable nano size with dopant concentration is shown in Fig. 5. The all measured values are listed in Table 1.

3.2. DC resistivity

DC resistivity of pure Ni0.5Zn0.5Fe2O4 and Zr Cu doped have been determined using the following equation

$$\rho = \rho_o \exp\left(\frac{\Delta E}{\kappa_B T}\right)$$

The compositional DC resistivity of ferrites is measured at temperature 373 K, the initial DC resistivity increased for x = 0.0 to 0.08 from 1.2×10^5 Ω-cm to 6.70×10^5 Ω-cm later it was found to decrease with increasing dopant concentration and the measured resistivity values are listed in Table 2. The initial increase in the DC resistivity for x = 0.0 to 0.08 is due to the formation of Fe^{2+}ions by substitute Zr and Cu ions later decrease in the DC resistivity assigned to the increase in formation of Fe^{3+} ions by the substitute ions. The presence of Fe^{3+} ions increases the electron hoping between the Fe^{2+} and Fe^{3+} hence the drift mobility of electron increased so as conduction is 4induced in ferrites according to Verway mechanism [8].For every substitution of Zr and Cu ions there is one Fe^{2+} ions formed by conversion of Fe^{3+} ions here site preference of substitution ions play an important role. Since Zr has strong preference for A-site and Cu prefers the B-site for their comfortable fit in the lattice sites, hence for every step of substitution Zr replace the Fe^{3+} ions from the A-site to B-site. To provide the accommodation in B-site for Fe^{3+} ions

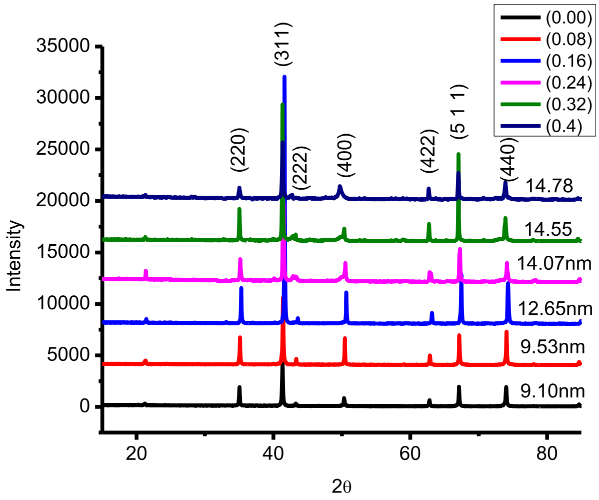

Fig. 1. X-ray diffraction patterns of $Ni_{0.5}\ Zn_{0.5}Zr_xCu_xFe_{2\text{-}2x}O_4$ samples with x = 0.0, 0.08, 0.16, 0.24, 0.32, and 0.4.