Materials Science in Semiconductor Processing 41 (2016) 508–512

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Synthesis of nickel–zinc–yttrium ferrites: Structural elucidation and dielectric behavior evaluation

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ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form
28 October 2015
Accepted 28 October 2015

Keywords:
XRD
FTIR
SEM
Electrical resistivity
Dielectric parameters

ABSTRACT

Novel $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}O_4$ soft spinel ferrites were prepared via double sintering ceramic route. The influence of Y^{3+} cations on structural, morphological, electrical and dielectric properties was investigated. X-ray diffraction (XRD) confirmed the formation of single phase spinel structure for $0 \le x \le 0.06$ and thereafter a small peak of orthorhombic phase ($FeYO_3$) appeared for $x > 0.06$. The incorporation of yttrium altered the lattice constant. The variation in lattice constant with respect to the Y^{3+} contents was non-linear. The variation of lattice constant may be attributed to larger ionic radius of Y^{3+} as compare to Fe^{3+} cations and solubility limit of substituted cations. Fourier transform infrared (FTIR) spectra showed two strong absorption bands around 600 cm^{-1} and 400 cm^{-1} which confirmed the spinel structure. The dc electrical resistivity was found to increase from 5.67×10^5 to 8.48×10^8 Ω cm with the increased Y^{3+} contents. The dielectric constant and dielectric loss tangent were significantly impeded by increasing the yttrium contents. The optimized electrical resistivity and reduced dielectric parameters suggest the possible use of these ferrites in the fabrication of microwave devices.

1. Introduction

Soft magnetic materials owing to their high electrical resistivity are important materials due to their high frequency and industrial applications. In the family of soft ferrites having semiconductor nature, the Ni–Zn ferrites exhibit the versatile characteristics by substituting various transition metal ions. The attractive properties of Ni–Zn ferrites are their high Curie temperature, low dielectric loss, chemical stability, high electrical resistivity and low eddy current losses. The small amount of iron deficiency in the composition of ferrites can increase the electrical resistivity and inhibit electron hopping between Fe^{2+} and Fe^{3+} ions at the octahedral sites in the spinel structure. It can also enhance the density of Ni–Zn ferrites. It has been observed that these are the best materials for wide-band transformers, pulse transformers, ferrite antennas and power transformers [1,2].

Several researchers [3,4] have explored the transport properties of Ni–Zn ferrites with addition of small amount of foreign metal ions. An improvement in the electrical transport properties by the addition of tetravalent ions has been reported in the literature [5,6]. The addition of pentavalent ions [7] in small quantity in Ni–Zn ferrites has also been reported to improve the electrical and dielectric properties. However, the influence of minor substitution of trivalent rare earth transition metal ions on electrical transport properties of Ni–Zn ferrites received little attention. It is known that the ions with large ionic radii and with a stable valency of 3+ are found to be the best substituent for improvements in the electrical properties of the soft magnets [8]. Yttrium is also a potential candidate for enhancement of electrical properties. There was a need to undertake the systematic study of Ni–Zn ferrites substituted with trivalent rare earth transition metals such as yttrium to investigate its influence on the structural, morphological, electrical and dielectric properties. To the best of our knowledge, no systematic information is available about the electrical transport properties of yttrium substituted Ni–Zn ferrites. Therefore, detailed investigation of structural and transport properties of $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}O_4$ (x=0.0–0.1; step: 0.02) ferrites was carried out and the results are presented in this article. The aim of the present work is to enhance the electrical transport properties to make these materials suitable for microwave devices applications.

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http://dx.doi.org/10.1016/j.mssp.2015.10.028

2. Materials and methods

Polycrystalline ferrites with chemical formula $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}O_4$ (x=0.0, 0.02, 0.04, 0.06, 0.08, 0.1) were prepared by standard double sintering ceramic technique in air using reagents of analytical grade. Stoichiometric calculations were carried out using the following chemical equation:

$$0.6\ NiO + 0.4\ ZnO + x\ Y_2O_3 + (1 - x)\ Fe_2O_3$$
$$\rightarrow Ni_{0.6}\ Zn_{0.4}\ Y_{2x}\ Fe_{2-2x}\ O_4$$

The metal oxides were mixed in the required stoichiometric ratio and wet milled for three hours. The fine dry powder was pre-sintered at 900 °C for 24 h. The mixture was wet milled again for three hours to improve the level of homogeneity. The mixture with 5% polyvinyl alcohol (PVA) was pressed into pellets at a pressure of 4 t/in.^{2}. The samples were finally sintered at 1200 °C for 8 h.

For FTIR analysis, the samples were prepared in the form of pellets in KBr medium. The FTIR spectra were recorded using Perkin Elmer FTIR Spectrometer (Spectrum 2000) at room temperature in the range of 370–1100 cm^{-1}. XRD measurements of powder samples were recorded at room temperature on Philips X' Pert analytical diffractometer with CuKα radiation source. The average value of the lattice constant 'a' for each composition was calculated using Nelson and Riley [9] extrapolation method. The X-ray density (D_x) was computed from the values of lattice parameter using the formula reported elsewhere [10]. The bulk density of each sample was measured using toluene by Archimedean principle. The bulk density (D) and porosity (P) were determined by using the equations reported in the literature [11]. The average grain size was calculated using the Scherrer's formula [9] from the width of the (311) peak. The surface morphology of all the compositions was studied using JEOL JSM-840 SEM.

The two probe method was employed to measure room temperature dc resistivity by a sensitive Keithley Electrometer 610-C. The surface of the samples were polished and then coated with silver paste as a contact material for electrical measurements. The effect of temperature on dc resistivity has been measured. Dielectric properties were investigated at room temperature over the frequency range from 10 Hz to 10 MHz by using the Solartron 1260 Impedance Analyzer. The values of dielectric constant (ε') and dielectric loss tangent (tan δ) were calculated using the equations reported in the literature [12].

3. Results and discussion

3.1. Structural and physical properties

XRD patterns of $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}\ O_4$ (x=0.0, 0.04, 0.1) ferrites are shown in Fig. 1. The XRD patterns were indexed and FCC cubic phase was identified as major phase. The presence of the peaks corresponding to the planes (111), (220), (311), (222), (400), (422), (333) and (440) reveal the formation of cubic spinel structure. The samples are single phase for $x \le 0.06$ and thereafter for $x \ge 0.08$, the samples exhibited the biphasic nature. The extra peak appeared at $2\theta = 33.1°$. The intensity of this peak increases with the increase of yttrium contents. This peak can be identified as the (1 2 1) reflection of the $YFeO_3$ phase (Yttrium Iron Oxide) matched with ICDD PDF # 39-1489. Similar orthorhombic phases of rare earth substituted ferrites have been observed earlier by several researchers [13–15]. The appearance of this second phase may be attributed to the high reactivity of Fe^{3+} ions with Y^{3+} ions at the grain boundaries. The phases precipitated and the variation of lattice constant of $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}\ O_4$ ferrites is given in Table 1. It can be observed that (Table 1) the lattice constant increases slightly for $0.0 \le x \le 0.06$ and for higher Y^{3+} concentration it decreased. The increase is attributed to the difference in ionic radii of the metal cations involved and decrease is owing to the formation of secondary phase ($YFeO_3$). Similar results have been reported in literature for Ho^{3+} substituted $CoFe_2O_4$ spinel ferrite [16]. It is reported that Y^{3+} ions reside on B-sites [17]. It is inferred that the replacement of the smaller Fe^{3+} ions (0.64 Å) with larger Y^{3+} ions (0.95 Å) causes an expansion of the host spinel lattice which results the increased lattice constant for $0.0 \le x \le 0.06$. This observation is in agreement with the results reported in the literature [17,18]. A possible explanation for the decrease of lattice constant for x=0.08, 0.1 is that some of the yttrium ions no longer dissolve in the spinel lattice however diffuse to the grain boundaries reacting with Fe^{3+} to form $YFeO_3$. It is also possible that the spinel lattice is compressed by the inter-granular secondary phase due to the differences in the thermal expansion coefficients [19].

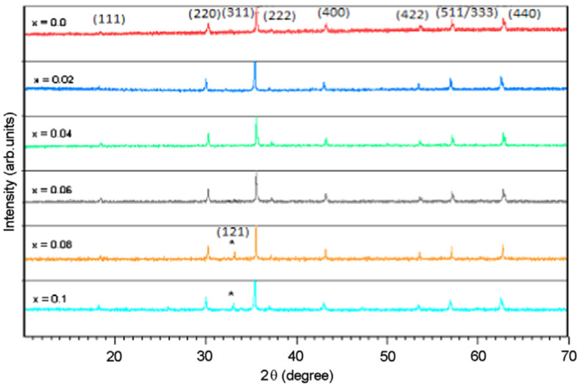

Fig. 1. X-ray diffraction patterns of $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}O_4$ (x=0.0, 0.02, 0.04, 0.06, 0.08, 0.1) ferrites.

The impact of Y^{3+} contents on X-ray density (D_x), physical density (D_p) and percentage porosity are given in Table 1. X-ray density (D_x) and physical density (D_p) show increasing trend with the increase in yttrium contents. X-ray density increases from 5.37 to 5.54 g/cm^3. The physical density also increases from 4.81 to 4.99 g/cm^3. This may be due to the fact that atomic weight of Y is greater than Fe [20]. The differences in physical and X-ray density indicate that the samples are porous in nature. In the present work, the porosity decreases with the increase of Y^{3+} contents. A similar increase of physical density and lowering of porosity with yttrium content was reported by Rezlescu et al. [18].

The crystallite size was determined by using Scherrer's formula (Table 1). The crystallite size was found to decrease with the increase of yttrium contents. It is an established fact that the size of crystallites depends upon grain boundary migration [14]. Some of the yttrium ions owing to their larger ionic radii might be diffused to the grain boundaries during sintering process. This will obstruct not only the grain boundary mobility but also impede the number of inner pores.

The SEM micrographs of some representative samples (x=0.0, 0.1) are shown in Fig. 2. These SEM images indicate the inhomogeneous grain size distribution. It is clear from SEM images that the morphology of yttrium substituted samples could not possess fine structured ferrites [14].

Fig. 3 shows the FTIR spectra of $Ni_{0.6}Zn_{0.4}Y_{2x}Fe_{2-2x}O_4$ (x=0.0, 0.02, 0.04, 0.06, 0.08, 0.1) ferrites. The position of bands for selected compositions is listed in Table 2. The absorption bands around 600 cm^{-1} (ν_1) and 400 cm^{-1} (ν_2) occurred. These bands are in the range of structural bands of spinel ferrites which confirmed the completion of solid state reaction [19]. The high frequency absorption band ν_1 lies in the range 576–579 cm^{-1} and low frequency absorption band ν_2 lies in the range 390–410 cm^{-1}. The