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Synthesis, microstructure, dielectric and magnetic properties of Cu substituted Ni–Li ferrites

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ABSTRACT

Cu substituted Ni–Li spinel ferrites were prepared by a conventional sol–gel auto-combustion method. The structure, surface morphology, dielectric and magnetic properties were investigated by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, impedance spectroscopy and vibrating sample magnetometer, respectively. X-ray diffraction studies reveal the single phase spinel structure of the ferrites and the crystallite size varies from 23 to 35 nm. Incorporation of Cu in the Ni–Li ferrites increases the grain size. The dielectric parameters such as ε, ε'', loss tan δ and ac conductivity (σ_{ac}) have been measured for the annealed samples in the temperature range from 35 to 200 °C and over the frequency range from 10^1 to 10^7 Hz. The saturation magnetization and coercivity show a dependence on the composition and microstructure. The values of saturation magnetization vary from 25.6 to 33.6 emu/g with increase in x for samples annealed at 600 °C. The values of the coercivity increase from 170 to 203 Oe with increase in x.

1. Introduction

Investigation of the nanosized spinel ferrites is one of the most vital and fastly growing areas of research in the field of nanotechnology. The excellent electrical and magnetic properties of some of the nanoferrites make them suitable for high frequency applications in the field of telecommunication. Ferrites can also be used as an electromagnetic wave absorber, multilayer chip indicator, transformer core and in surface mounting devices [1,2]. The electrical and magnetic properties of ferrites, having general formula MFe_2O_4, are dependent on the distribution of metal cation ($M=Ni^{2+}$, Cu^{2+}, Mg^{2+}, Zn^{2+}, Li^{+}) at tetrahedral A-site and at octahedral B-site [3]. The Ni–Li ferrites have been widely used in microwave devices such as circulators, insulators and phase shifters because of their high resistivity, low dielectric loss and excellent magnetic properties. Lithium and substituted ferrites have proved to be very good alternatives for garnets in microwave devices due to their low cost. Several investigations on the transition metal substituted lithium ferrite have been carried out to improve the properties of lithium ferrite. However, no reports have been found in the literature on dielectric properties of the Ni–Li–Cu ferrites [4–7]. The substitution of Li^+ ions by Cu^{2+} ions in the Ni–Li ferrites influences the dielectric properties, namely, ε', ε'' and tangent loss (tan δ) because the Li^+ ions occupy the tetrahedral A-site and Cu^{2+} ions can occupy both the A and B-sites. The properties of the spinel ferrites are also dependent on its microstructure, which in turn is sensitive to the manufacturing technique. Different techniques have been developed for the preparation of the nanosized ferrites, namely, sol–gel, microemulsion, double sintering, hydrothermal, co-precipitation, ball milling and microwave heating to improve the performance of the nanoferrites [8–11]. Sol–gel auto-combustion is the simplest methodology to synthesize the nanosized ferrites with good homogeneity at low annealing temperature. The aim of the present work is to investigate the effect of Li^+ ions substitution by Cu^{2+} ions on the properties of the $Ni_{0.5}Li_{1.0}Fe_2O_4$ ferrites.

2. Experimental

The spinel ferrites with composition $Ni_{0.5}Li_{1.0-2x}Cu_xFe_2O_4$ ($0.0 \le x \le 0.5$) were prepared by sol–gel auto-combustion method. Analytical grade nickel nitrate, copper nitrate, lithium nitrate and ferric nitrate were taken in stoichiometric proportion and were dissolved in 100 ml deionized water with subsequent addition of citric acid. The ratio of citric acid to total metal nitrates was 1:1 and that of Ni:Li:Cu:Fe was 0.5:(1−2x):x:2. After complete mixing of the metal nitrates and citric acid, the pH of the sol was adjusted to 7 using ammonia solution. The sol was heated at 100 °C to transform it into gel. The gel was dried for 24 h in an oven at 110 °C. Thereafter, the dried gel was ignited to transform it into a fluffy powder [8,12]. The as-prepared powder was annealed at three different annealing temperatures (T_a=400, 600 and 800 °C) for 5 h to yield ferrite nanoparticles. The X-ray diffraction patterns of the samples were recorded using MiniFlex-II X-ray diffractometer (Rigaku). The pellets of the samples were prepared using KBr for

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recording infrared spectra in the range from 400 to 4400 cm^{-1} using Spectrum BX FTIR spectrometer (Perkin-Elmer). The scanning electron microscopy was performed using a scanning electron microscope (JSM 6100, JEOL). Pellets (13 mm in diameter) of samples were used for measuring the dielectric properties using an impedance/gain phase analyzer (Newtons4th Ltd.) in the frequency range from 10^1 to 10^7 Hz. The real (ε') and imaginary (ε") parts of dielectric constant, loss tangent (tan δ) and conductivity were calculated using the following relations:

$$\varepsilon' = Ct/\varepsilon_0 A, \quad (1)$$

$$\varepsilon'' = \varepsilon' \tan\delta, \quad (2)$$

$$\sigma = \varepsilon_0 \varepsilon' \omega \tan\delta, \quad (3)$$

where C is the capacitance, t the thickness of the sample, A the cross-sectional area, ε_o the free space permittivity and ω the angular frequency. The magnetic measurements at room temperature were carried out using vibrating sample magnetometer (PAR 155).

3. Results and discussion

3.1. Structural studies

The X-ray powder diffraction patterns of the $Ni_{0.5}Li_{1.0-2x}Cu_xFe_2O_4$ ($0.0 \leq x \leq 0.5$) ferrites annealed at 600 °C are shown in Fig. 1(a). It is observed that all the peaks in the pattern belong to the spinel structure (ICDD # 86-2267) and it is confirmed that the samples have pure spinel phase [7]. Based on the site preference of the cations, the cation distribution of the Cu-doped Ni–Li ferrites can be described by the following relation: $(Fe^{3+}_{(1-y)}Cu^{2+}_{y})[Ni^{2+}_{0.5}Li^{+}_{(0.5+0.5-2x)}Cu^{2+}_{(x-y)}Fe^{3+}_{(1+y-a)}Fe^{2+}_{a}]O_4$, where parenthesis and square bracket denote the distribution of cations at the tetrahedral and the octahedral sites, respectively. $Li^{+}_{0.5+0.5}$ denotes that the Li^+ ions replace Fe^{3+} ions partially at the octahedral sites and fill partially into the octahedral interstices [7]. It is observed that the concentration of Fe^{2+} ions increases with increase in x. The average crystallite size of the prepared samples has been calculated using the following Debye–Scherrer's formula:

$$D = K\lambda/\beta \cos\theta \quad (4)$$

where K is a constant and it depends on the shape of the particle, λ the X-ray wavelength, β the full width at half maximum of the most intense peak (3 1 1) and θ is the diffraction angle of the peak [13]. The average crystallite size is 26–29 nm for different values of x (Table 1). Fig. 1(b) shows the XRD patterns of the $Ni_{0.5}Li_{0.2}Cu_{0.4}Fe_2O_4$ ferrites annealed at different temperatures and it is observed the intensities of all the peaks increase with increase in the annealing temperature. This increase in intensities of all the peaks may be attributed to the increase in grain growth with the increase in the annealing temperature.

Lattice constant (L) of the sample has also been calculated from the XRD data and it increases almost linearly with the increase in the annealing temperature for the $Ni_{0.5}Li_{0.2}Cu_{0.4}Fe_2O_4$ ferrite samples (Fig. 2). This increase in lattice constant may be attributed to the increase in grain growth with increase in the annealing temperature. Further, the lattice constant of the samples also increases with the increase in the concentration of the Cu^{2+} ions (inset Fig. 2). This may be due to the larger ionic radii of Cu^{2+} ions (0.72 Å) in comparison to that of Li^+ ions (0.71 Å). Fig. 3 shows the IR spectra of the ferrite samples (annealed at 600 °C) in the range from 400 to 700 cm^{-1}. It is observed that, there are two main frequency bands, namely, high frequency band ν_1 (575–580 cm^{-1}) and low frequency band ν_2 (around 400 cm^{-1}). These two observed bands (ν_1 and ν_2) correspond to the intrinsic vibrations of tetrahedral and octahedral Fe^{3+}–O^{2-} complexes, respectively, and are the characteristics of all the ferrite composites. The different band positions of ν_1 and ν_2 are expected because of different Fe^{3+}–O^{2-} bond lengths for tetrahedral and octahedral sites. The shifting of the ν_1 and ν_2 bands towards lower frequencies, with increase in the concentration of Cu^{2+} ions, may be attributed to the increase in the unit cell dimensions as evidenced by the variation in the lattice constant. The increase in the unit cell dimensions affects the Fe^{3+}–O^{2-} stretching vibrations and this is a prominent cause of change in band positions. The presence of Fe^{2+-}–O^{2-} in the ferrites can also cause splitting of the bands due to the Jahn–Teller distortion. This splitting of the octahedral band due to Fe^{2+}–O^{2-} vibration occurs at around 470 cm^{-1}. The other observed shoulders in the range

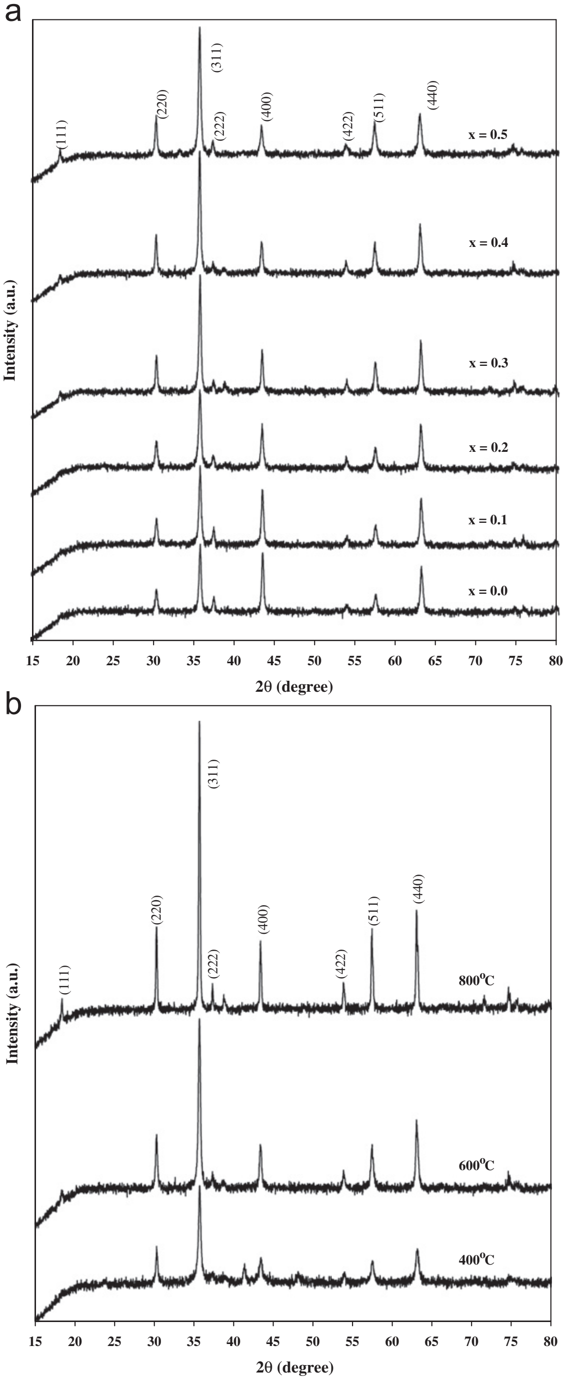

Fig. 1. (a) X-ray diffraction patterns of $Ni_{0.5}Li_{1.0-2x}Cu_xFe_2O_4$ ferrites annealed at 600 °C. (b) X-ray diffraction patterns of $Ni_{0.5}Li_{0.2}Cu_{0.4}Fe_2O_4$ ferrites annealed at different temperatures.