Effect of Al$^{3+}$ substitution on the electrical and magnetic properties of Li-base ferrites

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Abstract

Aluminum substituted lithium ferrites with chemical formula $Li_{0.6}(NiCo)_{0.2}Al_xFe_{2.2-x}O_4$ ($x = 0.0, 0.15, 0.3, 0.45, 0.6$) have been synthesized by sol-gel method and sintered at $900 \degree C$ for 5 h. The samples were characterized by XRD, electrical, dielectric and VSM measurements. X-ray diffraction studies confirmed that all the samples exhibit single phase cubic spinel structure with space group Fd3m. The crystallite size, bond lengths, x-ray density and lattice parameters decrease with the increase of Al$^{3+}$ concentration. Dielectric properties such as dielectric constant ($\varepsilon'$), complex dielectric constant ($\varepsilon''$), tangent loss (tan$\delta$) and ac conductivity ($\sigma_{ac}$) of all the samples were measured and evaluated as a function of frequency at room temperature. The variation of dielectric properties; $\varepsilon'$, $\varepsilon''$, tan$\delta$ and $\sigma_{ac}$ versus frequency reveals that the dispersion is due to Maxwell–Wagner type of interfacial polarization in general and the hopping of charge between Fe$^{2+}$ and Fe$^{3+}$. The Al-doped nano-crystalline lithium ferrite samples exhibit a very large value of dielectric constant of the order of $10^4$. The room temperature resistivity and activation energy increases with the increase of Al$^{3+}$ concentration. The temperature dependent resistivity of all samples decreases with increase of temperature indicating the semiconducting behavior. The room temperature DC resistivity increases from $1.65 \times 10^{10}$ to $2.23 \times 10^{11}$ ohm-cm. The small value of magnetization may be due to cation superparamagnetic spins at the surface of the samples. The decrease in the magnitude of magnetization value may also be due to the presence of Al$^{3+}$ paramagnetic ions with spin-down orientation instead of Fe$^{3+}$ cations with spin-up orientation in the octahedral sites. The squareness ratio (Mr/Ms) is less than 1 which indicates single domain behavior. The increase in coercivity is attributed to lattice defects and decrease is associated with the superparamagnetic behavior.

1. Introduction

From the last two decades, metallic oxides have been focused as novel functional materials. Lithium ferrites are the centre of attention for long time and were developed to replace the garnets like YIG that have got lowest FMR linewidth [1]. This is possible owing to high Curie temperature and saturation magnetization. Lithium ferrites are important part of microwave devices such as isolators, circulators, attenuators, phase shifters and memory cores owing to versatile properties of Lithium [2]. Due to inverse nature [3] of the Li ferrites it is observed that magnetization is equal to the difference of A & B-sublattice magnetizations. Due to monovalent Li the Lithium ferrite possess few cation vacancies in the sample. These vacancies may contribute in the enhancement of resistivity and other magnetic properties. The doping of transition metal ions with 3d electrons when substituted with iron ions can alter the properties of LiFe$_2$O$_4$. Al-doped lithium ferrites prepared by conventional solid state reaction method have been investigated for electrical and magnetic characteristics and for cation distribution on A and B sites [4, 5]. The maximum value of resistivity is reported $\sim 10^{11}$ ohm-cm [6] and the dielectric constant reported is $\sim 81–12$ at 1 MHz [7]. The maximum saturation magnetization observed is 309 gauss [6] and coercivity $\sim 2478–995$ Oe [8]. Li ferrite (LiFe$_2$O$_4$) is a useful material due to high microwave absorption

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The heating process is continued till solution is converted into greenish gel. Gel is then heated on a magnetic hot-plate stirrer for several hours. During heating and stirring pH value 7 is maintained by using ammonia solution drop. The mortar and pestle were rinsed with acetone each time before use. A small amount of citric acid was also mixed separately in 100 ml de-ionized water, it act as chelating agent. For making homogeneous solution all these solutions were mixed together in a 1000 ml beaker by stirring on magnetic hot-plate for 2 h. The solution is heated at 70 °C–80 °C with continuous stirring for several hours. During heating and stirring pH value 7 is maintained by using ammonia solution drop by drop. The heating process is continued till solution is converted into greenish gel. Gel is then heated on 270 °C to convert it into ash. The fine gray powder was obtained from ash by grinding for 30 min with the help of agate mortar and pestle. The mortar and pestle were rinsed with acetone each time before use. A small amount of fine powder is then pressed in Hydraulic pressing machine using metallic die under the load of 30 kN. Each pellet was then sintered using ceramics boats in tube furnace at 900 °C for 5 h followed by furnace cooling.

The phase purity of sintered pellets was identified by x-ray diffraction. The magnetic hysteresis loops were recorded at room temperature using vibrating sample magnetometer.

The samples were indexed by x-ray diffraction. The magnetic hysteresis loops were recorded at room temperature using vibrating sample magnetometer.

Table 1. Stoichiometric amounts of Nitrates for the preparation of Li0.6(NiCo)0.2AlxFe2.2−xO4 (x = 0.0, 0.15, 0.3, 0.45, 0.6) ferrites.

| Al3⁺ Contents (x) | LiNO3 | Al(NO3)3·9H2O | Co(NO3)3·2H2O | Ni(NO3)2·6H2O | Fe(NO3)3·9H2O | C6H5OH (COOH)3 |
|-------------------|-------|---------------|---------------|---------------|---------------|----------------|
| 0.00              | 0.4137 g | 0.000 g     | 0.5821 g   | 0.5816 g   | 8.888 g     | 9.2217 g       |
| 0.15              | 0.4137 g | 0.5627 g     | 0.5821 g   | 0.5816 g   | 8.888 g     | 9.2217 g       |
| 0.3               | 0.4137 g | 1.1254 g     | 0.5821 g   | 0.5816 g   | 7.676 g     | 9.2217 g       |
| 0.45              | 0.4137 g | 2.2508 g     | 0.5821 g   | 0.5816 g   | 7.070 g     | 9.2217 g       |
| 0.6               | 0.4137 g | 2.2508 g     | 0.5821 g   | 0.5816 g   | 6.464 g     | 9.2217 g       |

2. Experimental techniques

The aluminum substituted lithium based spinel ferrite 

Li0.6(NiCo)0.2AlxFe2.2−xO4 were synthesized by sol-gel auto combustion method. The stoichiometric amounts of the nitrates were weighed on the calibrated electronic balance with accuracy of 10−4 g. The stoichiometric amounts of precursors used are listed in table 1.

The weighed amount of each salt is mixed in deionized water in 100 ml beaker with proper stirring on magnetic hot-plate stirrer to obtain stock solution. The citric acid was also mixed separately in 100 ml de-ionized water, it act as chelating agent. For making homogeneous solution all these solutions were mixed together in a 1000 ml beaker by stirring on magnetic hot-plate for 2 h. The solution is heated at 70 °C–80 °C with continuous stirring for several hours. During heating and stirring pH value 7 is maintained by using ammonia solution drop by drop. The heating process is continued till solution is converted into greenish gel. Gel is then heated on 270 °C to convert it into ash. The fine gray powder was obtained from ash by grinding for 30 min with the help of agate mortar and pestle. The mortar and pestle were rinsed with acetone each time before use. A small amount of fine powder is then pressed in Hydraulic pressing machine using metallic die under the load of 30 kN. Each pellet was then sintered using ceramics boats in tube furnace at 900 °C for 5 h followed by furnace cooling.

The phase purity of sintered pellets was identified by x-ray diffraction. The magnetic hysteresis loops were recorded at room temperature using vibrating sample magnetometer.

The samples were indexed by ab-initio method. The d-values were determined for all the samples by using formula [9]:

\[ 2d_{hkl} \sin \theta_{hkl} = n \lambda \]

Where \( n \) = order of diffraction, \( d_{hkl} \) = interplanar spacing, Average crystallite size of the sample was calculated using Scherrer’s formula [10];

\[ \text{Crystallite size} = K\lambda / \beta \cos \theta \]

Where \( K \) = constant = 0.94, \( \theta \) = Bragg’s angle, \( \beta \) = Intensity full width at half maximum, \( \lambda \) = wavelength of Cu-Kα, radiations = 0.154 nm.

The hopping length (bond length) of tetrahedral (A-sites) and an octahedral (B-sites) was calculated using the following expressions [11]:

\[ r_B = \frac{1}{2}[0.6r_{Li}^{+} + 0.2r_{Ni}^{2+} + 0.2r_{Co}^{2+} + Xr_{Al}^{3+} + (2.2 - X)r_{Fe}^{3+}] \]

\[ u = \frac{5}{8} - \left( r_B + r_o^{2-} \right) / a \]

\[ r_A = \left( u - 1/4 \right) a(3)^{1/2} - r_o^{2-} \]

Bond length (hopping length) of A – sites = \( L_A = a(3)^{1/2}(\Delta + 1/8) \)

Bond length (hopping length) of B – sites = \( L_B = a(3\Delta^2 - \Delta/2 + 1/16)^{1/2} \)

\[ \Delta = u - 0.375 \]

Where \( r_B \) = average ionic radius of octahedral (B-site), \( r_A \) = average ionic radius of tetrahedral (A-site), \( u \) = oxygen parameter.

Two probe method was used to measure dc resistivity of samples at room temperature and at elevated temperature. The dc resistivity was calculated by the following equation [12]:
\[
R = RA \quad \text{and} \quad t = \text{thickness of pellet}, \quad \pi = \text{area of pellet}, \quad \ell = \text{radius of pellet.}
\]

The dielectric properties were investigated by using LCR meter model LC 8101 in the frequency range from 20 Hz to 1 MHz. The experimentally measured values of capacitance \( C \) and dissipation \( D \) were used to calculate AC conductivity \( \sigma_{ac} \), dielectric constant \( \varepsilon' \) and dielectric loss \( \varepsilon'' \). The dielectric constant was measured using the following equation:

\[
\varepsilon' = \frac{CL}{A\varepsilon_0}
\]

(10)

Where \( \varepsilon' = \text{material's dielectric constant}, \ell = \text{thickness of pellet}, \epsilon_0 = \text{permittivity of free space} \times 10^{-12} \text{ F m}^{-1} \).

The complex dielectric constant is calculated by the following equation:

\[
\varepsilon'' = \tan \delta \varepsilon'
\]

(11)

The ac conductivity of the sample was calculated using following expression;

\[
\sigma_{ac} = 2 \pi f \varepsilon_0 \varepsilon' \tan \delta
\]

(12)

3. Results and discussions

3.1. Structural analysis

The XRD patterns of Al doped lithium ferrites are taken at room temperature. Figure 1 shows x-ray diffraction patterns of spinel ferrites with composition \( \text{Li}_{0.6} (\text{NiCo})_{0.2} \text{Al}_x \text{Fe}_{2.2-x} \text{O}_4 \) where \( x = 0.00, 0.15, 0.3, 0.45, 0.6 \). The reflections observed were \( 220, 311, 400, 333, 440 \) and \( 622 \) which are characteristics of F.C.C. spinel structure with space group Fd3m.

The experimental results revealed that crystallite size varies from 56.55–56.59 nm as listed in table 2. It was observed that crystallite size first increases and then decreases with the...
increase of concentration of Al$^{3+}$ doping[13], depending on the peak broadening of (311) reflection [10]. The calculated values of lattice constant ($a$), crystallite size ($D$) and hopping lengths are given in the table 2.

3.2. Dielectric properties

The dielectric properties of ferrites depend on several factors together with method of sintering temperature, preparation, amount of substitution, sintering time, type and particle size, etc. Dielectric properties were measured in the frequency range 20–1 MHz.

3.2.1. Dielectric constant

Figure 2 shows the electrical permittivity of all the samples versus frequency. The dielectric constant ($\varepsilon'$) was calculated by the formula given by;

$$\varepsilon' = \frac{Cd}{A\varepsilon_0} \quad (13)$$

Where $c =$ capacitance, $d =$ thickness of pellet, $A =$ cross sectional area of flat surface of pellet.

It can be seen that the dielectric constant decreases as the Al$^{3+}$ content increases. This is due to increase in resistivity and restriction in hopping when Al$^{3+}$ ions replace the Fe$^{3+}$ ions at B-sites. As a result of paucity of Fe$^{2+}$ ions the electron exchange is reduced [14, 15]. It is observed from graph that dielectric constant decreased with the increase of frequency. At high frequency dielectric constant approximately becomes constant. The high value of dielectric constant at low frequency is due to interfacial polarization, which is attributed to the grain boundaries with high resistance. The low value of dielectric constant at high frequency is due to low resistive grains that play active role. Our results are consistent with the results reported by Rezlescu [10] and Murthy [16].

It was observed that the electronic exchange between Fe$^{2+}$ and Fe$^{3+}$ results in local displacement of the electrons in the direction of electric field, which governs the polarization of the ferrites. The polarization decreases with the increase of frequency, and then reached at constant value. It is basically due to fact that after certain frequency of external field, the exchange frequency of Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ can’t follow the alternating applied field. The highest value of dielectric constant observed for the composition Li$_{0.6}$(NiCo)$_{0.2}$Fe$_{2.2}$O$_4$ may be due to low resistivity.

3.2.2. Dielectric loss

The dielectric loss $\varepsilon''$ was calculated given by the formula;

$$\varepsilon'' = \tan \delta \varepsilon' \quad (14)$$

Figure 3 shows the plot of dielectric loss versus log frequency for Li$_{0.6}$(NiCo)$_{0.2}$Al$_x$Fe$_{2.2-x}$O$_4$ ferrites.

The dielectric loss decreases as function Al$^{3+}$ contents. This is attributed to increased magnitude of the resistivity with the increase of Al$^{3+}$ content as shown in figure 5. The graph shows that complex dielectric constant decreases with the increase of frequency [17]. The dielectric loss represents the energy loss because of high frequency due to the presence of defects and pores in the samples [18].
3.2.3. AC conductivity

AC conductivity was calculated using the formula given by;

\[
\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon''
\]

Figure 4 depicts ac conductivity versus log frequency.

It was observed that ac conductivity increases with increase of frequency. At low frequencies the dipoles feels the resistance due to grain boundaries that restrict the hopping process. At high frequency the hopping process becomes frequent within the less resistive grains. This behavior of ac conductivity can be explained on Maxwell-Wagner model and Koop’s theory [19–22]. The model assumes that ferrite sample consists of conducting grains separated by non-conducting grain boundaries.

3.3. Resistivity measurements

Dc resistivity was measured by two probe method. Resistance of the samples was calculated from I-V curves. Resistivity was measured by using the following expression;

\[
\rho = RA/t
\]

where \( R \) = resistance, \( A \) = cross sectional area of pellets, \( t \) = thickness of pellets.

3.3.1. Room temperature resistivity

Figure 5 depicts the room temperature resistivity versus Al\(^{3+}\) concentration.

The graph revealed that room temperature resistivity increases with increasing aluminum concentration. The increase in resistivity is due to restricted hopping between Fe\(^{3+}\) and Fe\(^{2+}\) ions due to Al\(^{3+}\) substitution on B-sites and decrease in Fe\(^{2+}\) ions concentration, thereby the resistivity increases [14].
3.3.2. Temperature dependent resistivity

Figure 6 shows the plot of $\ln \rho$ versus $1000/T$ for all the prepared samples. The resistivity increases in magnitude as the $\text{Al}^{3+}$ ions are substituted in $\text{Li}_{0.6}(\text{Ni Co})_{0.2}\text{Al}_x\text{Fe}_{2.2-x}\text{O}_4$ ($x = 0.00, 0.15, 0.3, 0.45, 0.6$) ferrites. This plot follows the Arrhenius equation;

$$\rho = \rho_0 \exp \left( \frac{E_a}{k_B T} \right)$$

Where $\rho_0 =$ resistivity at $T = 0 \text{ K}$, $E_a =$ activation energy, $k_B =$ Boltzmann’s constant.

It is observed that the resistivity of these ferrites decrease with increasing the temperature. This shows the semiconducting behavior which is related to increase in lattice vibration with increasing temperature and that leads to increase in hopping process.

3.3.3. Activation energy

Figure 7 shows activation energy increases with increasing Aluminum concentration. It has been observed that activation energy and room temperature resistivity exhibit similar behavior [6]. It shows that sample with high resistivity have high activation energy and vice versa.

3.4. Magnetic properties

Figure 8 shows MH loops for Aluminum substituted lithium ferrites, $\text{Li}_{0.6}(\text{NiCo})_{0.2}\text{Al}_x\text{Fe}_{2.2-x}\text{O}_4$ ($x = 0.00, 0.15, 0.3, 0.45, 0.6$).
The loops are narrow s-shaped, showing that these samples are soft ferrites. The values of saturation magnetization, remanance and coercivity obtained from M-H loops are listed in Table 3.

The magnitude of magnetization is very small maximum up to 11 emu g$^{-1}$, this may be due to canting superparamagnetic spins at the surface of the samples. This decrease in the magnitude of magnetization value may also be due to the presence of Al$^{3+}$ paramagnetic ions with down-spin configuration instead of Fe$^{3+}$ cations with up-spin configuration in the octahedral sites [23]. Figure 7 shows that $H_c$ values versus Al$^{3+}$ concentration ($x$).

The increase in coercivity up to $x = 0.3$ may be attributed to lattice defects produced due to monovalent Li$^{+}$ and Al$^{3+}$ ions at B-sublattice. The domain wall pinning by grain boundaries or dislocations under the limit.
of single domain size causes coercivity to increase. The decrease in coercivity of nano-crystalline materials may
be due to close proximity to superparamagnetic limit in last two samples follows \[24\]. It is observed from table 3
that the squaresness ratio (Mr/Ms) is less than 1 which indicates single domain behavior.

4. Conclusions

The Li\(_{0.6}\)(Ni Co)\(_{0.2}\)Al\(_x\)Fe\(_{2.2-x}\)O\(_4\) \((x = 0.00,0.15,0.3,0.45,0.6)\) ferrites were obtained in single phase fcc structure
confirmed by XRD analysis. The Lattice constant varies in the range 8.3267 to 8.2701 Å. The calculated values of
hopping length decrease in the range 2.39 to 2.356 Å which is attributed to the difference in the ionic size of Fe\(^{3+}\)
and Al\(^{3+}\). The Crystallite size is observed to decreases with the increasing Al\(^{3+}\) concentration, the dielectric
constant, complex constant and tangent loss decreased with the increase of frequency due to electronic exchange
between Fe\(^{2+}\) and Fe\(^{3+}\) ions consistent with Maxwell-Wagner model. Room temperature resistivity increases
from \(1.65 \times 10^{10}\) to \(2.23 \times 10^{11}\) ohm-cm with increasing Al\(^{3+}\) concentration. Semiconductor behavior of these
samples was observed from Arrhenius equation. The activation energy increases from 0.29 to 0.70 eV with the
increase of Al\(^{3+}\) content. It shows the similar trend as that of room temperature resistivity. The values of
activation energies show that hopping is the likely the conduction mechanism. The magnitude of magnetization
is small, this is attributed to the canting of superparamagnetic particle spins at the surface of the samples. This
decline in the magnitude of magnetization value may also be due to the presence of Al\(^{3+}\) paramagnetic ions
with down-spin configuration instead of Fe\(^{3+}\) cations with up-spin configuration in the octahedral sites \[23\].
The increase in coercivity up to \(x = 0.3\) is attributed to domain wall pinning at lattice defects produced due to
monovalent Li\(^{+}\) and Al\(^{3+}\) ions at B-sublattice. The decrease in coercivity of nano-crystalline materials may be
due to close proximity to superparamagnetic limit. Based on the investigations these ferrites Li\(_{0.6}\)(NiCo)\(_{0.2}\)Al\(_{0.6}\)Fe\(_{2.2}\)O\(_4\) are useful for the microwave devices and memory cores.

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