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Electrical and Dielectric Properties of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (0.0≤x≤0.2) Nanoparticles Synthesized by Sol-Gel auto combustion method

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Abstract: Ferrites are technologically useful materials due to their unique electric and dielectric properties. The co-substitution of metal ions in nickel ferrites are one of the most attractive classes of materials for researchers and scientist. $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (0.0 ≤ x ≤ 0.2) spinel ferrite nanoparticles were synthesized by sol-gel auto combustion method. The DC electrical resistivity of prepared nanoparticles was studied using two probe methods as a function of temperature. The dielectric parameters such as dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tan δ) were measured at room temperature in the frequency range 50 Hz to 5 MHz. All the dielectrical parameters show compositional as a function of frequency dependences. At lower frequencies, it is observed that the dielectric constant (ε′), dielectric loss (ε’’) and loss tangent (tan δ) are high.

Keywords: Activation energy; nanoparticles; Dielectric properties.

I. INTRODUCTION

Ferrites have wide applications from microwave to radio frequencies [1, 2]. They exhibit relatively high resistivity at carrier frequencies, sufficiently low losses for microwave applications and a wide range of other electrical properties [3, 4]. The nickel ferrite possesses an inverse spinel structure and the degree of inversion depends upon the heat treatment [5, 6]. Nickel ferrite materials have been used in research for many years due to their useful electromagnetic characteristics for a large number of applications [7, 8]. The performance of these materials in their bulk form where the grain dimensions are in micrometer scales is limited to a few megahertz frequency due to their higher electrical conductivity and domain wall resonance [9]. However, the recent technological advances in electronic industry demand even more compact cores for work at higher frequencies [10, 11]. One way to solve this problem is by synthesizing the ferrite particles in nano-metric scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multi domain formation, the particle is in a single domain state. Domain wall resonance is avoided, and the material can work at higher frequencies [8]. Spinel ferrites are widely used in many electronics devices [12, 13]. They preferred because of their saturation magnetization, high Curie temperature and high permeability, high electrical resistivity [14, 15]. Mechanical properties of spinel ferrites depend on the chemical composition, heat treatment and type of substitution [16]. The magnetic properties of several mixed spinel ferrites with the spinel type crystal structure have been the subject of many investigations [5, 17].

The magnetic properties of spinel ferrite strongly depend on the distribution of cation over the tetrahedral and octahedral sites [18, 19]. Cations in spinel ferrite can occupy either an interstitial site of tetrahedral symmetry or octahedral symmetry with a closed packed oxygen lattice. The substitution on non-magnetic and magnetic ions like tetravalent ions Al^{3+} in nickel ferrite may give rise to interesting electrical and magnetic properties like spin structure [20, 21]. Nickel ferrite has totally inverse spinel structure with half of the ferric ions on tetrahedral sites and the rest occupy the octahedral sites [22, 23]. In Ni-Al-Cr ferrites, the nickel ions occupy the octahedral sites, while some of the aluminium and chromium ions prefer to occupy the tetrahedral sites and rest are stable in the octahedral sites [24, 25].In the literature, very less reports are available for the synthesis and characterization of nickel ferrite substituted with various cations like Al, Cr. These studies revealed that the structural, electrical and magnetic properties of nickel ferrite are strongly influenced with the substitution of multivalent cations. In particular, the co-substitution of Cr^{3+} and Al^{3+} ions at the Fe^{3+} site are known to produce very interesting physical and chemical properties in spinel ferrites [26, 27]. The substitution of Al^{3+} and Cr^{3+} ions in the crystal structure of nickel ferrite can significantly affect on structural and magnetic properties by changing the magneto-crystalline anisotropy field [26]. Here, by replacing the Fe^{3+} ions by Al^{3+} and Cr^{3+} ions, we expected to obtain the nickel ferrite that possess high anisotropy field. Also, the electrical and dielectric properties are expected to be significantly changed. Thus, it will be interesting to study the electrical

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and magnetic properties of Al and Cr co-substituted nickel ferrite nanoparticles [28, 29]. The investigations of electrical and dielectric properties as a function of frequency dependence of Al and Cr doped in nickel ferrite nanoparticles are important from the point of view of its use in electrical and electronic applications like high frequency device application. To our knowledge, the effect of co-substitution of Al^{3+} and Cr^{3+}ions in nickel ferrite on the electrical and dielectric properties has not been reported in the literature. In the previous report we have reported structural, morphological, compositional and infra-red properties of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ ($0.0 \leq x \leq 0.2$) nanoparticles.

In view of the above facts, the aim of the present work is to investigate the electrical properties as a function of temperature dependence and dielectric properties as a function of frequency and composition dependence of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (for x = 0.0, 0.1, 0.2) nanoparticles and to find correlation between the various properties.

II. EXPERIMENTAL

2.1 Synthesis of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ nanoparticles

Analytical Reagent (AR) grade nickel nitrate $Ni(NO_3)_2.6H_2O$, ferric nitrate $Fe(NO_3)_3.9H_2O$, aluminum nitrate $Al(NO_3)_3.9H_2O$, chromium nitrate $Cr(NO_3)_3.9H_2O$ and citric acid $C_6H_8O_7.H_2O$ as a fuel were used as starting materials. According to the composition of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ **(**where x = 0.0, 0.1, 0.2) all the nitrates were separately dissolved in minimum amount of distilled water and stirred on magnetic stirrer for 10 min. All the solutions were mixed together and stirred on a magnetic stirrer until the nitrates were completely dissolved. The metal nitrate to citric acid ratio was taken as 1:3. The solutions were stirred with continuous stirring on magnetic stirrer; drop by drop ammonia solution was added to adjust the pH value to 7. Then the solution was heated on hot plate at 90 ˚C with constant stirring until gel was formed. Instantaneously gel ignites with the formation of large amount of gas, resulting in to light weight voluminous powder. The resulting precursor powder was annealed at 800 ˚C for 12 h to obtain $NiAl_{2x}Cr_xFe_{2-3x}O_4$ nano-powder.

2.2 Characterizations

The electrical properties such as DC electrical resistivity of the nano-particles were measured using the two probe technique. The measurements were performed in the temperature range 300-800 K. The temperature of the sample was sensed by chromel-alumel thermocouple with an accuracy of ± 5 K. For measuring dc resistivity the samples in the form of circular pellets of the dimensions 10 mm diameter and 3 mm thickness were used. The surface of the pellets was coated with silver paste for good Ohmic contact. The dielectric constant ε', dielectric loss ε'' and dielectric loss tangent (tanδ) were obtained by measuring the capacitance of the nanoparticles in the pellet form at room temperature using LCR-Q-meter bridge (Hewlett Packard, model 4284-A) in the frequency range 20 Hz - 5 MHz.

III. RESULTS AND DISCUSSION

3.1 DC electrical resistivity

The room temperature DC electrical resistivity values were calculated by measuring resistance (R) of each sample. The temperature dependence of electrical resistivity was studied in the temperature range 300-800 K.

The resistivity of the samples was calculated by using the Arrhenius relation [30, 31].

$$\rho = \rho_0 \exp(E\rho/kT) \quad (1)$$

where, E_ρ represents an activation energy, k is Boltzmann constant, ρ is the resistivity at absolute temperature T, and ρ_0 represents the resistivity at 0 K.

The plot between logarithm of resistivity (log ρ) and reciprocal of temperature is shown in Fig.1.

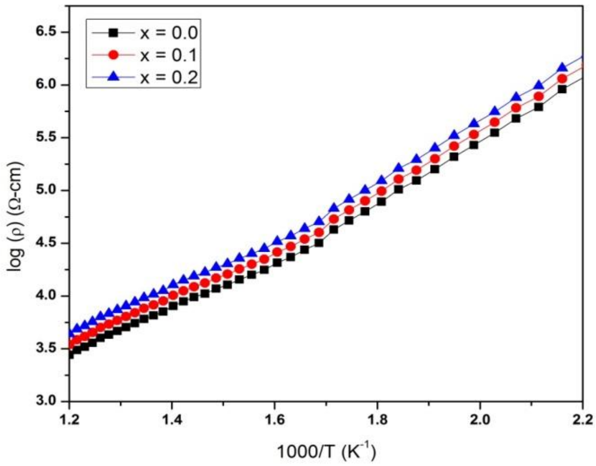

Fig. 1. Variation of DC electrical resistivity with reciprocal of temperature of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ ($0.0 \leq x \leq 0.2$) nanoparticles

It is observed from figure that the resistivity decreases as temperature increases. Ferrites behave like semiconductor and their resistivity decreases with increase in temperature according to the relation (1). The plot of logρ versus 1000/T shows a straight line in most of the ferrite sample with a slope corresponding to Eρ. In some ferrite a change in slope is found in the curve showing different activation energy values. The change in slope generally occurs at temperature range approaching to Curie temperature of the sample [32].

In the present study, the plot of logρ versus 1000/T show change in slope which creates two straight lines or regions namely ferrimagnetic region (low temperature region, $T<T_c$) and paramagnetic region (high temperature region, $T>T_c$). The variation in resistivity as function of temperature obeys Arrhenius relation (Eq.5.1). The activation energy ΔE for each sample in the ferrimagnetic and paramagnetic region was calculated from the resistivity plots. The values of activation energies for all Al-Cr substituted nickel spinel ferrite samples are listed in Table 1.

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It can be observed that the activation energy in general decreases with aluminum and chromium concentration 'x' increases [33]. Within the ferrimagnetic region of each sample, the activation energy E_f values of the samples under investigation are found to be in the range 0.397 to 0.274 eV. Similarly the activation energy values for paramagnetic region E_p are found to be in the range 0.442 to 0.755 eV. As expected, activation energy values for paramagnetic region are greater than that of ferrimagnetic region. The results of activation energy are well supported by literature reports [34-36].

TABLE I Activation energy in paramagnetic (E_p) and ferrimagnetic (E_f) region of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ ($0.0 \le x \le 0.2$) nanoparticles

x	Ep (eV)	Ef (eV)	ΔE (eV)
0.0	0.755	0.397	0.358
0.1	0.713	0.378	0.335
0.2	0.675	0.354	0.321

3.2 Dielectric properties

The dielectric properties for the present samples can be explained on the basis of the mechanism of polarization process in ferrite, which is similar to that of conduction process. The electronic exchange $Fe^{3+} \leftrightarrow Fe^{2+}$ gives the local displacement of electrons in the direction of an applied field, which induces polarization in ferrites [37].

3.2.1 Frequency dependence of dielectric properties

Dielectric constant (ε')

The dielectric properties of $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (x = 0.0, 0.1 and 0.2) ferrite nano-particles were investigated as a function of frequency using LCR-Q meter in the frequency range 20 Hz to 5 MHz .The measurements were carried out in the frequency range 20 Hz - 5 MHz at room temperature on disc shaped pellets of 10 mm diameter and 2-3 mm thickness.

Fig.2 (a) represents the variation of dielectric constant with frequency. It can be seen that as frequency increases, the dielectric constant (ε′) found to decrease. The decrease in dielectric constants is exponential in nature. At higher frequency the dielectric constant remains almost constant. The decrease of dielectric constant with increase of frequency is a normal dielectric behaviour of spinel ferrites. The similar behaviour was also observed in other spinel ferrites [38-40].

Further, it can be noticed from Fig. 2 (a) shows that the dispersion in ε′ is similar to Maxwell-Wagner interfacial polarization [41-43] in agreement with Koop's phenomenological theory [44, 45]. The decrease in dielectric constant is because beyond a certain frequency of a externally applied field the electronic exchange between ferrous and ferric ions cannot follow the alternating field.

Dielectric loss (ε″)

Fig. 2 (b) shows the variation of dielectric loss (ε″) with frequency. It is observed from figure Fig. 2 (b) that the dielectric loss also decreases with increase in frequency similar to dielectric constant [38].

It can also be noticed from figure that the dielectric loss remains almost constant at higher frequency whereas at lower frequency the dielectric loss shows significant values. The decrease in dielectric loss (ε″) as a function of frequency was also observed in other well known ferrite. Similar behaviour of dielectric loss has been observed in other literature [38, 41, 46]

Dielectric loss tangent (tan δ)

Fig. 2 (c) shows the variation of dielectric loss tangent (tan δ) as a function of frequency. It can be observed from Fig. 2 (c) that the dielectric loss tangent decreases with frequency. It is well known that there is a strong co-relation between the conduction mechanism and dielectric behaviour of ferrite.

All the samples exhibit dispersion due Maxwell-Wagner interfacial type polarization [43]. The values of dielectric loss tangent (tan δ) depend on many factors such as stoichiometric, concentration Fe^{3+} ions etc [47, 48], which in turn depends on the composition and annealing temperature of the sample.

3.2.2 Compositional dependence of dielectric properties

Dielectric constant (ε')

The dielectric constant of prepared $NiAl_{2x}Cr_xFe_{2-3x}O_4$ nanoparticles at different composition is shown in Fig. 2 (a). It is evident from Fig. 2 (a) that the dielectric constant decreases as Al-Cr concentration x increases.

The decreases in dielectric constant for the prepared materials is due to the impact of grain size that lies in the nanometer dimension, which makes these materials suitable for the miniaturization of high- frequency applications [49, 50].

Dielectric loss (ε'')

The dielectric loss of prepared $NiAl_{2x}Cr_xFe_{2-3x}O_4$ samples at different composition is shown in Fig. 2 (b). It is evident from Fig. 2 (b) that the dielectric loss decreases as Al-Cr concentration x increases. However, the values of dielectric loss are sufficiently larger than the values of dielectric constant [51].

Dielectric loss tangent (tan δ)

The dielectric loss tangent of prepared $NiAl_{2x}Cr_xFe_{2-3x}O_4$ samples at different composition is shown in Fig. 2 (c).

It is evident from Fig. 2 (c) that the dielectric loss tangent (tanδ) decrease with increase Al-Cr concentration x. The decrease in dielectric loss tangent (tanδ) as a function of Al-Cr concentration x is observed at all frequencies studied.

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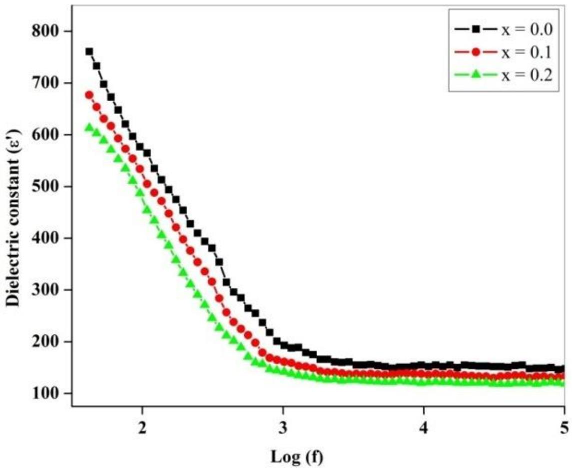

Fig. 2 (a): Variation of dielectric constant ε′ with log (f) for $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (0.0≤x≤0.2) nanoparticles

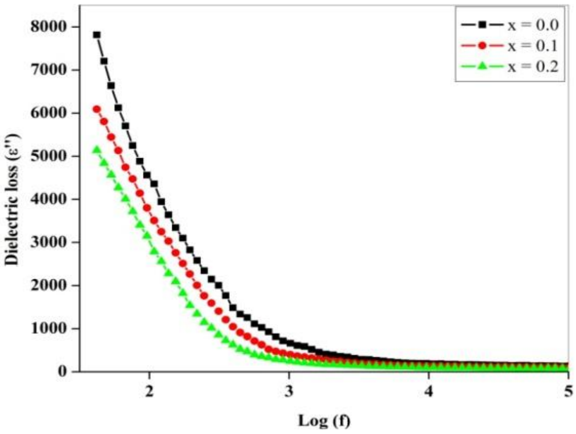

Fig. 2 (b): Variation of dielectric loss ε″ with log (f) for $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (0.0≤x≤0.6) nanoparticles

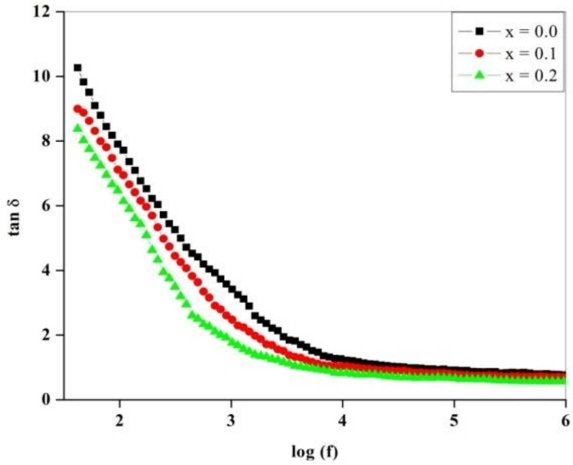

Fig. 2(c): Variation of dielectric loss tangent (tanδ) with log (f) for $NiAl_{2x}Cr_xFe_{2-3x}O_4$ (0.0≤x≤0.2) nanoparticles

IV. CONCLUSION

Al^{3+} and Cr^{3+} co-substituted $NiAl_{2x}Cr_xFe_{2-3x}O_4$ nanoparticles were successfully synthesized via sol-gel auto combustion method. DC electrical resistivity increases with Al-Cr concentration 'x' increases. The plot of log ρ versus reciprocal of temperature indicates that the resistivity decreases with temperature increases. The activation energy in paramagnetic region is more than that of ferrimagnetic region. Dielectric properties such as dielectric constant (ε), dielectric loss (ε'') and dielectric loss tangent (tan δ) decreases with increase in frequency and Al-Cr content 'x'. Thus, the prepared materials having high dielectric constant at lower frequency and concentration of Al- Cr, therefore, these kinds of materials can be useful for microwave device applications.

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