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Structural, Dielectric and Morphological Spectroscopy of $Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$/Chitosan Modified Reduced Graphene Oxide (rGO) Nanocomposites*

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ABSTRACT

A laboratory experiment was conducted for Structural, Dielectric and Morphological Spectroscopy of $Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$/Chitosan Modified Reduced Graphene Oxide (rGO) Nanocomposites. Sol-Gel synthesized Al^{3+}-Mg^{2+} cobalt ferrite ($Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$) was successfully embedded on functionalized reduced graphene oxide. The sample was characterised using XRD, FTIR, FESEM. Phase analysis show the formation of cobalt ferrite with space group Fd3m. FTIR analysis gives an idea of the formation of cobalt ferrites by the appearance of two prominent peaks at 405 and 525 cm^{-1}. The morphology of the sample shows particles with shapes close to cubic structure. Raman spectra show the presence of D and G band. The dielectric properties were discussed based on Maxwell-Wagner model and Koop's phenomenological theory. Cobalt ferrite exhibits interesting structural, dielectric, and impedance properties that make it suitable for various applications, such as microwave devices, sensors, and magnetic recording media.

Keywords: *Spinel ferrite, magnetic properties, structural properties.*

1. Introduction

Development of nanomaterials for technological application has prompt renew interest in the synthesis and characterization of nanomaterials [1][2][3][4]. In particular, spinal ferrites shows exceptional magnetic and dielectric properties which include high Curie temperature, large magneto crystalline anisotropy, high coercively, moderate saturation

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magnetization, large magnetostrictive coefficient, excellent chemical stability and mechanical hardness [5][6][7]. These properties makes spinel ferrites useful in microwave absorption and used in high density magnetic recording media [8][9]. Graphene oxide (GO) was used to prepared Reduced graphene oxide (rGO). The properties of Reduced graphene oxide (rGO) are usually thermal stability, excellent electrical conductivity, light weight and high surface area. [10][11].

Dielectric measurements show that the dielectric constant and dielectric loss decrease with increasing frequency [17][18][19]. This behavior is attributed to the space charge polarization and the Maxwell-Wagner type interfacial polarization [17][19]. Impedance spectroscopy is used to understand the conduction mechanism and study the effect of grain and grain boundary on the electrical properties [17][19][20]. The prominent effects in dielectric measurements are observed, and it is found that the effect of resistance in grains and grain boundaries is significant [21].

The properties of spinel ferrites depend on several factors such as method of synthesis, precursor material and sintering temperature. sol-gel auto-combustion method offer several advantages over traditional solid state reaction and coprecipitation, these advantages include homogeneity of the mixture of precursor materials, low calcination temperature, low cost, and low reaction time [12][13][14]. Hence, in this method we adopt sol-gel auto-combustion method and synthesize $Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$. Graphene oxide was synthesized using hummers method and reduced in the presence of chitosan in order to avoid restacking of the reduced grapheme oxide Nanosheets. The prepared Nancomposites was characterised using XRD, FTIR, FESEM.

2.0 Experimental Procedure

2.1 Synthesis of Co-dopped Aluminium Ferrite ($Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$)

AR grade chemicals were used to synthesize spinel ferrites with chemical composition ($Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$) using sol-gel auto-combustion method. The chemicals which are Aluminium nitrate, cobalt nitrate, ferric nitrate, magnesium nitrate, and poly vinyl pyrrolidone have been used without further purification. Stoichiometric amount of the chemicals was weighed and dissolved in 100ml of distilled water to form the salt solution. The solution was heated on a hot plate with constant and continuous magnetic stirring at 80-100 °C so as to evaporate the water. A brown gel was obtained which upon further heating at 280-300 °C gives the precursor material. The precursor material crushes in powder using mortar and pestle. The final powder was calcinated at 700°C for 5 hours in electric furnace.

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Co(0.9)	Molar ratio of the reagent Al(0.1)	Fe(0.9)	Mg(0.1)	Sample	Polymer (PVP)	
	291.03	375.13	404	256.41	B1	40000
	261.927	37.513	767.6	25.641	B2	
	10.47708	1.50052	30.704	1.02564	B3	9gm

2.2 Synthesis of pre-oxidized graphite

Concentrated sulphuric acid was taken in a beaker. Potassium persulfate was added to the beaker containing sulfuric acid, followed by addition of 5g of phosphorous pentoxide and 10g natural graphite. The reaction mixture was then homogenised thoroughly at medium heating for 2 hours and 30 minutes using a magnetic stirrer. This led to the formation of a dark blue mixture. The dark blue mixture allowed cooling down at room temperature. Then it was filtered, and the material obtained in the filter paper was washed with distilled water. Then it allowed drying under ambient (under room temperature and pressure). Given that pre-oxidized graphite powder.

2.3 Synthesis of reducing graphene (rGO)

A 5g of pre-oxidized graphite was poured in a beaker containing 200 ml concentrated sulphuric acid. The procedure was carried out in an ice bath under continuous magnetic stirring. A 15ml of potassium permanganate was added gradually (manually dropped) to the above and left the mixture under magnetic stirrer with stirring and keeping the temperature below 100°C, and obtained a thick viscous mixture. 100ml of concentrated sulphuric acid added to the viscous mixture for dissolution. The solution was again stirred for 2 hours at 100°C. Again, we used a laboratory thermometer to maintain the temperature of this mixture. The resulting mixture was the shift to a water bath and maintained at 40°C 1 hr. The beaker containing the above-said mixture was removed from the water bath. It was then diluted with distilled water (~ 1 liter). 20 ml of hydrogen peroxide (H_2O_2) and 2 ml of hydrogen chloride was added to this diluted mixture. The color of the mixture changed from dark-brown to brown-yellow in color gradually. It believed that colorless change of soluble manganese sulphate was formed because of residual reduction of permanganate and manganese oxide is responsible for color change in the reaction mixture. The mixture then filtered and washed with dilute HCl to remove any residual metal ions. Dilute HCl was prepared in the laboratory by adding distilled water in concentrated HCl in the ratio of 1:10.

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2.4 Methods of formation of composites of doped Co-ferrites with rGO

Sample with ID number B1 was not used for the preparation of composite. Sample with IDs number B2 and B3 were mixed with rGO (as discussed above in sec. 2.3) to form a composite.

- **Preparation of composite (B2 and rGO):** 2.6 g of B2 was weighed in a watch glass. 0.26 g of rGO (i.e. 10% by weight of B2) was weighed in another watch glass. These two materials were transferred in a mortar and pestle. These were grounded thoroughly manually for ~ 10 minutes. The sample/composite obtained this in a way that was named as BB2.

- **Preparation of composite (B3 and rGO):** 2.6 g of B3 was weighed in a watch glass. 0.52 g (i.e. 20% by weight of B3) was weighed in another watch glass. The two substances were transferred in a mortal and a pestle (ceramic). These two materials were mixed thoroughly manually by using a pestle for about ~ 10 minutes. The composite was named as BB3.

3. Characterization details

XRD pattern of the prepared samples was obtained in the range 20°–80° using Cu-Kα radiation operating at 40 kV and 35 mA with step size 0.02° (Bruker AXS D8 advance diffractometer) was used to carry out phase identification. Fourier transform infrared (FTIR) spectrometer [Nicolet FTIR interferometer IR prestige-21 (model-8400S)] was used to study the attached functional groups, room temperature FTIR spectra was recorded in the wavenumber range 4000 cm^{-1} and 400 cm^{-1}. Field-emission scanning electron microscope (FESEM) (Joel 6390LV) operating at a voltage of 20 kV was used to study the morphology and elemental analysis of the prepared samples.

4.0 Results and discussions

4.1 Phase identification

X-ray diffraction (XRD) patterns of the sample indicate according to the standard JCPDS card 221086 and 75-2078 for rGO. The diffraction lines (h k l) belonging to the peaks (211), (220), (310), (222), (321), (400), (422), (440), and (620) which indicate the simple cubic spinal structure in a crystal form (Fig. 1).

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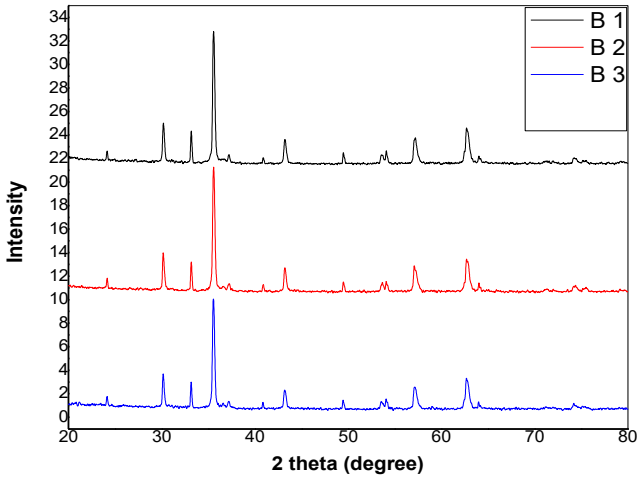

Fig. 1 XRD patterns of $Co_{(1-x)}Al_xFe_{(2-x)}Mg_xO_4$ /Reduced Graphene Oxide Nanocomposites (B1, B2 and B3)

X-ray diffraction (XRD) spectra of $Co_{(1-x)}Al_xFe_{(2-x)}Mg_xO_4$ Nano composites shows that the diffraction peaks occur as a result of small impurities in the sample, which indicates the single-phase cubic crystal spinel structure was formed. This suggests that dopants occupy space in the simple cubic structure, without any major improvement in its phase. The Miller indices and θ are the diffraction angle of h k l plane. The value of 2θ is inversely proportional to a lattice constant so that the lattice constant increases and hence the peak shift to the lower hkl value at 355. So the value decreases with the increase of the constant lattice, such that the x-ray density is inversely proportional to the constant lattice. Where lattice constant is *an* inter-planer spacing is ***dhkl***, crystallite size ***D*** and Volume of the unit cell ***V*** were determined from the following equations; [6]

$$V_{cell} = 0.8666\,a^2c \text{ Or } a^3 \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$D = \frac{0.89\lambda}{\beta \cos\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$a = dhkl\sqrt{h^2 + k^2 + l^2} \ldots\ldots\ldots\ldots\ldots (3)$$

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Table 1 Lattice variables (parameters) of $Co_{(1-x)}Al_xFe_{(2-x)}Mg_xO_4$

Sample	2θ	a (Å)	d (Å)	β (nm)	D (nm)	V_{cell} (Å^3)
B1	37.08	9.6904	2.4226	0.23042	7.30657	910
B2	37.21	9.6568	2.4142	0.25731	6.03634	901
B3	37.03	9.7032	2.4258	0.35781	4.88533	914

Where d_{hkl} is the d spacing between the planes, hkl are the miller indices, β is the full width at half maximum (in radian), θ is the Braggs angle and λ is the X-ray wavelength (1.54056 Å). From above table 1, shows that lattice Constant, crystallite thickness, and volume increase due to the increase in Aluminium and Magnesium doping concentration. That is because the dopant with a higher atomic radius replaces the Cobalt and iron atom with a lower atomic radius on the octahedral sites is inversely proportion to the lattice constant, therefore the lattice constant increases with a lower change to 355 peaks. The large diffraction peak indicates the presence of rGO in the Nano composite at approximately $2\theta = 26.57^{0}$. [15][9] [16]

4.2 FTIR analysis

Fourier transforms infrared spectroscopy (FTIR) used to examine (investigate) the molecular bands that attached in the functional groups of the samples (Fig 2).

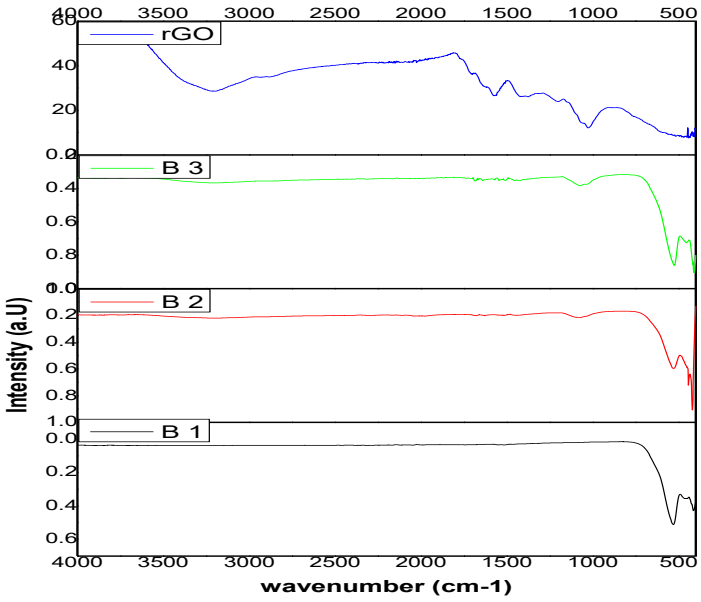

Fig 2 FTIR of B1, B2, B3 and rGO

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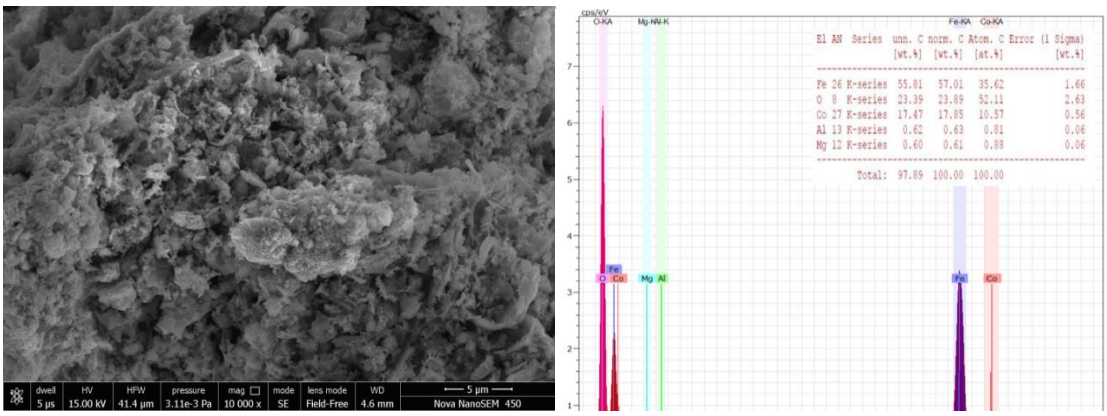
Fig. 2 has shown that Fourier transforms infrared spectrometer (FTIR) spectra of the $Co_{(1-x)}Al_xFe_{(2-x)}Mg_xO_4$ (B 1,B 2,B 3) ferrite and rGO system recorded between 4000 and 400 cm^{-1}. Stretching vibration in the tetrahedral combination showed in the graph absorption band (ν 1) at 600 cm^{-1} and stretching absorption band (ν 2) of the octahedral complex at around 400 cm^{-1}. With increasing the concentration of aluminium and magnesium, the absorption band υ1 shifted to a lower point and the position of υ2 changed. The reduced graphene oxide rGO bands characterize between 1000-1500 cm^{-1} as stretching vibrations of C–O alkoxy, stretching vibrations of C–O epoxy, deformation of O–H, stretching vibrations of C–C and C=O bonds showed the reduced graphene as in Fig 2 (rGO). The chemical substances were absorbed around the surface of the ferrite sample correspondent to the tetrahedral and octahedral complex vibrations respectively. The bond's intrinsic stretching vibrations are attributed to the high-frequency absorption band, while the lower frequency band is due to the reduction of graphene oxide (rGO). [6][11]

4.3 Surface features analysis (FESEM/EDX Analysis for B 1and B 2)

Fig. 3 shown FESEM (Field emission scanning electron microscope) and EDX (Energy dispersive x-ray) spectrum of $Co_{(1-x)}Al_xFe_{(2-x)}Mg_xO_4$ Nano composite at various magnifications for the study of particle morphology, microstructure, and imaging of synthesized nanoparticles. For the FESEM, measurement was been performed and the irregular particle morphology of synthesized samples was shown. The EDX figure clearly shows the presence of Co, Al, Mg, C, and Fe and O ions with no significant impurity in the prepared ferrites and the final products confirm the purity of the sample. Silky waves reflect the rGO (B 2) sheets with some wrinkles at the edges, due to the escape from the GO surface of oxygen-containing groups. [6][11] Detail analysis of prepared ferrites by element shown in the figure.



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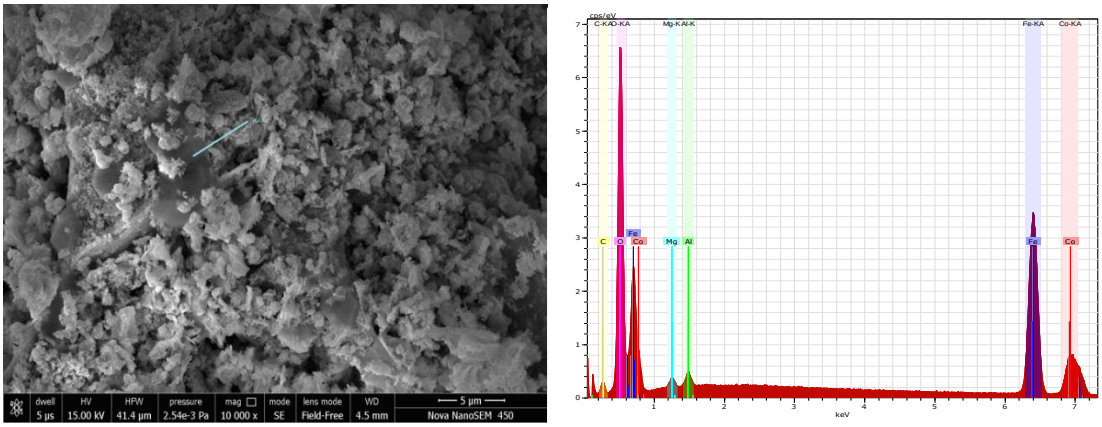

Fig. 3 EDX spectra and mapping of $Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$/Reduced Graphene Oxide Nano composites B1 and B2

5. CONCLUSION

The $Co_{0.9}Al_{0.1}Fe_{1.9}Mg_{0.1}O_4$ Nanoparticles have been successfully synthesis by using Sol-gel method. The X-ray diffraction analysis of the sample confirms the simple cubic crystalline structure. Structural analysis using X-ray diffraction (XRD) confirms the formation of a single-phase cubic spinel structure of cobalt ferrite Nanoparticles. Fourier-transform infrared (FT-IR) spectroscopy provides information about the chemical and molecular structure changes in the ferrite due to changes in the Fe^{3+} - O^{2+} bond and observed the particles size decrease with the increase and doping the materials. Cobalt ferrite exhibits interesting structural, dielectric, and impedance properties that make it suitable for various applications, such as microwave devices, sensors, and magnetic recording media.

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