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Effect Of Ni^{2+} Doping On, Structural, Electrical, Dielectric And Optical Properties Of Magnesium Spinel Ferrite

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Abstract

Nano-ferrites of the composition $Ni_xMg_{1-x}Fe_2O_4$ (x=0.1, 0.2,0.3) were synthesized by sol-gel auto combustion method. as synthesized powders were sintered at 800^0c for four hours NPs possess unique physical and chemical properties due to their high surface area and nanoscale size and were characterized by X-ray diffraction (XRD) which confirmed the formation of cubic spinel structure of ferrites with an average crystallite size in the range of 23-31 nm. The dielectric constant decreases with increase in frequency shows dielectric dispersion behavior. AC conductivity increases with increase in frequency shows small polarons type of conduction mechanism. The FTIR spectral studies at room temperature in the range of 400 to 40000cm^{-1} shows The high frequency band (v_1) around 600 cm^{-1} and the low frequency band (v_2) around 400 cm^{-1} sharps bands is due to tetrahedral and octahedral complexes.

Keywords Ferrites, XRD, Fourier Transform Infrared Spectroscopy (FTIR),Dielectric and electric properties.

1. Introduction

Spinel ferrites are polycrystalline ceramic magnetic semiconductor materials. The general formula of ferrites are AB_2O_4. A represent the tetrahedral A site and B represent the octahedral site of spinel. Depending on the composition and cation distribution on A and B sites spinel ferrites shows various magnetic and electrical properties [1]. Due to their higher surface to volume ratio spinel ferrites

have different physical and chemical properties corresponding to bulk materials [2]. Due to high magnetic permeability and low magnetic losses (Giannakopoulou et al.2002).High electrical resistance and lower saturation magnetization makes spinel- ferrites used in many electronic magnetic and magneto-optical devices [3][4].

In recent year they have attracted attention in high frequency applications such as magnetic drug delivery [3], high density information storage [4],ferrofluids [5], photocatalysis [6],gas sensors [7] etc.

Among several spinel ferrite, we are interested in Ni^{2+} substituted magnesium spinel ferrites. $MgFe_2O_4$ is inverse spinel ferrites with Mg^{2+} ions mainly on octahedral sites (B sites) and Fe^{3+} ions are distributed at the (tetrahedral sites)A-sites and (octahedral sites) B-sites,. $NiFe_2O_4$ is also a inverse spinel ferrites. The replacement of non-magnetic ion Mg^{2+} with magnetic ion Ni^{2+} prefer the octahedral sites causes magnetic ordering of the compounds changes and magnetization increases [8]. The distribution of cations over the two interstitial sites is strongly affected by the variations of lattice constants, size of crystallites, and bond angles-bond length between the cations [9].

Recently, various fabrication methods have been reported, for preparation of spinel ferrites, including the sol–gel [10], co-precipitation [11], solid-state reaction [12], ball milling [13], hydrothermal method [14], and combustion technique [15] etc.In the present work, Sol-gel method were used for the synthesis of Ni^{2+} substituted magnesium spinel ferrites, then obtained precursor were synthesized at 800^0C temperature and their structural, electrical and optical properties were studied by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), Impedance Analyzer.

2 Material and Method

Nickel substituted Magnesium spinel ferrite nanoparticles ($Ni_{1-x}Mg_xFe_2O_4$) of different compositions with (x = 0.1, 0.2, 0.3,) were synthesized by Sol-gel auto combution method.

ferric nitrate ($Fe(NO_3)_39H_2O$, 98%) and magnesium nitrate ($Mg(NO_3)_2.6H_2O$) Nickel nitrates [$Ni(NO_3)_2.3H_2O$] were used as precursors and urea as a fuel for this reaction. All these nitrates were weight in required molar proportion according to the stoichiometry and dissolved in deionized water. The mixture of the nitrates is then stirred continuously and heated to a temperature of 80^0C till the sol is formed. after the formation of gel, it kept in a microwave for few minutes, gel burns within few minutes and leave the ash of ferrites. Then, this ash powder were calcined at 800 °C for 4 h. and get required ferrites sample for characterization.

3. Result and Discussion

I . Structural Analysis

X-rd were used to analyze the structure and phase purity of the samples.Fig1 shows the X-ray diffraction pattern of $Ni_xMg_{1-x}Fe_2O_4$ samples prepared with substitution of Ni^{2+} cation 0.1,0.2,0.3) in magnesium spinel ferrites. The high intensity diffraction peaks observed at 2θ of 30.6°, 35.9°, 43.7°, 57.7° and 63.2° express the high crystalline nature of the as-prepared nanoparticles corresponds to the reflections of (220), (311), (400), (511) and (440) planes confirmed the existence of cubic spinel structure of ferrites without any impurities [16]. The crystallite size of ferrites was estimated from the high intense diffraction peak i.e. (3 1 1) by using the Debye-Scherer equation. The average crystallite size D_{311}, cell volume V_c, X-ray density dx were calculated from XRD data, while the bulk density was measured by considering mass to volume ratio and the results are listed in Table

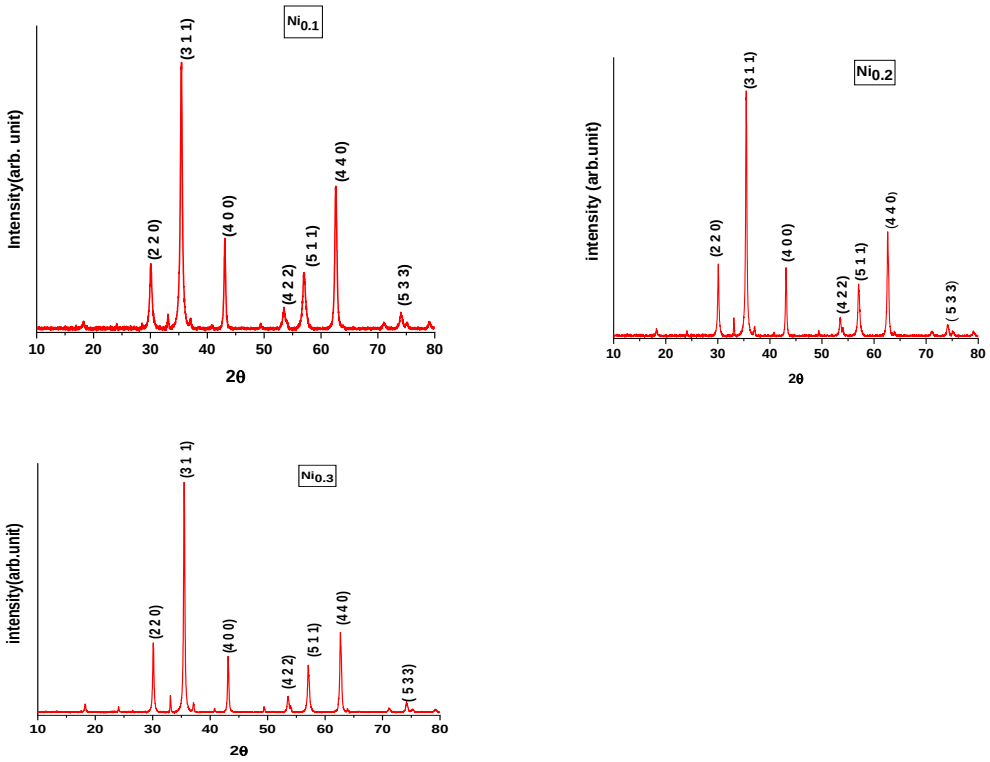

Fig.1 XRD pattern of Ni_x Mg $_{1-x}Fe_2O_4$ (x=0.1,0.2,0.3)

Table1: Structural parameters from XRD data for $Ni_xMg_{1-x}Fe_2O_4$ (x=0.1, 0.2, 0.3) of different composition

Composition	Lattice Parameter(a) (Å)	Volume "a^3" $(Å)^3$	Bulk Density "D_b"(gm/cm^3)	X-ray Density "D_x"(gm/cm^3)	Porosity "P"(%)	Particle Size(nm)
$Ni_{0.1}Mg_{0.9}Fe_2O_4$	8.3933	591.286	4.10	4.569	10.3	23.26
$Ni_{0.2}Mg_{0.8}Fe_2O_4$	8.3897	590.52	3.89	4.653	16	26.94
$Ni_{0.3}Mg_{0.7}Fe_2O_4$	8.3840	589.32	3.90	4.740	17.7	31.10

The average crystallite size in the Ni substituted samples was found to be in the range of 23.26 nm to 31.10 nm. lattice constant decreases with the substitution of the smaller ionic radius Ni^{2+} (0.695 Å) ions in place of large Mg^{2+} (0.72 Å) ions. from the table observed that value of X-ray density increases and bulk density deceases ,it is due to the presence of pores created during the sintering process.

II . Dielectric Properties of Ferrites

The variations of dielectric constant with frequency for all ferrite samples are as

the ferrites depend upon the method of preparation, chemical composition, grain size and sintering temperature [17]. shown in Fig1. The electrical properties of Initially at the low frequency region, the dielectric constant decreases rapidly, and in the high frequency region, it remains constant. This behavior based on the Maxwell–Wagner type interfacial polarization, which is in good agreement with Koop's phenomenological theory [18] [19]. The dielectric constant (ε') of the ferrites decreases with increase in frequency due to the

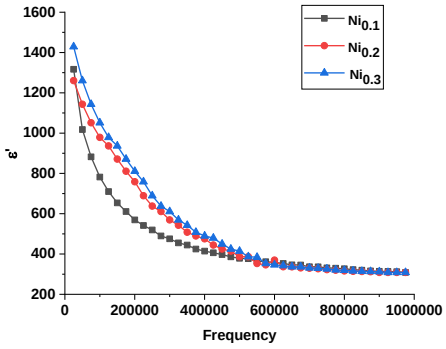

Fig.2 variation of dielectric constant with frequency

hopping of electrons between Fe^{2+} to Fe^{3+} ions Beyond the certain frequency region the dielectric constant fails to follow the applied electric field [20].

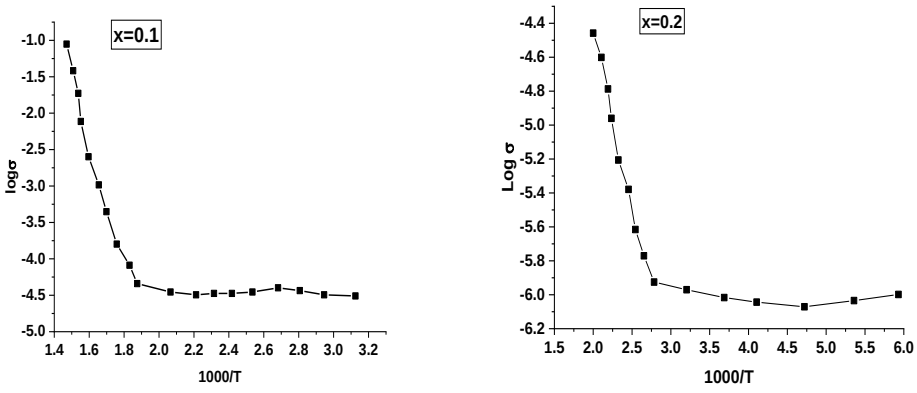

Fig. 3 Variation of logσ with inverse of temperature for $Ni_xMg_{1-x}Fe_2O_4$

Fig.3 shows the temperature dependent dc electrical conductivity of Ni substituted Mg spinel ferrites was measured in the range of 100K-550K.

The relationship between conductivity and temperature may be expressed as by the relation (Verwey and Heilman 1947),

$$\sigma = \sigma_0 \exp\left(\Delta E / KT\right) \quad \text{.....(1)}$$

The electrical properties of ferrites are affected by the distribution of cations in the octahedral and tetrahedral sites,the electronic conduction in ferrites is mainly due to hopping of electrons between the ions of the same element present in more than one valence state" i.e. (Fe^{3+} and Fe^{2+} ions), It is explained on the basis of Verwey's hopping mechanism [21].

The above fig. shows the logσ against $10^3/T$ of pure Ni-Mg spinel ferrites. The kink occurs in each curve of composition $Ni_xMg_{1-x}Fe_2O_4$ (x=0.1,0.2) at the particular temperature called transition temperature T_c, Above the transition temperature, the synthesized Ni-Mg ferrite samples exhibit paramagnetic nature where it has disordered character.

III. FTIR study of Ferrites

The IR Spectra were recorded in the frequency range 400-4000 cm^{-1} for $Ni_xMg_{1-x}Fe_2O_4$ (x=0.1,0.2) are shown in fig.3 . The FTIR spectra show sharp bands and variation in spectrum due to the vibration of ions in samples sinerted at temperature 800^0c. Two main bands in spinel ferrites for tetrahedral and octahedral appear in the frequency range 390-450 and 540-600 cm^{-1} are shown in fig.4

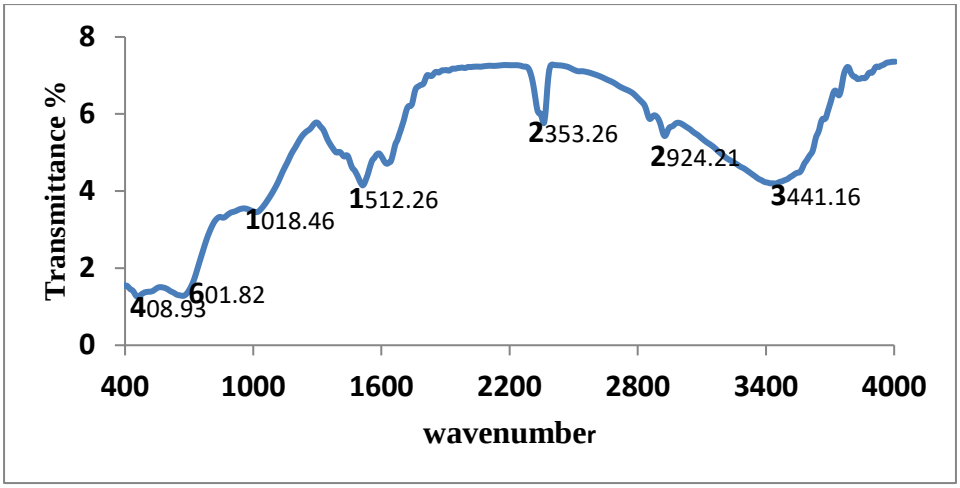

Fig 4. FTIR spectra of $Ni_{0.1}Mg_{0.9}Fe_2O_4$

The absorption band ν_1 is caused by the stretching vibrations of tetrahedral metal-oxygen bond, and the absorption band ν_2 is caused by the stretching vibrations of octahedral metal-oxygen bond. These splitting of the bond occur at around 400 cm^{-1} and 600 cm^{-1} due to Fe^{3+}– O^{2-} vibrations. The absorption band are shown in the expanded view of the FTIR.

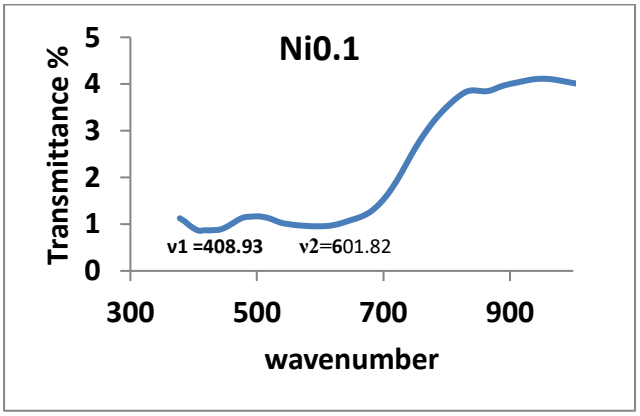

Fig 5. Expanded view of FTIR Spectra

IV.Conclusion

Nickel substituted magnesium spinel ferrites were successfully synthesized by Sol-gel auto combustion method for structural, dielectric ,electric and optical studies. The XRD analysis confirmed that the formation of single phase spinel structure. The mean crystallite sizes for the sintered mixed ferrites were calculated using Debye Sherrer formula indicating that the synthesized ferrites are nano in nature. The decrease of dielectric constant with increase in frequency shows the dielectric dispersion behavior,it was explained on the basis of Maxwell-Wagner two layer models and Koop's theory. FTIR absorption bands observed around 408.91 cm^{-1} and 601.82 cm^{-1} corresponds to tetrahedral and octahedral sites which confirmed the formation of single phase cubic

structure of ferrites. The variations of logσ against $10^3/T$ shows the transition temperature of samples.

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