

Synthesis and Dielectric properties of nanocrystalline Gd³⁺ substituted Nickel-Cadmium ferrites

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ABSTRACT

Nanocrystalline Gd³⁺ substituted Ni-Cd spinel ferrites having general formula Cd_xNi_{1-x}Gd_yFe_{2-y}O₄ with x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 and y = 0.00, 0.05 and 0.1 were synthesized by oxalate co-precipitation method using Sulphates. XRD analysis confirms that all the composition exhibits a single phase cubic spinel structure excluding the presence of any intermediate phase. Room temperature dielectric properties such as dielectric constant, dielectric loss factor, loss tangent, ac conductivity for all samples were investigated as a function of composition and frequency range between 20 Hz to 1 MHz. These dielectric studies indicates that the dielectric constant, dielectric loss and loss tangent for all composition shows usual dielectric dispersion which is due to Maxwell-Wagner type interfacial polarization.

Key Words: Dielectric constant, loss tangent, loss factor, co precipitation, Gd³⁺ substitution.

INTRODUCTION

Spinel ferrites have attracted a lot of attention of researchers due to their wide range of technological applications. Ferrite materials are widely used in many technical fields such as telecommunication, digital memories, multilayer chip inductor, radar and satellite communication, gas sensors, photoelectric devices, microwave devices and biomedical applications [1, 2, 3].

They have good dielectric properties and large number of application from microwave to radio frequency. The dielectric properties of ferrites are depend upon the method of preparation, sintering time and sintering temperature, chemical composition, type and quantity of substituent [4,5]. For high frequency applications, the knowledge of dielectric properties of ferrites is necessary and the parameters such as dielectric constant, dielectric loss, loss tangent and AC conductivity could be evaluated. These dielectric properties provide information about the behavior of localized electric charge carriers leading to greater understanding of mechanism of dielectric polarization in the sample [6]. Generally the ferrite materials were synthesized using conventional ceramic oxide method which suffers from many drawbacks such as requirement of high sintering temperature and more time. The particles obtained from ceramic method are large and non uniform in size resulting in the formation of voids and low density material [7]. To overcome these limitations of ceramic methods, many chemical methods such as co-precipitation, sol-gel, combustion, hydrothermal, oxalate precursor, microwave syntheses have been used for the preparation of high density ferrites [9–14]. The objective of the present work is to synthesize the Ni-Cd and Gd³⁺ substituted Ni-Cd ferrites using co-precipitation method and to study the effect of Gd³⁺ substitution on the dielectric properties.

METHODOLOGY

The ferrite system CdxNi_{1-x}GdyFe_{2-y}O₄ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 with y = 0.0, 0.05, 0.10) was prepared by oxalate co-precipitation method. The high purity AR grade nickel sulphate, cadmium sulphate, gadolinium sulphate and ferrous sulphate were weighed carefully on single pan microbalance to have proper stoichiometric proportion required in the final product. The oxalate co-precipitation method for the preparation of present ferrite system is discussed elsewhere [15]. The dry powder was presintered at 600°C for one hour in air. The pellets of 10 mm diameter were formed with hydraulic press by applying the pressure of 5 tones inch⁻² for five minutes. Finally the prepared pellets were sintered at 1000°C for two hours.

The structural formation was confirmed by taking X-ray diffractograms of all the samples, recorded with Philips PW 3710 powder diffractometer by continuous scanning in the range of 0 to 100°. The dielectric measurements were carried out at room temperature in the frequency range 20 Hz to 1MHz with HEWLETT PACKARD, precision LCR meter model HP 4284A.

The dielectric constant (ϵ') of ferrite sample was calculated using a relation [8, 31].

$$\epsilon' = \frac{C_p \times t}{\epsilon_0 A} \text{ ----- [1]}$$

Where ϵ' is dielectric constant, ϵ_0 is free space permittivity, C_p is capacitance of sample, t is thickness of the sample and A is area of cross section. The dielectric loss tangent ($\tan\delta$) was calculated using a relation

$$\tan\delta = \frac{1}{Q} \text{ ----- [2]}$$

Where Q is the quality factor

The dielectric loss factor (ϵ'') of the ferrite samples is given by

$$\epsilon'' = \epsilon' \times \tan\delta \text{ ----- [3]}$$

The ac conductivity in the frequency range 1 KHz - 1MHz was determined using the values of dielectric constant and dielectric loss tangent in the relation [26]

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan\delta \text{ ----- [4]}$$

Where σ_{ac} is ac conductivity and ω is angular frequency.

RESULT AND DISCUSSION

X-RAY diffraction:

Fig. 1 shows a typical X - ray diffraction pattern for CdxNi_{1-x}GdyFe_{2-y}O₄ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 with y = 0.0, 0.05, 0.10) sintered at 1000°C for 2 hours. All the sintered compositions show all the characteristics reflections of cubic spinel ferrites with most intense [311] reflection which confirms the formation of cubic spinel structure without any signature of secondary phase in sintered ferrite compositions. An absence of any extra peak ensures that the synthesized products are phase pure. The crystallite size of all samples was calculated using the Debye-Scherrer formula and it was found to be in 40 to 50 nm regime.

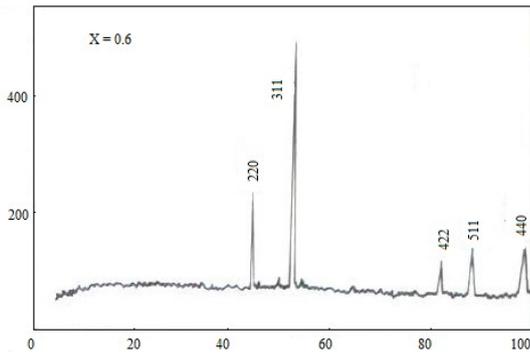


Fig. 1: Typical XRD pattern for $Cd_xNi_{1-x}Gd_{0.05}Fe_{1.95}O_4$ with $x = 0.6$

Compositional variation of ϵ' , ϵ'' , $\tan\delta$ AND σ_{ac} :

Table 1 represents the values of dielectric parameters as a function of composition at frequency 5 KHz for $y = 0.00, 0.05$ and 0.1 . It is observed that all the dielectric parameters show similar trend/ behaviour for all composition series. For $y = 0.00$, the dielectric parameters ϵ' , ϵ'' , $\tan\delta$ decreases with increase in x content. For Gd^{3+} substituted composition with $y = 0.05$, the ϵ' , ϵ'' , $\tan\delta$ increase initially up to $x = 0.2$, then reaches maximum thereafter decreases for its further substitution. For $y = 0.1$, they increase up to $x = 0.4$, thereafter again decrease. Jadhav et al [9] have observed an initial increase in dielectric constant with increase in Zn up to $x = 0.3$ and then decrease with further increase in Zn content for Ni-Zn ferrites and this behaviour is attributed to fluctuating in hopping mechanism between Fe^{3+} and Fe^{2+} ions. Kolekar [16] have investigated the dielectric studies of Gd^{3+} substituted Cu-Cd ferrites as function of

compositions. Iwachi [17] reported that the strong relation between the conduction mechanism and dielectric behaviour of ferrites starting with assumption that the conduction mechanism and polarization are quite similar processes to each other. They observed that an electronic exchange between $Fe^{2+} = Fe^{3+}$ results in local polarization and determines its dielectric behaviour. Hence, similar explanation may be proposed for the compositional variation of dielectric constant in present ferrite system. D. Ravinder [18] concluded that the number of ferrous ions on octahedral site plays a dominant role in the process of conduction mechanism and hence dielectric polarization. The high dielectric constant composition has maximum number of ferrous ions and thus it reveals maximum dielectric polarization in case of Erbium substituted Mn-Zn ferrites. Batoo [19] have observed the decrease in dielectric constant with increasing Al content and concluded that when Al is doped in Mn ferrite, it occupies the octahedral site resulting in decrease in number of Fe ions and is responsible for the polarization in the system. The value of $\tan\delta$ depends on many factors such as Fe^{2+} content, stoichiometry and sintering temperature [20]. Table 1 shows that dielectric loss tangent also depend on the composition. It is also observed that when Gd^{3+} is substituted in Ni-Cd ferrites the dielectric loss tangent decreases. For $y = 0.00$ ac conductivity decrease faster initially, from $x = 0.4$ it decrease very slowly and for $y = 0.05$ & 0.1 , there is no particular trend with composition. It is also observed that after substitution of Gd^{3+} in Ni-Cd ferrites the conductivity decreases.

Table 1: Data on dielectric constant (ϵ'), dielectric loss factor (ϵ''), dielectric loss tangent ($\tan\delta$) and AC conductivity σ_{ac} for $Cd_xNi_{1-x}Gd_yFe_{2-y}O_4$ ferrite system

$x \downarrow$	ϵ'			ϵ''			$\tan\delta$			$\sigma_{ac} \times 10^{-8}$ $\Omega^{-1}cm^{-1}$		
	0.00	0.05	0.1	0.00	0.05	0.1	0.00	0.05	0.1	0.00	0.05	0.1
0.00	269	395	351	121	67	59	0.45	0.17	0.17	33.8	18.6	16.7
0.2	235	459	237	91	94	45	0.38	0.20	0.18	25.2	26.2	12.4
0.4	177	438	339	29	66	56	0.16	0.15	0.16	8.16	18.4	15.6
0.6	150	408	250	20	67	33	0.13	0.16	0.13	5.54	18.7	9.2
0.8	101	381	280	21	42	40	0.20	0.11	0.14	5.79	11.7	11.2
1.0	76	265	255	18	35	47	0.23	0.09	0.18	4.98	9.9	13.1

FREQUENCY VARIATION OF ϵ' , ϵ'' , $\tan\delta$ AND σ_{ac} :

Figs. 2(a, b, c), 3(a, b, c) and 5(a, b, c) shows the variation of dielectric constant (ϵ'), dielectric loss factor (ϵ''), dielectric loss tangent ($\tan\delta$) and AC conductivity (σ_{ac}) as a function of frequency for the present ferrite system with $y = 0.00, 0.05$ and 0.1 respectively at room temperature in the frequency range 1 KHz to 1MHz. From Figs., it is clearly seen that ϵ' , ϵ'' and $\tan\delta$ decrease as the frequency increases showing usual dielectric dispersion. The dispersion is sharp at lower frequencies and almost level off at higher frequencies. This type of nature can be explained by Maxwell [21] Wagner [22] and Koops [28] phenomenological theory. The decrease in dielectric constant at higher frequency can be explained on the basis that the dielectric medium is assumed to be composed of well conducting grains which are separated by non-conducting grain boundaries. The grain boundaries are found to be more effective at lower frequency while ferrite grains are more effective at higher frequency [27]. When electrons reach non conducting grain boundaries through the hopping, the resistance of grain boundary is high; hence electrons pile up at grain boundaries and produce the polarization. At higher frequency, beyond a certain limit, the electron does not follow the alternating field. This decreases the possibility of electron reaching the grain boundary which results decrease in polarization (Maxwell-Wagner [21,22]). The explanation about the polarization process was given by Rabinkin and Novikova [30]. They pointed out that the polarization in ferrite is quite similar to the conduction process. The electron exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ results in local displacement of electron in the direction of applied field, hence determines the polarization. The polarization decreases with increase in frequency is due to the fact that beyond a certain frequency of external field the exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ does not follow the alternating field [29]. The high value of dielectric constant at low frequency is due to Fe^{2+} ions and grain boundary defects [21, 22].

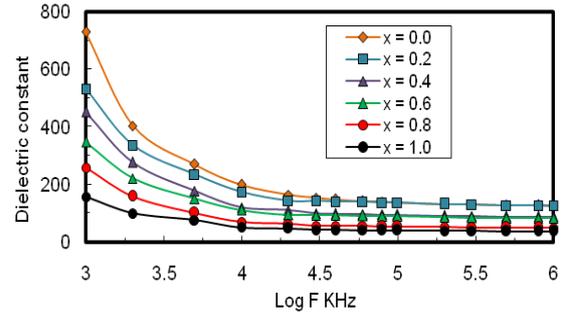


Fig. 2(a): Variation of Dielectric constant with frequency of $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$. For $y = 0.00$.

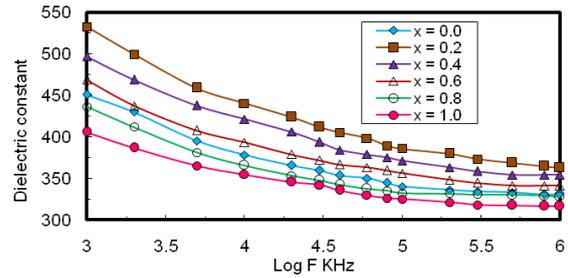


Fig. 2(b): Variation of dielectric constant with frequency of $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$. For $y = 0.05$.

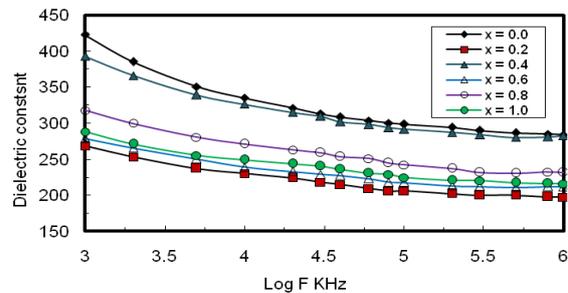


Fig. 2(c): Variation of Dielectric constant with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ For $y = 0.10$.

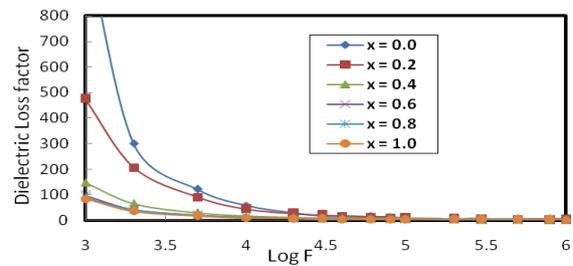


Fig. 3(a) Variation of dielectric loss factor with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.00$

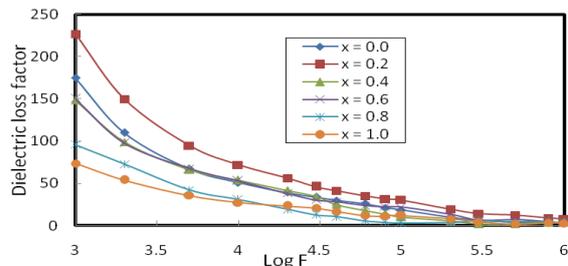


Fig. 3(b): Variation of dielectric loss factor with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.05$

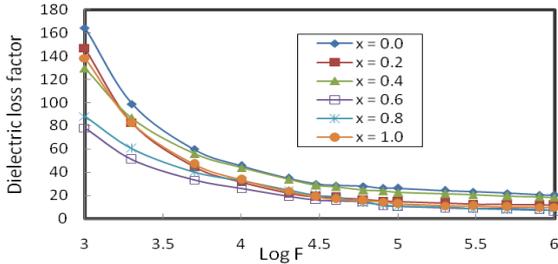


Fig. 3(c): Variation of dielectric loss factor with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.10$

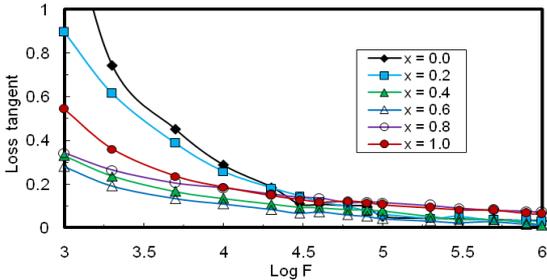


Fig. 4(a): Variation of Dielectric loss tangent with frequency of $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$. For $y = 0.00$.

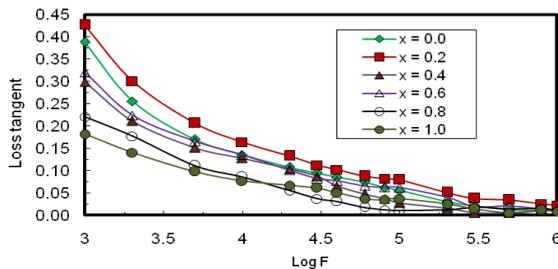


Fig. 4(b): Variation of Dielectric loss tangent with frequency, of $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$. For $y = 0.05$.

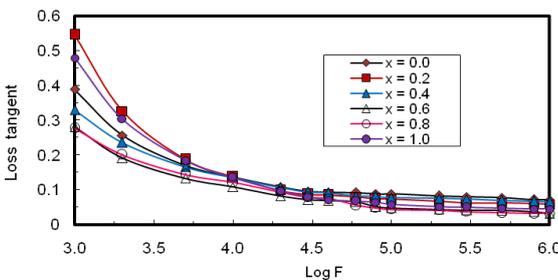


Fig. 4(c): Variation of dielectric loss tangent with frequency of $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$. For $y = 0.10$.

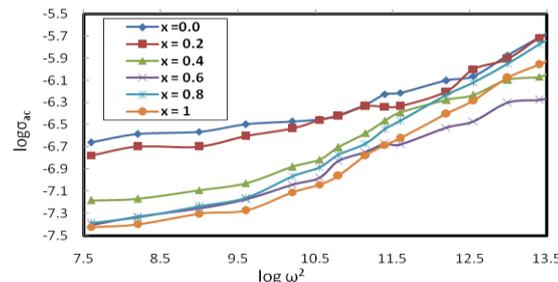


Fig. 5(a) Variation of ac conductivity with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.00$

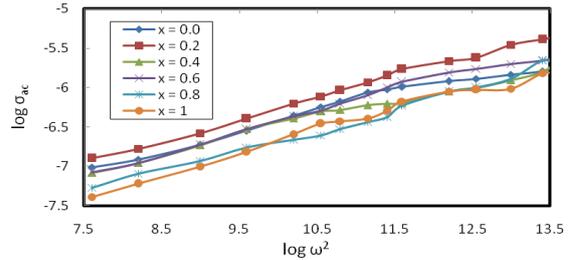


Fig. 5(b) Variation of ac conductivity with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.05$

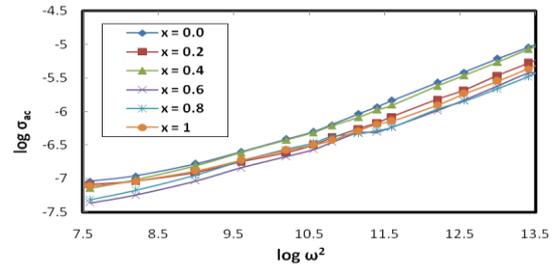


Fig. 5(c) Variation of ac conductivity with frequency for $Cd_xNi_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.1$

It is necessary to understand the conduction mechanism and type of polarons responsible for the conduction. The variation of AC conductivity as a function of frequency for all compositions with $y = 0.00, 0.05$ and 0.1 is represented in Figs. 5(a, b, c). The frequency dependence of ac conductivity is given by Batoo [19]

$$\sigma_{tot.} = \sigma_B(T) + \sigma(\omega, t)$$

$\sigma_B(T)$ is the conductivity due to band conduction and frequency independent function and predominant in low frequency and at high temperature while $\sigma(\omega, t)$ is pure ac conductivity due to hopping process at octahedral site. It is frequency dependent function and predominant in high frequency region and at low temperature. The frequency dependence of the second term can be expressed as $\sigma_{AC} = A\omega^n$, where A is the constant having unit of conductivity, n is temperature dependent function, σ is real part of conductivity and ω is the angular frequency.

It is well known that in large polaron hopping ac conductivity decreases with frequency while in small polaron hopping it increases with frequency [23-25]. Austin and Mott [25] have explained the electrical conduction mechanism in terms of electron and polaron hopping. From the variation of $\log \sigma_{AC}$ versus $\log(\omega^2)$, it is seen that ac conductivity increases with increase in frequency which is a normal behavior for

ferrite materials. For the present ferrite system, the plots of ac conductivity measurement are observed to be linear and indicate the conduction is due to small polaron. The increase in ac conductivity can be explained, as the frequency of applied field increases the conductive grains becomes more active and promoting the electron hopping between two octahedral sites and a transition between Fe^{2+} and Fe^{3+} ions thereby increases the hopping conduction. R. C. Kambale et al [7] have reported a linear response in ac conductivity measurement and attributed to the small polaron type hopping mechanism in Ni-Zn ferrites.

CONCLUSION

The Ni-Cd-Gd ferrite nanoparticles having general formula $\text{Cd}_x\text{Ni}_{1-x}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 with $y = 0.0, 0.05, 0.10$) were successfully synthesized by co-precipitation techniques using sulphates. The X-ray diffraction pattern reveals the formation of single phase cubic spinel structure excluding the presence of any undesirable secondary structure. The dielectric parameters such as dielectric constant (ϵ'), dielectric loss factor (ϵ''), dielectric loss tangent ($\tan\delta$) decrease as the frequency increases exhibiting a normal behaviour of ferrites. The dependence of dielectric properties on frequency of alternating applied field is in accordance with Maxwell-Wagner model and Koops phenomenological theory. AC conductivity (σ_{ac}) increases with increase in frequency. The plots of AC conductivity measurements are almost linear, indicating that the conduction is due to small polaron hopping.

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