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SEM, FTIR AND DIELECTRIC PROPERTIES OF COBALT SUBSTITUTED SPINEL FERRITES

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A series of Gd-substituted Cobalt based ferrites of nominal composition $CoGd_{2x}Fe_{2-2x}O_4$ for x= 0.00-0.25 in steps of 0.05 was produced by conventional ceramic technique. The synthesized samples were characterized by Scanning Electron Microscopy, Fourier transform infrared (FTIR) spectroscopy, and dielectric measurements. SEM was used to study the morphology of samples. The average grain size of the synthesized samples was found in the range8– 12 μm. The dielectric constant, complex dielectric constant and loss tangent of these samples decreased with the increase of Gd-concentration, following the Maxwell–Wagner two-layer model. The reduced dielectric properties make the synthesized materials suitable for high frequency applications.

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Fourier transform infrared (FTIR) spectroscopy, A.C Conductivity,
Cobalt Spinel ferrites.

1. Introduction

Ferrites are the mixed metal oxides with iron oxide as their main component [1]. Ferrites are important materials on account of their electrical and magnetic properties [2]. Ferrites are preferred in the field of electronics and telecommunication industry because of their novel electrical properties which make them useful in radiofrequency circuits, high quality factors, rod antennas, transformer core, read/write heads for high density digital tapes and other devices. Hence it is important to study their dielectric behavior at different frequencies. The dielectric properties of ferrites are dependent on several factors, such as method of preparation, heat treatment, sintering conditions chemical composition, cation distribution and crystallite size [2, 3]. The ferrites behave as inhomogeneous dielectric materials in which individual high-conducting grains are separated by either air gaps or low-conducting layers. Substitution of rare earth ions into the spinel structure lead to structural distortion which modify the electrical transport properties. Electric and magnetic properties are particularly useful in radio frequency region, due to high resistivity, mechanical hardness and chemical stability [4]. Sattar et al. [5, 6] have studied the electrical and magnetic properties cobalt ferrites doped with different rare earth ions and reported the modification in structural properties due to substitution of rare earth ions. The solid state sintering route of producing these materials requires high sintering temperature, as well as long sintering time. It suffers from other disadvantages like chemical inhomogeneity and hard agglomerates of particles [7]. In this paper, the structural, FTIR and dielectric properties of Cobalt based Gadolinium substituted spinel ferrites have been studied.

2. Experimental

The parent oxide materials (99.99% pure) Co_3O_4, Gd_2O_3 and Fe_2O_3 were weighed using electronic balance having an accuracy up to 10^{-4} grams. The weighed amount of parent oxide materials were mixed homogeneously in an agate mortar by grinding for four hours. Before and after this process the mortar and pestle were rinsed with acetone. This powder was then palletized by using hydraulic pressing machine (PAUL-OTTOWEBER). Each pellet was pressed under the pressure of 30KN/mm^2 for about one minute. By using the same procedure the other samples were ground and palletized under the same conditions. In first step, heat treatment of the samples was carried out in a box furnace for about 40 hours at 1250 C° and finally sintered at 1300 C° for 03 hours in tube furnace. After final heat treatment the samples were furnaced cool.

The surface morphology was studied using a Hitachi S4160 scanning electron microscopy (SEM). Samples were coated with carbon prior to SEM analysis. FTIR transmission spectra were taken on Mattson Satellite Infrared Spectrometer from 4000 to 400 cm^{-1} in order to investigate the nature of the chemical bonds formed. Dielectric properties were studied by using RF impedance/Material analyzer Agilent in the frequency range of 1 MHz–3 GHz.

3. Results and Discussions

3.1 Scanning Electron Microscopy (SEM)

To study the surface morphology of the $CoGd_{2x}Fe_{2-2x}O_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25) ferrites, JEOL JSM-840 Scanning Electron Microscope (SEM) was used.

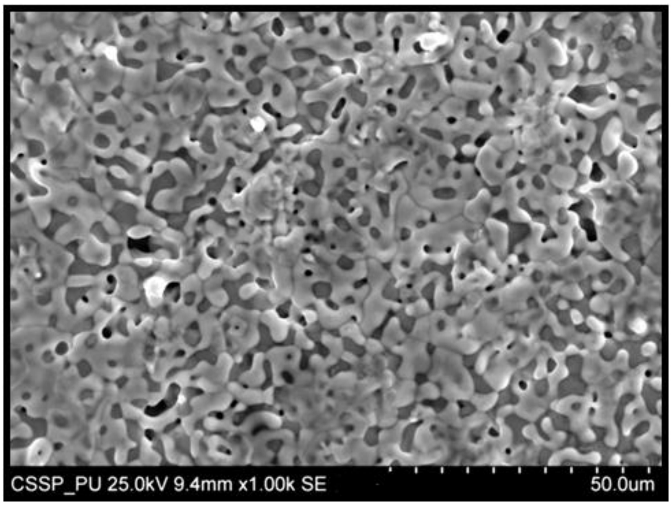

Fig. 1a. SEM micrograph of $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.0) ferrites.*

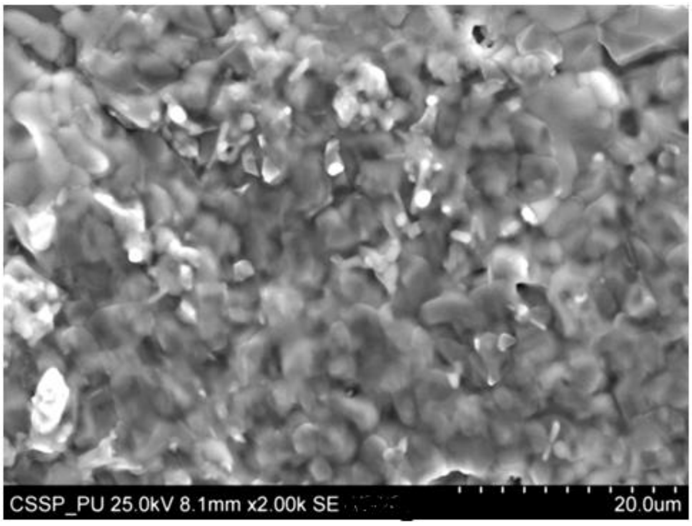

Fig. 1b. SEM micrograph of $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.05) ferrites.*

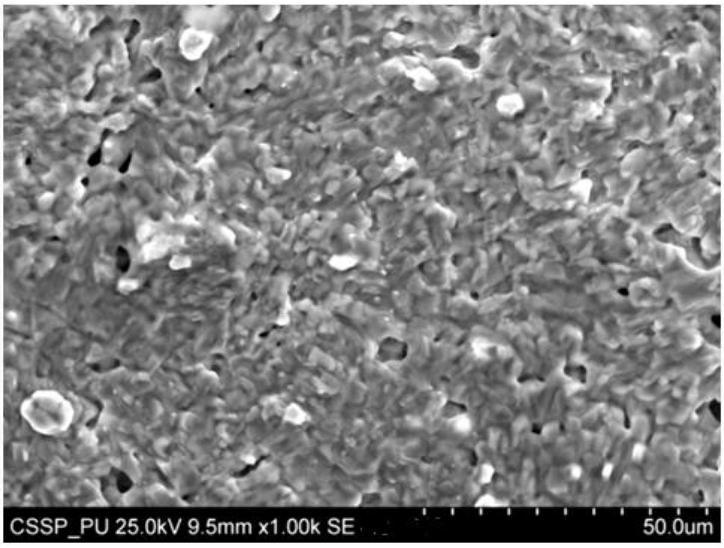

Fig. 1c. SEM micrograph of $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.10) ferrites.*

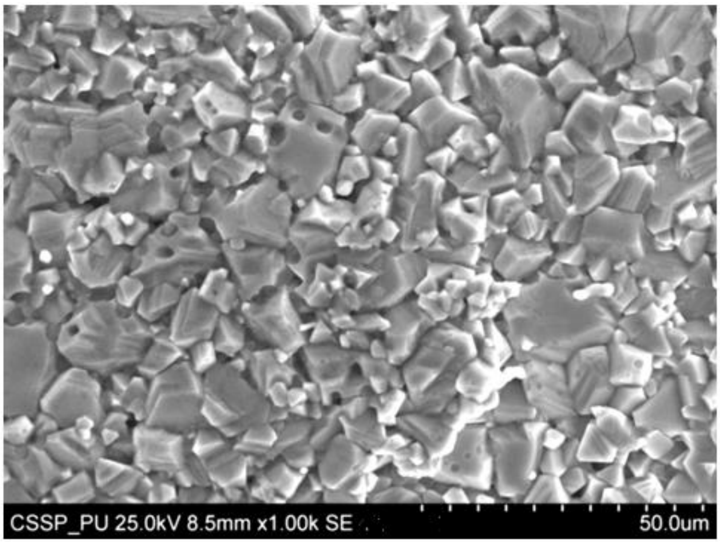

Fig. 1d. SEM micrograph of $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.15) ferrites.*

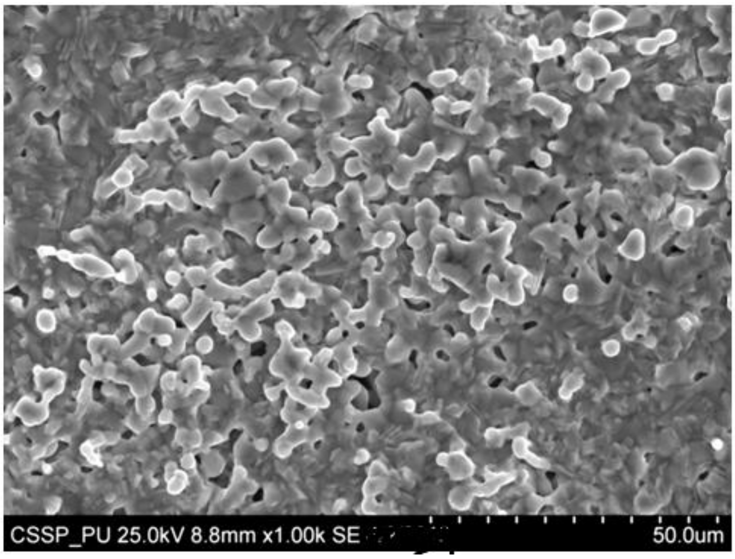

Fig. 1e. SEM micrograph of $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.20) ferrites.*

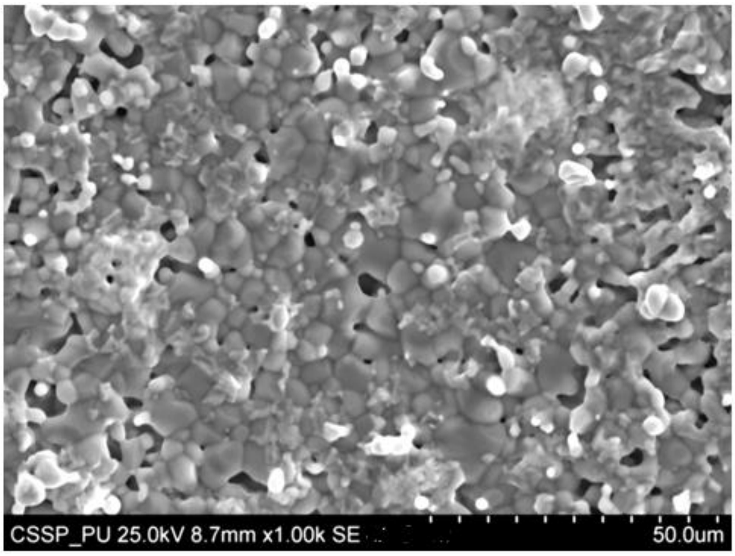

Fig. 1f. SEM micrograph of $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.25) ferrites.*

SEM images of all the ferrite samples are shown in figures.1a–1f, reflecting inhomogeneous grain size distribution, well packed and are almost crack free. Few agglomerates however in the composition x= 0.15 were observed. The appearance of these agglomerates may be attributed to sintering process as a result of chemical reaction. Magnetic forces or even relatively weak Vander Waals bonds might be responsible to hold these agglomerates together [8]. The uniqueness of these agglomerates can be maintained under quite insistent forces. By using the Line-intercept method, average grain size was measured from SEM micrographs [9]. With average grain size falling in the range of 8– 12 μm, they decrease with the increase substitution of Gadolinium element. The mobility of grain boundaries play a vital role in grain growth therefore presence of Gadolinium ions near or at the grain boundaries confines the grain boundary movement subsequently the grain size decreases with increasing Gadolinium substitution [10].

3.2 FT-IR Spectroscopy

The IR spectra show the bands arising from inter atomic vibrations. The structural changes brought about by the metal ions strongly influenced the lattice vibrations. The lattice vibrations also depend on the cations mass, the cation oxygen and the bonding force.

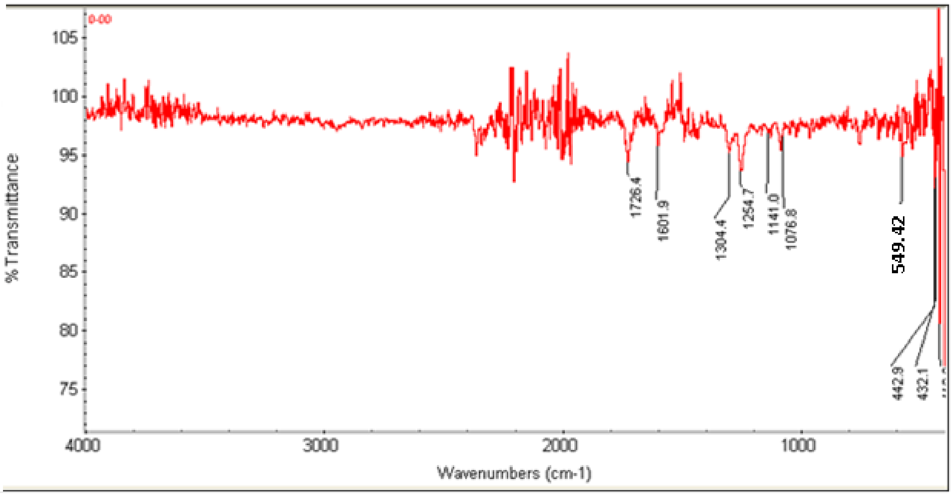

Fig. 2. FTIR Spectra $CoGd_{2x}Fe_{2-2x}O_4$ *(x = 0.15) ferrites.*

Figure 2 shows the representative room temperature FTIR spectrum of for $CoGd_{2x}Fe_{2-2x}O_4$ (x = 0.15) ferrites. The representative spectrum of these ferrites obtained at room temperature manifest absorption peaks located at about 420, 432.1, 442.9, 549.3, 755.9, 1076.8, 1141.0, 1254.7, 1304.4, 1601.9, 1726.4, in the range of 400–4000 cm^{-1}. The inset indicates two absorption bands which is a common feature of all ferrites [11]. The two main absorption bands corresponding to the stretching vibration of the tetrahedral and octahedral sites are around 550 and 400 cm^{-1}, respectively [12]. In figure 2, the bands observed 420, 432, 442 cm^{-1}assigned to octahedral group complexes[13]while the band 549 cm^{-1} attributed to the tetrahedral group complexes. The tetrahedral bands are shifted from lower bands to higher bands i.e., 520–558 cm^{-1} , that can be ascribed to the shifting of Fe $^{3+}$ ions towards oxygen ion on the tetrahedral site which decreases Fe^{3+}–O^2 distances. The band at 1076.8 cm^{-1} is attributed to the formation of Co substituted spinel ferrites [14]. The band at 1652.1 cm1 is ascribed to the presence of absorbed water (H–O–H) [15].

3.3 Dielectric properties

3.3.1 Compositional Effect on Electrical Permittivity

The plot graphs of (ε_o) versus log frequency for $CoGd_{2x}Fe_{2-2x}O_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25) ferrites at room temperature are shown in figure 4. It is concluded from the figure 4, that ε_o decrease with the increase of Gadolinium concentration. And results show that the electronic exchange between Fe^{2+} and Fe^{3+} in local displacements, determining the polarization of charges in these spinel ferrites. Thus, it is the number of Fe^{2+} ions on octahedral sites that play a prominent role in the process of conduction and dielectric polarization. Due to larger ionic radius, Gd^{3+} ions occupy octahedral sites [16]. The concentration of Fe^{3+} ions at B-sites decreases as the concentration of Gadolinium increases up to x = 0.10. At x > 0.10, ε_o and complex dielectric constant decrease remarkable with increasing concentration of Gadolinium. It is due to depicting concentration of iron ions at B-sites which play an important role in dielectric polarization due to the presence of secondary phase. The electron transfer between ferrous and ferric ions will be slowed down i.e. the polarization decreases. Consequently, dielectric (ε_o) decrease with Gadolinium contents [17].

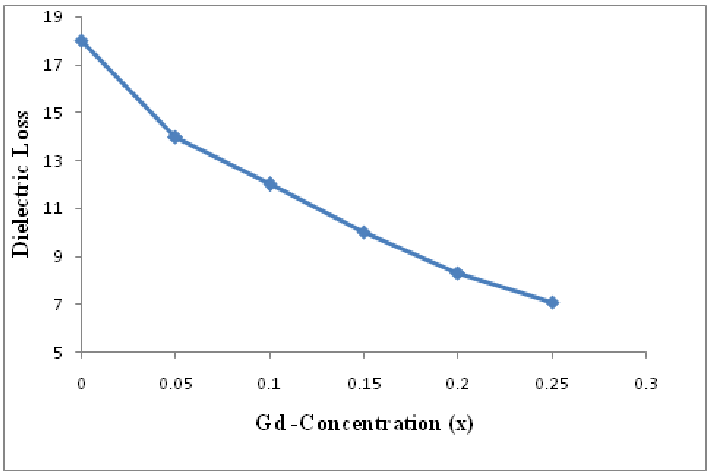

Fig. 3. Dielectric Loss vs Gd-Concentration (x) for $CoGd_{2x}Fe_{2-2x}O_4$ ferrites (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25).

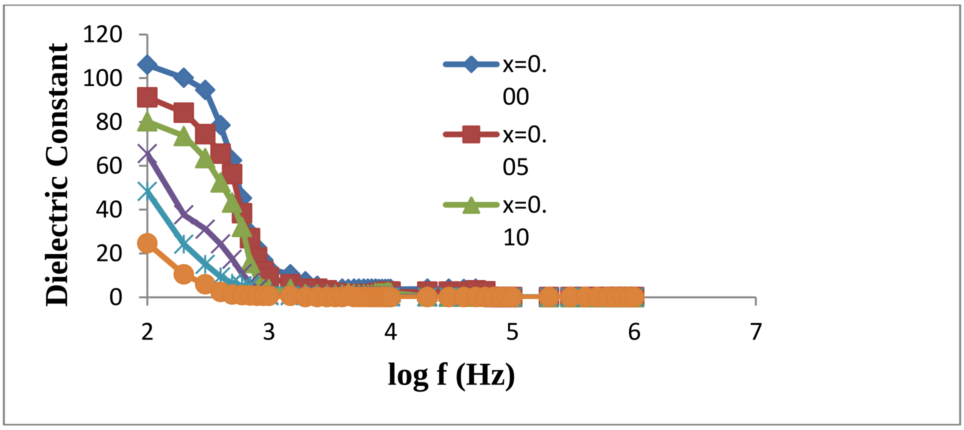

Fig. 4. Dielectric Constant vs log f (Hz) for $CoGd_{2x}Fe_{2-2x}O_4$ ferrites (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25).

3.3.2. Effect of frequency on dielectric and complex dielectric constant

Variations of the real ($\varepsilon^{/}$) and imaginary ($\varepsilon^{//}$) parts of the dielectric constant versus log frequency(Hz) for $CoGd_{2x}Fe_{2-2x}O_4$ ferrites at room temperature for all the samples are plotted in figures 5 and 6. From plots it can be seen that both real and imaginary parts of dielectric constants decrease as the frequency increases. The values of both $\varepsilon^{/}$ and $\varepsilon^{//}$ are high at low frequency and then decreases rapidly with the increase in frequency for all the compositions which is a general trend for all the ferrite samples [18]. This behavior depicts the dispersion due to Maxwell Wagner type interfacial polarization in agreement with Koop's phenomenological theory [18, 19].

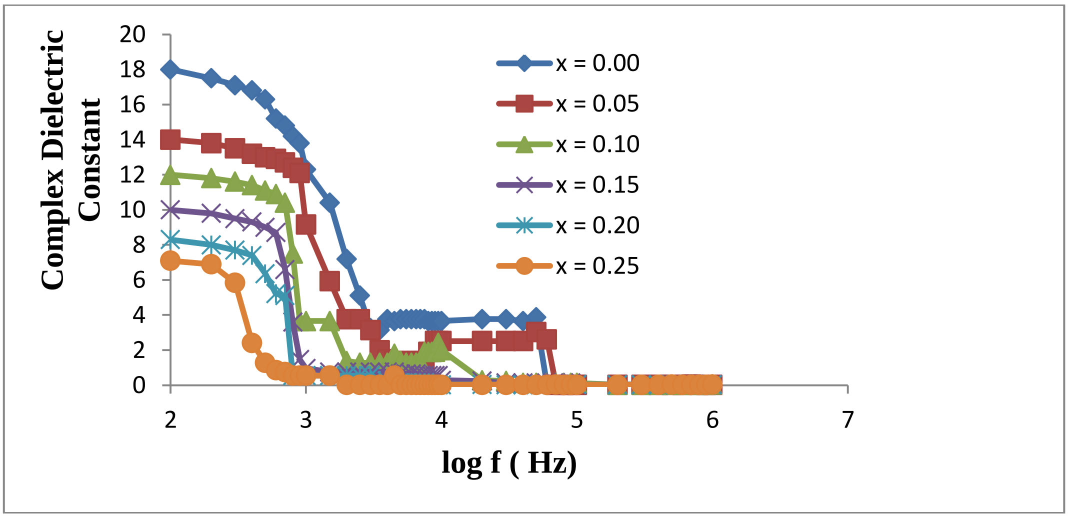

Fig. 5. Complex Dielectric Constant vs log f (Hz) for $CoGd_{2x}Fe_{2-2x}O_4$ *ferrites (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25).*

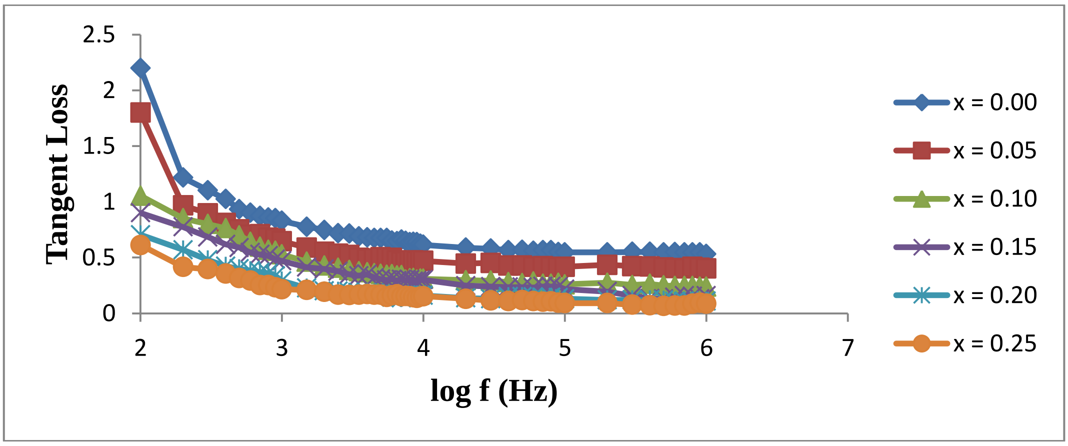

Fig. 6. Tangent Loss vs log f (Hz) for $CoGd_{2x}Fe_{2-2x}O_4$ *ferrites (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25).*

The phenomenon of electron exchange between Fe^{2+} and Fe^{3+} ions give rise to local displacement of charges in the direction of an applied electric field, which subsequently determines the polarization. The polarization decreases substantially with increase in frequency and reaches a constant value due to the fact that beyond a certain frequency of external field, the electron exchange between Fe^{2+} and Fe^{3+} ions cannot follow the alternating field [18, 20-22]. At lower frequency region both interfacial and dipolar polarization play their role where as at high frequency region only the electronic polarization contributes in hopping process. Moreover, the higher values of dielectric constant observed at lower frequencies, may be due to the

predominance of species like Fe^{2+} ions, due to which interfacial dislocation piles-up oxygen vacancies and grain boundary defects etc. The decrease in both $\varepsilon^{/}$ and $\varepsilon^{//}$ with frequency is due to the fact that any species contributing to polarizability are bound to show the lagging behind the applied field at higher frequencies [23-25]. At high frequency, several resonance peaks which are the characteristics of real dielectrics appeared due to undamped dipoles [26].
As for achieving the maximum in dielectric loss of material, condition is;

$$\omega_{\max}\tau = 1 \tag{1}$$

Here $\omega_{\max}\tau = 2\pi f_{\max}$. Relaxation time τ is the jumping probability per unit time 'p' for the ionic/interfacial /electronic polarization as;

$$\tau = \frac{1}{\omega_{\max}} = 2P \tag{2}$$

Eq. (2) depicts that the Debye relaxation process occurs when the rate of hopping of electrons from Fe^{2+} to Fe^{3+} is almost equal to the applied ac frequency and this phenomenon is known as ferromagnetic resonance [27]. Moreover if an ion has got two equilibrium states A and B with the sample potential energies and separated by some potential barrier, the probability of jumping for both the ions stands same. The frequency at which ion changes its position at either side is called its natural frequency. So when both the natural and external applied field frequencies become equal, then maximum electrical energy is transferred to the oscillating ions subsequently there is an increase in power loss. It results to the occurrence of resonance phenomenon and eventually the formation of resonance peaks [26, 28, 29].

3.3.3. Dielectric Loss Tangent

The variation of dielectric loss tangent (tanδ) with frequency for mixed $CoGd_{2x}Fe_{2-2x}O_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25) ferrites is shown in figure. 6. It is clear from the figure 6, that tan δ decreases with increasing frequency. When the frequency of the applied ac electric field is much smaller than hopping frequency of electrons between Fe^{2+} and Fe^{3+} ions at adjacent octahedral sites, the electrons follow the field and hence the loss is maximum. At higher frequencies of the applied electric field, the hopping frequency of the electron exchange between Fe^{2+} and Fe^{3+} ions cannot follow the applied field beyond certain critical frequency and the loss is minimum [30,31].At low frequency (tan δ) is high and decreases rapidly at high frequency in accordance with Koops phenomenological theory. Therefore, it is expected that energy loss is high at low frequency region while it is low at high frequency region [21,22].

3.3.4. AC Conductivity

The variation in ac conductivity (σ_{ac}) of all the samples at room temperature of mixed $CoGd_{2x}Fe_{2-2x}O_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25) ferrites was observed. The ac conductivity data is tabulated by using equation

$$\sigma_{ac} = 2\pi f\varepsilon_o D \tag{3}$$

Here ''f'' is the frequency and ''D'' is the Loss co-efficient. It is seen that ac conductivity of all the samples have same increasing trend at low frequency region however dispersion behavior is exhibited at higher range of frequencies. Both Maxwell–Wagner model and Koops phenomenological theory reveals that ferrite materials consist of conducting grains separated by resistive thin layers of grain boundaries. As conduction processes is related to the dielectric polarization [23]so almost a plane and similar region is observed for all the samples due to affected grain boundaries with high resistance at low frequency region. On the other hand at higher frequency region, grain effect and increasing trend of hopping of charge carriers Fe^{2+}-Fe^{3+}at adjacent octahedral sites play a vital role thereby increasing conductivity [32,33].

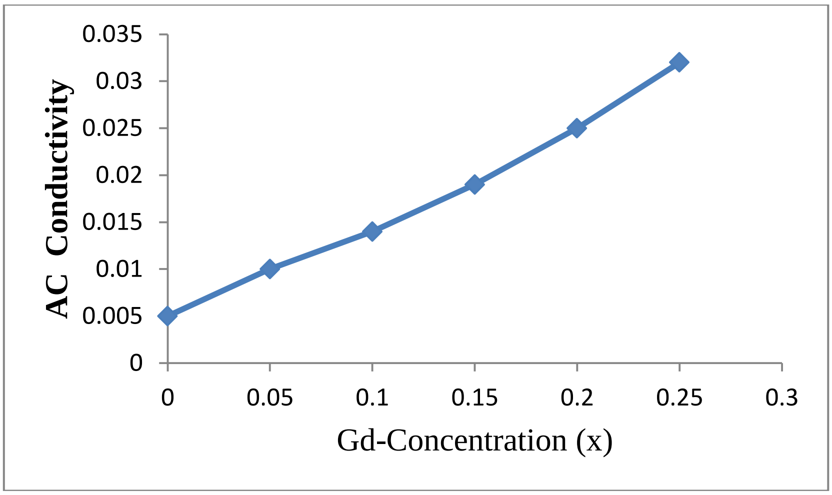

Fig. 7. AC Conductivity (Ω*-cm)*$^{-1}$*vs Gd-Concentration (x) for* $CoGd_{2x}Fe_{2-2x}O_4$ *ferrites (x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25).*

The increase in conductivity vs Gd-content is shown in Figure 7, depicts the fact that magnitude of the electronic exchange depends on the concentration of Fe^{3+}/Fe^{2+} ion pairs located at B-sites [34,35].It is observed from the plots that with the substitution of Gadolinium ac conductivity increases gradually. It increases by the substitution of Rare Earth element from x = 0.00 to 0.25. Maximum value of ac conductivity is achieved for x = 0.25. The increase in conductivity can also be attributed to decrease in porosity. It is observed that at low frequencies ac conductivity shows the grain boundaries contribution however at very high frequency the dispersion trend can be attributed to the conducting nature of grains [36, 37].

4. Conclusions

The Gd^{3+} substituted cobalt ferrites have been prepared successfully by using standard ceramic method at a sintering temperature 13000 °C for 3 h. The average grain size of the synthesized samples was found in the range 8– 12 μm. Two major absorption bands are found in the frequency range $5.49\times10^4 m^{-1}$ to $4.32\times10^4 m^{-1}$. The substitution of Gd^{3+} broadens suggesting the occupancy of Gd^{3+}on octahedral B-site. Dielectric constant and loss decreases rapidly with increasing frequency. All the substituted samples have low dielectric constant than the basic composition without cobalt. The ac conductivity has been discussed in the light of ferrous ion concentration. The ac conductivity showed semiconducting behavior over a wide range of frequency.

References

[1] B. Viswanathan, V.R.K. Murthy, Ferrite Materials, Springer-VerlagNarosa Publishing, House New Delhi,(1990).
[2] J. Smit and H.P. Wijn , “ferrites” Physical properties of ferromagnetic oxides in relation to their technicalapplications(Philips,Eindhoven) ,(1959).
[3] M. A. Dar, K.M.Batoo, V.Verma ,W.A.Siddiui, J.AlloysCompds. **493**, 553(2010).
[4] EMelagiriyappa, HSJayanna, BKChougale, Materials of Chemistry and Physics **112(1)**, 68(2008).
[5] AASatter, Egypt J Sol. **26(2)**, 113–121(2003).

[6] AASatter, AMSamy, J Mat Sci. **37**, 4499 (2002).
[7] KCPatil, SSunder Manoharan, D. Gajpathy,Handbook ofceramic and composites,(1990).
[8]William E. Lee, W. Mark Rainforth, Ceramic Microstructures: Property Controlby Processing, Kluwer Academic Publishers, (1994).
[9]P.S. Aghav, Vinod N. Dhage, Maheshkumar L. Mane, D.R. Shengule, R.G. Dorik, K.M. Jadhav, Physica B **406**, 4350 (2011).
[10]A.B. Gadkari, T.J. Shinde, P.N. Vasambekar, Materials of Chemistry and Physics **114**, 505 (2009).
[11]C.G. Ramankutty, S. Sugunan, Appl. Catal. A: Gen. **218**, 39(2001).
[12]J. Liu, T. Xu, M. Gong, F. Yu, Y. Fu, J. Memb. Sci. **283**, 190(2006).
[13]A. Maqsood, K. Khan, M. Anis-ur-Rehman, M.A. Malik, Journal of Alloys and Compounds **509**, 7493 (2011).
[14] P. Pulišová, J. Kovác, A. Voigt, P. Raschman, Journal of Magnetism and magnetic materials. **341**,93 (2013).
[15] M. Kaur, S. Rana, P.S. Tarsikka, Ceramic International **38**, 4319 (2012).
[16] Tatina N. brusentosva, Viatcheslva D. kuznetsov, Journal of Magnetism and magnetic Materials **311**, 22(2007).
[17] T.M. Meaza, S.M. Attiab, A.M. Abo El Ataa, Journal of Magnetism and magnetic materials **257**, 296(2003).
[18] D. Ravinder, Materials Letter **40**, 205(1999).
[19] B. Ramesh, D. Ravinder, Materials Letter.**62**, 2043(2008).
[20] G. Ranga Mohan, D. Ravinder, A.V. Ramana Reddy, B.S. Boyanov, Materials Letter **40**, 39(1999).
[21] S.F. Mansour, Egypt J. Solids. **28(2)**,211(2005).
[22] ZeljkaCveji, SrdanRaki, StevanJankov, Sonja Skuban, AgneKapor, Journal of Alloys and Compounds **480,** 241(2009).
[23] C.G. Koops, Phys. Rev.**83**, 121(1951).
[24] J.C. Maxwell, Electricity and Magnetism, vol. 1, Oxford University Press, Oxford, Section 328(1929).
[25] M. AsifIqbal, Misbah-ul-Islam, Irshad Ali, Hasan M. Khan, Ghulam Mustafa,Ihsan Ali, Ceramic International **39**,1539(2013).
[26] P.J Harrop, Dielectrics, London Butterworths, (1972).
[27] Muhammad NaeemAshiq, Muhammad Javed Iqbal, Iftikhar Hussain Gul, Journal of Magnetism and magnetic materials **323**, 259(2011).
[28] Muhammad Javed Iqbal, Muhammad NaeemAshiq, Pablo Hernandez-Gomez,Jose Maria Munos, Journal of Magnetism and magnetic. **320**, 881(2008).
[29] Jian-Ping Zhou, Li Lv, Xian-Zhi Chen, J. Ceram. Process.Res. **2(11)**, 263(2010).
[30] U.B. Shinde, Sagar E. Shirsath, S.M. Patange, S.P. Jadhav, K.M. Jadhav, V.L. Patil,Ceramic International **39**, 5227(2013).
[31] M. Ishaque, M.U. Islam, M. Azhar Khan, I.Z. Rahman, A. Genson, S. Hampshire, Physica B **405**, 1532(2010).
[32] M.A. Amer, Phyics. Status Solidi (b) **237(2)**, 459(2003).
[33] A.K.M. AktherHossain, M.A. Rahman, S.F.U. Farhad, B. Vilquinc, HidekazuTanaka, Physica B **406**, 1506(2011).
[34] M.A. Elkestawy, Journal of Alloys and Compounds **492**, 616(2010).
[35] L.G. Van Uitert, J. Chem. Phys. **23**, 1883(1955).
[36] Navneet Singh, Ashish Agarwal and Sujata Sanghi, CurrentAppllied Physics **11**, 783 (2011).
[37] H. Bottger, V.V. Bryksin, Hopping Conduction in Solids, Akademie-Verlag, Berlin, (1985).