Materials Research Express

**PAPER**

Structural, magnetic and dielectric properties of cobalt doped Gd$_{Fe}$O$_3$ orthoferrites

C Sai Vandana and B Hemalatha Rudramadevi

Department of Physics, Sri Venkateswara University, Tirupati-517 502, India

E-mail: drbhrd@gmail.com

**Keywords:** perovskite, orthoferrites, ferromagnetic material, GdFeO$_3$

**Abstract**

In this present work deals with the structural and magnetoelectric behaviour of Cobalt substituted GdFeO$_3$ orthoferrites synthesized by solid state reaction technique. X-ray diffraction and FTIR studies of GdCoxFe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) orthoferrites disclosed the orthorhombic Pbnm structure and Co induced vibrational modes in GdFeO$_3$ orthoferrites respectively. Cationic displacements confirmed from the crystallite size calculations and deviations in lattice parameters affected the magnetic and electrical nature of the GdCoxFe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) orthoferrites. Co substitution promoted a drastic improvement in the magnetic nature of Cobalt substituted GdFeO$_3$ orthoferrites than that of GdFeO$_3$. Antiferromagnetic GdFeO$_3$ has turned out to be strong ferromagnetic material on Co substitution. Higher coercive values 1620.4 Oe and 4035.06 Oe were recorded for GdCo$_{0.2}$Fe$_{0.8}$O$_3$ ferrites whereas for GdFeO$_3$ they were seen to be 527.62 Oe and 360.61 Oe at 300K and 150K temperatures respectively. Dielectric studies revealed a decrease in dielectric constant and loss tangent values with frequency at room temperature. AC conductivity is seen to be increasing at higher frequencies and a maximum value is obtained at Co content of x = 0.2. The significance of cobalt in mutating the structural, magnetic and electrical properties of GdCoxFe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites is clearly seen by making them useful for high frequency applications.

**Introduction**

Rare earth perovskites, ReMO$_3$ (e.g. Re = Gd, Eu, Dy etc and M = transition metal ions) were focused for the past several years because of their intriguing magnetic and electrical properties. Magnetic and electrical properties of many rare earth perovskites have been observed, based on the type of rare earth cation, oxygen non-stoichiometry, and aliovalent cationic substitution. It was earlier reported that europium niobate (EuNbO$_3$) exhibits ferromagnetic nature and due to the presence of oxygen vacancies it gets transformed into a superconductor with a critical temperature about 6 K [1–4]. Among many rare earth perovskites, rare earth orthoferrites with distorted perovskite structure attained importance owing to their notable and unconventional magnetic ground states arises primarily due to challenging interactions among charge, spin and orbital degrees of freedom [5]. The undistorted symmetric structure of these perovskites gets disturbed due to distortion or tilting of BO$_6$ octahedra and (iii) differences in cationic site occupancies due to B ions movement within the polyhedra with respect to oxygen octahedra. These distortions cause a misalignment in the magnetic moments according to applied magnetic field direction [6, 7]. GdFeO$_3$, in Pnma space group is a rare earth orthoferrite with orthorhombic structure. In GdFeO$_3$, symmetric structure is distorted by FeO$_6$ octahedral tilting. A typical feature of GdFeO$_3$ is it shows antiferromagnetic ordering as well as ferroelectric behaviour simultaneously above room temperature due to its mixed ionic and electronic conductivity This peculiar nature of GdFeO$_3$ is due to the interactions between Gd 4f spin and Fe 3d spin resulting in diverse magnetic transitions at different temperatures [8–10]. Apart from this electric and magnetic fields can effectively control the ferroelectric polarization and magnetization in GdFeO$_3$. Yusuke Tokunaga et al had already proposed that the domain wall in GdFeO$_3$ crystal determines the efficiency of their mutual controllability in GdFeO$_3$ crystal and has an important
role in practical devices. Complex impedance spectroscopic technique is employed to correlate the microstructure and electrical properties to analyze the electrical behaviour of these ferrites in wide-ranging of frequencies. Cationic displacements related lattice distortions in Co substituted GdFeO$_3$ results in the coupling of magnetic and electric behaviour when an electric field or a magnetic field is applied. This coupling offers new ways in the design of data storage devices, high frequency applications, sensors, etc [11, 12].

The magnetic and electrically good Co$^{2+}$ inserted into the GdFeO$_3$ matrix induced magnetic phase transitions and changes in electrical behaviour of GdFeO$_3$ at room temperature. In our present work we have shown the impact of Co$^{2+}$ ions on structural, electrical and magnetic properties of GdFeO$_3$ ferrites in turn emphasizing the Co$^{2+}$ ions role in modulating the electrical and magnetic response of GdFeO$_3$ ferrites.

Experimental studies

GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites were prepared by conventional solid state reaction technique from analytical grade Gd$_2$O$_3$, Fe$_2$O$_3$, Co$_3$O$_4$ chemicals. Stoichiometric quantities of Gd$_2$O$_3$ and Fe$_2$O$_3$ were well grinded in an agate mortar for 1 h. A small amount of acetone is added for homogenous mixing and the powders were sintered at 1000 °C for 4h in an electrical muffle furnace. Later on stoichiometric ratios of 0, 10, 20 and 30 mol% Co doped GdFeO$_3$ ferrites were weighed and grinded for 1 h and sintered at 1000 °C for 4 h. The products obtained were sent for further characterizations. For x-ray diffraction analysis a Philips diffractometer with Cu K$_{\alpha}$ radiation is used. Magnetic measurements were taken in an applied magnetic field range of $-15000$ Oe to $+15000$ Oe. Lakeshore, USA, Model 7407 Vibrating Sample Magnetometer (VSM) is used for magnetic measurements at different temperatures. Temperature dependent magnetization studies were performed in zero field cooling (ZFC) and field cooling (FC) modes. In FC mode, the samples were primarily cooled to 20 K and later on the data was recorded during the warming process in a field of 1000 Oe. A PSM 1700 LCR METER is used for dielectric measurements at room temperature in a frequency range of 100 Hz—1 MHz.

Results and discussion

XRD analysis

The x-ray diffraction patterns of GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites were shown in figure 1. The peaks observed were well matched with the JCPDS card No. 47-0067 which is related to Gadolinium Orthoferrite GdFeO$_3$. The distorted perovskite structure of GdFeO$_3$ is due to tilted FeO$_6$ octahedra in which Fe$^{3+}$ ions occupy octahedral sites with six O$^2-$ ions surrounding the Fe$^{3+}$ ions. As Fe$^{3+}$ cation is too small for 12-coordination, this tilting
increases the coulombic attractions in the lattice [13, 14]. These tilts and distortions result orthorhombic GdFeO₃ along with a small amount of cubic garnet phase Gd₃Fe₅O₁₂.

The crystal sizes and lattice parameters of all the GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites were calculated and tabulated in Table 1. The Debye–Schererr formula, 

$$D = \frac{0.9 \lambda}{βCosθ}$$

is used to calculate the crystallite sizes, where D denotes crystallite size in nm, λ is wavelength of Cu-Kα radiation in nm and β is full width at half maximum of intense peak in radians. From Table 1 the crystallite sizes are found to be varying around 45–85 nm with increasing Co concentration. This variation can be explained by the following reasons: (i) the difference in ionic radii of substituted cobalt ions (0.88 Å) and Fe⁺³ (0.79 Å) ions and (ii) the charge fluctuations between Co⁵⁺ and Co⁴⁺ ions. A highest crystallite size of 85 nm was acquired for GdCo₀.₂Fe₀.₈O₃ ferrite. The substitution of cobalt ions brings out a difference in cationic radii and thus the crystallites were inclined to get agglomerated by themselves with higher crystallite sizes resulting in formation of spinel ferrite CoFe₂O₄. The formation of a spinel ferrite phase is confirmed from the appearance of new peak at around 35.5° that is highlighted (in green) in 0.2 and 0.3 mol% concentration of Co²⁺ in figure 1. A decrease in crystallite size at 30 mol% of Co concentration is observed due to the internal strain introduced in the lattice because of crystal point defects, surface defects and dislocations. The internal lattice strain developed due to different ionic size and valence of dopant Co²⁺ ions also affects the unit cell size and volume. To maximize the stabilization energy and to minimize the lattice strain, cationic displacements resulting in an increase in crystallite size of the synthesized ferrites is observed. So the above structural changes have a significant effect on the electrical and magnetic behaviour of the synthesized GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites [15, 16].

**FTIR spectra**

Figure 2 shows the FTIR spectra of GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites. The bands at 1524 cm⁻¹ & 2387 cm⁻¹ are related to the Co–OH bending and O = C = O stretching vibrations. The band around 2925 cm⁻¹ is characteristic to antisymmetric stretching of C–H group in all the synthesized ferrites. Usually, the 400–1000 cm⁻¹ wavenumber range, the broad metal–oxygen bands are observed in the FTIR spectra of all samples. The characteristic absorption peak at 1692 cm⁻¹ may be attributed to C=O stretching frequency. [17–19]. The difference in intensity of the bands arises because of the changes in the bond length of Fe³⁺–O²⁻ at octahedral B-sites and tetrahedral A-sites. Substitution of Co in GdFe₂O₄ creates strain and in turn results in migration of Fe³⁺ ions from tetrahedral to octahedral sites which results in increase of the ionic radii at tetrahedral and octahedral sites [20].

**FESEM**

Figures 3(a) and (b) show FESEM images and EDAX analysis of GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites respectively. In pure GdFeO₃, grains in different orientations were observed through Field Emission Scanning electron microscopy. All the above figures confirm that the grains are hexagonal with flake shape. The geometric morphology revealed there is an appreciable agglomeration because of the magnetostatic interaction between the particles. We have observed that on increasing the Co content in GdFeO₃, a decrease in grain size is observed. The decrease in particle size with increasing Co content is due to the considerable difference in ionic radius of Co compared to the other metal cations present in pure GdFeO₃. The higher ionic radius of Co compared to Fe ions inhibits the formation of larger nuclei during the crystallization process in Co doped GdFeO₃ ferrites. The effect of this physical process leads to a reduction in grain size [20, 21]. Figure 3(b) shows the EDAX elemental analysis of the GdFeO₃ samples with different concentrations of Co. Based on these profiles we have confirmed the presence of the Gadolinium (Gd), Iron (Fe) and Oxygen (O) and Cobalt (Co).

**Magnetic studies**

In GdFeO₃, Gd–Gd, Gd–Fe and Fe–Fe interactions result in its antiferromagnetic behaviour along with a weak ferromagnetic nature. There are two magnetic subsystems Fe³⁺ and Gd⁴⁺ in GdFeO₃ because of different magnetic moment values of Gd(4f⁷6s²) atoms in 4f group and Fe(3d⁶4s²) atoms in 3d group which develops
some challenging phenomena in these materials. At cube corners all Fe ions were coupled to six nearest Fe ions by means of super exchange interaction. A weak ferromagnetism is provoked in antiferromagnetic materials because of the compatibility between tilting of spins and super exchange interaction in FeO₆ octahedra [22, 23]. Among all the interactions, Fe³⁺–Fe³⁺ interaction influences the magnetic behaviour of GdFeO₃ ferrites because of spin coupling of 3d electrons. Cobalt substitution changes the cationic site occupancies of GdFeO₃ lattice and alters the exchange interactions and magnetic nature of the material [24, 25]. Apart from cationic site occupancies, chemical composition and particle sizes also determine the magnetic property of a material. So a difference in particle size also affects the magnetic behaviour of these ferrites. Figure 4 shows the room temperature magnetic hysteresis (M-H) loops of GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites. Pure Gadolinium ferrite is having a coercivity of 527 Oe, which increases to 1020 Oe for GdCo₀.₁Fe₀.₉O₃ at room temperature. The observed enhancement in coercivity is due to the reason that Co²⁺ ion has a feeble crystal field and stronger L-S coupling causing a strong magnetocrystalline anisotropy in Cobalt substituted Gadolinium orthoferrite. From table 2 it is clear that there is a drastic improvement in coercive values and a transition from antiferromagnetic to ferromagnetic behaviour is seen in Co substituted GdFeO₃ at room temperature. The magnetic properties of substituted ferrites mainly arise due to strong superexchange interactions between A and B-sites cations in the inverse spinel ferrites [5, 26]. At higher concentrations the coercive values of GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites were slightly reduced because of the crystal defects and dislocations as discussed in XRD results [27].

Figure 5 shows the temperature dependent magnetization curves in ZFC and FC modes of GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites. The temperature dependent magnetization of GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites was verified in a temperature range of 20 K–300 K in an applied field of 1000 Oe. In undoped GdFeO₃, there is an overlap between the ZFC and FC lines suggesting an antiferromagnetic behaviour as well as there is no magnetic transition in 20 K–300 K temperature range. On Co²⁺ substitution a slight split between ZFC and FC lines is observed initially for GdCo₀.₁Fe₀.₉O₃ and later on the split is seen to be increased drastically suggesting high magnetic moments at lower temperatures and a strong ferromagnetic behaviour of the GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites at higher Co concentrations [28].

Improved magnetic moment values were observed when GdCoₓFe₁₋ₓO₃ (0 ≤ x ≤ 0.3) ferrites are cooled to 150 K and then to 20 K as depicted in figure 6. This behaviour is due to the fact that at low temperatures random movement of atoms and random alignment of magnetic domains were restricted improving the magnetic properties. There is also an increase in the saturation values which can be attributed to the variation in cationic occupancies because of the substitution of Cobalt ions as explained in XRD analysis [29].
Magnetic parameters evaluated from the hysteresis curves such as saturation magnetization $M_s$ (emu/g), remnant magnetization $M_r$ (emu/g) and coercivity $H_c$ (Oe) values for GdFeO$_3$, GdCo$_{0.1}$Fe$_{0.9}$O$_3$, GdCo$_{0.2}$Fe$_{0.8}$O$_3$ and GdCo$_{0.3}$Fe$_{0.7}$O$_3$ ferrites were listed in tables 2 and 3.

![Figure 3](image-url)
Dielectric studies
The dielectric properties of GdCoxFe1-xO3 (0 ≤ x ≤ 0.3) ferrites were studied at room temperature in a range of frequency 100 Hz to 1 MHz. The dielectric constants of the GdCoxFe1-xO3 (0 ≤ x ≤ 0.3) ferrites were calculated from the parallel plate capacitance formula,

\[ \varepsilon' = \frac{Cd}{\varepsilon_0 A} \]

Where C is the capacitance, d is the separation distance between plates and A denotes the area of parallel plates. The value of real part of dielectric constant \( \varepsilon' \) decreases sharply at lower frequencies and attains a constant limiting value at higher frequencies where \( \varepsilon' \) becomes almost frequency independent [30, 31]. Figure 7 shows real (\( \varepsilon' \)) and imaginary parts (\( \varepsilon'' \)) of dielectric constant with frequency at room temperature in GdCoxFe1-xO3 (0 ≤ x ≤ 0.3) ferrites.

The GdCoxFe1-xO3 (0 ≤ x ≤ 0.3) ferrites attain higher values of dielectric constant at lower frequencies due to the piling up of charges at the interfaces of electrodes and the sample. An electric field can modulate the polarization ability of the dipoles accumulated at the interface which affects the dielectric behaviour of the material. Here the strength of the applied field decides the ability of dipoles to orient themselves in the direction of the field. At lower frequencies the dipoles can easily get oriented along the field direction giving larger values of \( \varepsilon' \). The maximum value of \( \varepsilon' \) we achieved was \( 3.2 \times 10^8 \) F/m for GdCo0.1Fe0.9O3. As the frequency increases further, the dipoles cannot cope up with the applied electric field resulting in the decrease of \( \varepsilon' \) values and those values become almost constant later. Hence the dielectric constant \( \varepsilon' \) decreases with an increase in frequency and exhibits almost frequency independent behaviour at higher frequencies. Maxwell–Wagner interfacial model suggests that the dielectric medium consists of conducting grains separated by resistive grain boundaries. Within these grains the opposite charges move in reverse direction due to external field. These moving charges get accumulated at the grain boundaries due to their resistive nature. Thus in the presence of external field, grains

![Figure 4. Magnetic hysteresis (M-H) curves of GdCo0.1Fe0.9O3 (0 ≤ x ≤ 0.3) ferrites at room temperature.](image)

Table 2. Variation of magnetic properties in GdFeO3, GdCo0.1Fe0.9O3, GdCo0.2Fe0.8O3 and GdCo0.3Fe0.7O3 ferrites at room temperature (300k).

| Composition (x) | GdCo0.1Fe1-xO3 formula | Coercivity, Hc (Oe) | Remnant Magnetization, Mr | Saturation Magnetization, Ms |
|-----------------|------------------------|---------------------|-------------------------|-----------------------------|
| 0               | GdFeO3                 | 527.62              | 2.93                    | 39.75                        |
| 0.1             | GdCo0.1Fe0.9O3         | 1040.60             | 6.18                    | 33.56                        |
| 0.2             | GdCo0.2Fe0.8O3         | 1620.40             | 93.93                   | 222.70                       |
| 0.3             | GdCo0.3Fe0.7O3         | 1535.00             | 81.19                   | 197.20                       |

Dielectric studies
The dielectric properties of GdCo0.1Fe1-xO3 (0 ≤ x ≤ 0.3) ferrites were studied at room temperature in a range of frequency 100 Hz to 1 MHz. The dielectric constants of the GdCo0.1Fe1-xO3 (0 ≤ x ≤ 0.3) ferrites were calculated from the parallel plate capacitance formula,
act as electric dipoles. This kind of polarization is termed as space charge or interfacial polarization. In GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites, Co doping creates large number of defects such as interstitials and vacancies at the grain boundaries in GdFeO$_3$ lattice. In perovskites, oxygen vacancies create critical impact on their properties due to oxygen-vacancy-related dielectric relaxation that appears typically in low frequency region. These defects induce charge carriers with different time constants. Increased charge carrier density by Co substitution is the main reason for high dielectric constant values in GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites [32, 33].

The frequency versus tanδ curves at room temperature for GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites are shown in figure 8. Tangent loss represents the dissipated energy in a dielectric system. The dispersion behaviour of

![Figure 5. Zero field cooled (ZFC) and field cooled (FC) temperature dependent magnetization measurements for GdFeO$_3$, GdCo$_{0.1}$Fe$_{0.9}$O$_3$, GdCo$_{0.2}$Fe$_{0.8}$O$_3$ and GdCo$_{0.3}$Fe$_{0.7}$O$_3$ ferrites under applied magnetic field of 1000 Oe.](image1)

![Figure 6. Magnetic hysteresis (M-H) curves of GdFeO$_3$, GdCo$_{0.1}$Fe$_{0.9}$O$_3$, GdCo$_{0.2}$Fe$_{0.8}$O$_3$ and GdCo$_{0.3}$Fe$_{0.7}$O$_3$ ferrites at 150k and 20k.](image2)
GdCo$_x$Fe$_{1-x}$O$_3$ ($x = 0, 0.1, 0.2, 0.3$) ferrites is similar to that of the dielectric constant. At higher frequency the losses are found to be low due to domain wall motion whereas at low frequencies their rotation predominates $^{[32]}$. 

Table 3. Variation of magnetic properties in GdFeO$_3$, GdCo$_0.1$Fe$_{0.9}$O$_3$, GdCo$_{0.2}$Fe$_{0.8}$O$_3$ and GdCo$_{0.3}$Fe$_{0.7}$O$_3$ ferrites at low temperature (20k).

| Composition ($x$) | GdCo$_x$Fe$_{1-x}$O$_3$ formula | Coercivity, $H_c$ (Oe) | Remnant Magnetization, $M_r$, $x \times 10^{-3}$ (emu) | Saturation Magnetization, $M_s$, $x \times 10^{-3}$ (emu) |
|------------------|----------------------------------|------------------------|---------------------------------|---------------------------------|
| 0                | GdFeO$_3$                        | 360.61                 | 33.02                           | 413.23                          |
| 0.1              | GdCo$_{0.1}$Fe$_{0.9}$O$_3$       | 1065.00                | 15.63                           | 197.78                          |
| 0.2              | GdCo$_{0.2}$Fe$_{0.8}$O$_3$       | 4035.06                | 146.67                          | 427.83                          |
| 0.3              | GdCo$_{0.3}$Fe$_{0.7}$O$_3$       | 3904.00                | 130.80                          | 382.70                          |

Figure 7. Dependence of the real ($\varepsilon'$) and imaginary parts ($\varepsilon''$) of dielectric constant on the frequency for GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites at room temperature.

Figure 8. Dielectric loss in GdCo$_x$Fe$_{1-x}$O$_3$ ($0 \leq x \leq 0.3$) ferrites with frequency variation at room temperature.
AC conductivity of GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites is calculated using the subsequent equation,

$$\sigma_{ac} = \frac{\omega \varepsilon_0\varepsilon'}{\tan \delta}$$

where $\varepsilon'$ is real permittivity, tan$\delta$ represents tangent loss, $\omega$ is angular frequency and $\sigma_{ac}$ is AC conductivity.

Alteration of ac conductivity with frequency ($\sigma_{ac}$) in GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites at room temperature is shown in figure 9. The plots were showing an initial decrease at lower frequencies but an increase in conductivity with dopant concentration is seen at higher frequencies. The highest ac conductivity value obtained is $8 \times 10^2$ (Ω cm)$^{-1}$. Co$^{2+}$ ions in GdFeO$_3$ lattice cause cationic displacements due to different ionic radii and results in alteration of AC conductivity. In low-frequency region dc conductivity is observed whereas in high-frequency region ac conductivity is observed. The electrical conductivity majorly depends on the number of free charge carriers and their portability. According to the ion-hopping process, the ionic conduction in Co doped GdFeO$_3$ ferrites arise because of the migration of replaceable channels and cavities of the grains boundaries and grains [33, 34]. This alteration of AC conductivity can be predicted in the following ways i) Fe$^{3+}$ to Fe$^{2+}$ and Co$^{2+}$ to Co$^{3+}$ conversions to sustain electrical neutrality. ii) Formation of an oxygen deficient phase and iii) both of the above changes may occur at the same time to maintain charge neutrality. In GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites it is expected that certain Fe$^{3+}$ ions are converted to Fe$^{2+}$ for enhancing the conductivity values [35].

Impedance spectroscopy is a great tool to study the electrical properties of different kinds of materials. Figure 10 represents the variation of the (a) real ($Z'$) and (b) imaginary ($Z''$) part of the impedance varying with frequency in GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites at room temperature. The (a) real ($Z'$) and (b) imaginary ($Z''$) part of the impedance were calculated using the formulae

$$Z' = \frac{R}{1 + (\omega RC)^2}$$

$$Z'' = \frac{\omega RC}{1 + (\omega RC)^2}$$

The dynamics of ac electrical conductivity is further studied from impedance spectral analysis of GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites in terms of grains and grain boundaries. It is observed that the $Z'$ and $Z''$ values are typically higher at low frequency region due to space charge polarization [36, 37]. It is also observed that the $Z'$ and $Z''$ steadily decrease with increasing frequency implying an increase in ac conductivity. The merger of the spectra at high frequencies, regardless of Co concentration, suggests a possible release of space charge and subsequent lowering of barrier properties in GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites. Higher impedance is seen on GdFeO$_3$ rather than in cobalt substituted GdFeO$_3$ ferrites. Finally, a good correlation is seen between the conductivity and complex impedance plots of the Co doped GdFeO$_3$ ferrites. A systematic decrease in impedance values with Co concentration can be related to the presence of more number of charge carriers in GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites at higher concentrations [38, 39, 40].

Figure 9. AC Conductivity profiles of GdCo$_x$Fe$_{1-x}$O$_3$ (0 ≤ x ≤ 0.3) ferrites at room temperature.
References

C Sai Vandana

Conclusions

Polycrystalline GdCo$_{x}$Fe$_{1-x}$O$_3$ $(0 \leq x \leq 0.3)$ ferrites were synthesized by solid state reaction method. XRD and FTIR studies revealed the structural changes induced in GdFeO$_3$ ferrites due to cobalt substitution. A maximum crystallite size of 86 nm for GdFe$_{0.8}$Co$_{0.2}$O$_3$ ferrite was obtained because of the difference in ionic radii of Co$^{2+}$ (0.88 Å) and Fe$^{3+}$ (0.79 Å) ions. This variation in ionic radii of host and dopant ions introduced defects and dislocations in the host lattice thereby modifying their magnetic and electrical properties. In Fourier transform infrared spectra two prominent absorption peaks were noticed at 539 and 1523 cm$^{-1}$. These peaks correspond to Gd-O and Co-O vibrations respectively. Antiferromagnetic nature of GdFeO$_3$ at room temperature is revealed from M-H hysteresis curves. It is also clear that substitution of Co$^{2+}$ provoked a magnetic phase transition from antiferromagnetic to strong ferromagnetic nature in GdCo$_{x}$Fe$_{1-x}$O$_3$ $(0 \leq x \leq 0.3)$ ferrites due to the long range magnetic ordering of domains at higher concentrations of Co. Impedance measurements revealed the dominance of grain boundary mechanism in conduction behaviour and the charge hopping between localized states. The maximum ac conductivity obtained is $8 \times 10^2$ (Ω cm)$^{-1}$. The obtained results have proved that there is a good enhancement in electrical properties and doping of Co controls the dielectric behaviour in GdCo$_{x}$Fe$_{1-x}$O$_3$ $(0 \leq x \leq 0.3)$ ferrites. The results obtained demonstrated the role of Co concentration in altering the microstructure, magnetic and electrical properties GdCo$_{x}$Fe$_{1-x}$O$_3$ $(0 \leq x \leq 0.3)$ ferrites with promising use in data storage devices, sensors and high frequency applications.

ORCID iDs

C Sai Vandana  https://orcid.org/0000-0002-7108-5887

References

[1] Zong Y, Fujita K, Akamatsu H, Murai S and Tanaka K 2010 J. Solid State Chem. 183 168–72
[2] Zubkov V G, Tryutynnik A P, Pereliasv V A, Shveikin G P, Kohler J, Kremer R K, Simon A and Svensson G 1995 J. Alloys Compd. 226 24–30
[3] Ishikawa K, Adachi G and Shiokawa J 1981 Mater. Res. Bull. 16 419–27
[4] Strukova G K, Shovkun D V, Zverev V N, Batov I E, Zverkov S A and Khasanov S S 2001 Physica C 351 363–70
[5] Biswas S, Khan M H, Pal S and Bose E 2013 J. Magn. Magn. Mater. 328 31–4
[6] Ahmed M A, Mansour S F, El-Dek S I and Abu-Abdeen M 2014 Mater. Res. Bull. 49 352–9
[7] Ribi D, Marlasca F G, Reinoso M, Bonville P and Levy P 2012 Mater. Sci. Eng. B 177 471–5
[8] Wgilusz R J, Kordek K, Malecka M, Ciupka A, Ptak M, Pazik R, Pohl P and Kaczorowski D 2015 Dalton. Trans. 44 20067–74
[9] Shibeshi P T and Veeraiah V 2014 J. Phys. Chem. Solids 75 1075–9
[10] Wu A, Wang Z, Wang B, Ban X, Jiang L, Xu J, Yuan S and Cao S 2014 Solid State Commun. 185 14–7
[11] Tokunaga Y, Iguchi S, Arima T and Tsuchiya Y 2008 Phys. Rev. Lett. 101 3–6
[12] Kumar M, Sati P C and Chhoker S 2014 J. Mater. Sci.: Mater. Electron. 25 5366–74
[13] Prakash B J, Rudramadevi B H and Buddhudu S 2014 Ferroelectr. Lett. Sect. 41 110–22
[14] Dolgos M, Adem U, Wan X, Xu Z, Bell J, Conyn T P, Stevenson T, Bennett J, Claridge J B and Rosseinsky M J 2012 Chem. Sci. 3 1426–35
[15] Moure C and Pena O 2013 J. Magn. Magn. Mater. 337–338 1–22
Fabbiyola S, Sailaja V, Kennedy L J, Bououdina M and Vijaya J J 2017 J. Alloys Compd. 694 522–31
Bennet J, Tholkappiyam R, Vishistaa K, Jaya N V and Hamed F 2016 Appl. Surf. Sci. 383 113–25
Djaja N F, Montja D A and Saleh R 2013 Adv. Mater. Phys. Chem. 3 33–41
Mishra M K 2016 Chem Sci Trans. 5 770–4
Routray K L, Saha S and Behera D 2019 Phys. Status Solidi b 256 1800676 (1-14)
Karmakar R, Neogi S K, Banerjee A and Bandyopadhyay S 2012 Appl. Surf. Sci. 263 671–7
Sharma Y, Sahoo S, Perez W, Mukherjee S, Gupta R, Garg A, Chatterjee R and Katiyar R S 2014 J. Appl. Phys. 115 183907 (1-9)
Shah J and Kotnala R K 2012 Scr. Mater. 67 316–9
Yadav S P, Shinde S S, Kadam A A and Raipure K Y 2013 J. Alloys Compd. 555 330–4
Heiba Z K, Imam N G and Mohamed M B 2015 J. Mol. Struct. 1095 61–8
Puli V S, Adireddy S and Ramana C V 2015 J. Alloys Compd. 644 470–5
Khomchenko V A, Shvartsman V V, Borisov P, Kleemann W, Kiselev D A, Bdikin I K, Vieira J M and Kholkin A L 2009 Acta Mater. 57 5137–45
Sun S, Chen Z, Wang G, Geng X, Xiao Z, Sun Z, Peng R and Lu Y 2018 Sci. Rep. 8 871
Wang M, Zeng L and Chen Q 2011 Dalton Trans. 40 597–601
Saleem M and Varshney D 2017 J. Alloys Compd. 708 397–403
Sultan K, Ikrarn M, Division M S, Asaf A, Marg A and Delhi N 2014 Vacuum 99 251–8
Ashokkumar M and Muthukumaran S 2015 J. Lumin. 162 97–103
Routray K L, Sanyal D and Behera D 2017 J. Appl. Phys. 122 224104
Karmakar S, Panda B, Sahoo B, Routray K L, Varma S and Behera D 2018 Mater. Sci. Semicond. Process. 88 198–206
Ahmed M A, Mansour S F, El Dek S I and Abdeen M A 2014 Mater. Res. Bull. 49 352–9
Izquierdo J I, Bolanos G, Zapata V H and Moran O 2014 Curr. Appl Phys. 14 1492–7
Murugesan C and Chandrasekar C 2015 RSC Adv. 5 73714–25
Kadam A A, Shinde S S, Yadav S P, Patil P S and Raipure K Y 2013 J. Magn. Magn. Mater. 329 59–64
Velhal N R, Patil N D, Shelke A R, Deshpane N G and Puri V R 2015 AIP Adv. 5 097166 (1-11)
Routray K L and Behera D 2018 J. Mater. Sci.: Mater. Electron. 29 14248–60