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**Investigation of negative magnetization and impedance spectroscopy of Sm-substituted gadolinium iron garnets**

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**Abstract**

Samarium substituted gadolinium iron garnet \( (\text{Gd}_{3-x}\text{Sm}_x\text{Fe}_5\text{O}_{12}) \) samples were synthesized in pure-phase form by solid-state chemical reaction method. The lattice constant increases (12.4624 Å to 12.5211 Å) with Sm-concentration. Magnetization measurements show an increase in ferrimagnetic (FIM) transition temperature \( (T_C = 567 \text{ K to 575 K}) \) and a decrease in magnetic compensation temperature \( (T_{comp} = 286 \text{ K to 70 K}) \) upon Sm-substitution. In addition to magnetic compensation, an interesting negative magnetization under field-cooled condition is achieved for a sample with \( x = 2.0 \), and it has been explained in terms of enhanced magnetic anisotropy due to Sm-substitution. A significant increase in saturation magnetization is attained at room temperature by Sm-substitution. Frequency dependence of complex impedance shows relaxation behavior and the relaxation frequency follows the Arrhenius power-law, along with an anomaly around FIM \( T_C \). Such anomaly is ascribed to magneto-electric coupling.

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**1. Introduction**

Rare-earth iron garnets (RIG: \( \text{R}_3\text{Fe}_5\text{O}_{12} \)) are of paramount importance in the field of research due to their noteworthy applications in memory storage, microwave devices, oscillators, waveguides and magneto-optical isolators [1–3]. Gadolinium iron garnet (GIG) is an important material in RIG series, having excellent magnetic and dielectric properties as well as potential applications in various magneto-optical, spintronic and magneto-caloric devices [4, 5]. The GIG is ferrimagnetic (FIM) in nature with the transition temperature, \( T_C \sim 550 \text{ K} \). The moments of \( \text{Fe}^{3+} \) ions located in octahedral \( (a) \) and tetrahedral \( (d) \) sites are coupled antiferromagnetically and the resultant moment is antiparallel to that of \( \text{Gd}^{3+} \) ions at dodecahedral \( (c) \) site [6–9]. Such coupling leads to a magnetic compensation around \( T_{comp} = 288 \text{ K} \). Similar magnetic compensation has been reported in other RIG (\( \text{R} = \text{Er}, \text{Dy}, \text{Ho} \) and \( \text{Tb} \)) and spinel ferrites [10, 11]. Even though the magnetic compensation is observed in the above discussed RIG, they generally do not show any negative magnetization for \( T < T_{comp} \); rather, the magnetization starts increasing as the temperature is reduced further. This can be attributed to the flipping of magnetic spins of all the three magnetic sublattices as a result of relatively small magnetic anisotropy [6, 12, 13]. Alternatively, some of the RIG such as Bi-substituted \( \text{Tb}_3\text{Fe}_5\text{O}_{12} \) and \( \text{Ho}_3\text{Fe}_5\text{O}_{12} \), exhibit negative magnetization below \( T_{comp} \) [14, 15]. In addition to RIG, several other systems such as spinel ferrite, spinel chromite, orthochromite, manganite, molecular magnets, etc., are known to show negative magnetization but with varied mechanisms. In spinel ferrites and chromites, the negative magnetization has been primarily explained in terms of the different temperature dependence of sublattice magnetization [16–18]. Orthoferrites and orthochromites exhibit a competition between the weak ferromagnetic (FM) moment due to spin canting and the paramagnetic (PM) moment under negative internal field; which eventually leads to magnetization reversal [19–21]. The different temperature dependence of spin and orbital moment of rare-earth elements and the significant moment of polarized conduction electrons result in negative magnetization in intermetallic alloys [22–24].

Besides magnetic properties, RIG exhibits novel electrical properties. Huang et al. [25] observed two dielectric relaxation peaks in RIG \( (\text{R} = \text{Eu and Gd}) \) at low and high-frequency regions. They are ascribed to
doubly ionized oxygen vacancies and electron hopping between $Fe^{2+} - Fe^{3+}$ ions, respectively. Ferroelectric materials, like $ATiO_2$ ($A = Ba, Pb$) are known to exhibit large dielectric constant ($\varepsilon' > 15$) as a result of their permanent dipoles. However, non-ferroelectric $CaCu_3Ti_4O_{12}$ is also known to exhibit a large dielectric constant due to the presence of Maxwell-Wagner type polarization [26–28]. The large dielectric constant usually coexists with large dielectric loss in many materials. Nevertheless, Huang et al. [29] reported a large dielectric constant as well as low dielectric loss in a broad temperature and frequency range in polycrystalline $Sm_2Fe_{17}O_{12}$. Moreover, magneto-dielectric properties have been observed in some of the RIG due to the presence of $Fe^{3+}$ and $Fe^{2+}$ ions [30–32]. The dielectric relaxation in these materials is assigned to the carriers hopping across mixed valent Fe ions, oxygen vacancies, Maxwell-Wagner relaxation, etc. [33–35]. Magneto-electric coupling is reported in a few RIG, based on the observed dielectric anomaly close to magnetic transition [36–39]. Therefore, the detailed investigation of magnetic and electrical properties of GIG is required, and the prime motivation behind this study of Sm-substitution at Gd site is to tune the structural, magnetic, as well as electrical properties. Such substitution can give rise to an increase in saturation magnetization along with negative magnetization behavior.

2. Experimental details:

Polycrystalline $Gd_{1-x}Sm_xFe_{17}O_{12}$ (Sm-GIG) samples with $x = 0, 0.5, 1.0, 2.0$ and $3.0$ were synthesized by the solid-state chemical reaction method as described in [37, 38]. The as-prepared samples were finally sintered at 1400 °C for 8 h in cylindrical pellet form. The crystal structure analysis and microstructural characterization were carried out using Rigaku (TTRAX-III) x-ray diffractometer (XRD) with x-ray wavelength of $\lambda = 1.5406$ Å and Zeiss (SIGMA model) Field Emission Scanning Electron Microscope (FESEM), respectively. The oxidation state of cations was determined with the help of an x-ray photoelectron spectrometer (Versa Probe II (PHI 5000), FEI Inc.) with Al Kx source. The temperature and field dependence of magnetization were measured using Lakeshore (7410 model) make Vibrating Sample Magnetometer (VSM). An LCR meter of Wayne Kerr (model number 4300) was used for complex impedance ($Z'$ and $Z''$) measurements in the frequency range of $10^2$–$10^5$ Hz at various temperature ranging from 303 K to 623 K. The XRD patterns were analyzed by the FullProf software based on the Rietveld refinement technique [40].

3. Results and discussion

3.1. Structural analysis

Figure 1(a) illustrates the XRD patterns of Sm-GIG samples for $x = 0, 0.5, 1.0, 2.0$ and $3.0$. All the patterns were Rietveld refined using $IA3d(O_0^g)$ space group and they confirm the single-phase nature of samples. Figure 1(b) shows the Rietveld refined XRD pattern (solid line) for $x = 2.0$ sample. The lattice constant $a$, and the unit cell volume $V$, determined from the above analysis, increase with Sm-concentration ($x$) as shown in figure 1(c), and they are consistent with larger Sm$^{3+}$ (1.02 Å) ions substituting at Gd$^{3+}$ (0.94 Å) site. The site occupation values of various cations determined from the above analysis are also consistent with starting composition. Figure 2 illustrates the bond length across $Fe(a) – Fe(d)$ ions, $Gd(c) – Fe(d)$ ions and $Gd(c) – Fe(a)$ ions and bond angles of $Fe(a) – O – Fe(d)$, $Gd(c) – O – Fe(d)$ and $Gd(c) – O – Fe(a)$ networks as a function of $x$. It is observed that the obtained bond length values increase with Sm-concentration in accordance with the substitution of larger Sm$^{3+}$ ions at the Gd$^{3+}$ site and the related stretching of interatomic distance. The $Fe(a) – O – Fe(d)$ bond angle is found to be increased from 126.2° ($x = 0$) to 127.8° ($x = 3.0$), which influences the magnetic properties as discussed later. The bond length and the bond angle values of the parent compound ($x = 0$) are comparable with the literature [41].

Figures 3(a), (b) show typical microstructural images of $x = 0.5$ and 2.0 samples. The average grain size values are 1.4, 4.2, 4.7, 5.8 and 7.2 μm for $x = 0, 0.5, 1.0, 2.0$ and 3.0, respectively. The possible reason for grain growth due to Sm-substitution is the reduction in melting point and hence, better mobility of grain boundaries leading to a larger grain size [42]. The presence of Gd/Sm and Fe elements has been witnessed as per the typical EDS spectra (figures 3(c), (d)) collected from the microscopic surface area marked in figures 3(a), (b) for $x = 0.5$ and 2.0 samples. The chemical composition is consistent with the nominal starting composition. For example, cationic ratio $Gd/Sm/Fe = 2.47: 0.48: 4.99$ and 0.98: 1.97: 4.98 for $x = 0.5$ and 2.0, respectively. The density of prepared pellets, determined from the Archimedes principle, shows that they lie in the range of 80 to 90% of the theoretical density.

Figures 4(a)–(d) shows the XPS spectra for Sm-GIG with $x = 1.0$ and 2.0. The binding energy peaks corresponding to $4d_{xz}$ and $4d_{yz}$ levels of Sm$^{3+}$ and Gd$^{3+}$ ions can be seen in figures 4(a), (b). Moreover, the binding energy peak corresponding to Sm$^{3+}$ ions is found to increase with Sm-concentration. The binding energy peaks corresponding to both $2p_{3/2}$ and $2p_{1/2}$ levels of Fe ions are observed around 710.6 eV and 725.2 eV, respectively, as shown in figures 4(c), (d). The broad and asymmetric nature of peaks is explained by taking the
contribution from Fe$^{3+}$ and Fe$^{2+}$ ions as per the profile fitting and their resolved binding energy values are 709 eV and 711 eV respectively for Fe-2$p_{3/2}$ level for $x = 1.0$ sample. The obtained binding energy values are comparable to those of respective elements\cite{29, 43, 44}. In addition to that, a satellite peak is observed at 717 eV, which is associated with large background noise.

3.2. Magnetic properties

The temperature ($T$) variation of magnetization ($M$) data were measured at an applied field of 200 Oe and they are shown in figure 5(a). They all undergo FIM transition with increase in $T_C$ from 567 K ($x = 0$) to 575 K ($x = 3.0$) as estimated from $dM/dT$ versus $T$ plots (figure 5(b)). Such increase in $T_C$ is because of the strengthening of super-exchange interaction across $\text{Fe}_8\text{O}_8$ networks, which is in accordance with the XRD analysis result. For $x = 0$, as the sample is cooled below $T_C$, the magnetization initially increases to a broad maximum value occurring at 450 K, and on further cooling, its value gradually approaches towards zero and reaching a magnetic compensation at $T_{\text{comp}} = 286$ K. However for $T < T_{\text{comp}}$, the magnetization starts increasing. The above observed trend along with $T_C$ and $T_{\text{comp}}$ values in $x = 0$ sample is comparable with the literature\cite{13}. A similar trend is observed for Sm-substituted samples; however the $T_{\text{comp}}$ is found to be decreased drastically from 286 K ($x = 0$) to 70 K ($x = 3.0$). For $x = 3.0$ sample, $T_{\text{comp}}$ is not observed due to small moment of Sm$^{3+}$ ions, which cannot drive the system into magnetic compensation within the measured temperature limit. The magnetic compensation in $x = 0$ sample, can be understood in terms of competition between magnetic moment of three Fe$^{3+}$ ions in the tetrahedral site ($3M_{\text{Fe}}(d)$) and the total magnetic moment of two Fe$^{2+}$ ions in the octahedral site ($2M_{\text{Fe}}(a)$) and the enhanced PM moment of three Gd$^{3+}$ ions at dodecahedral site ($3M_{\text{Gd}}(c)$), i.e., $[2M_{\text{Fe}}(a) + 3M_{\text{Gd}}(c)]$. So, the net magnetic moment per formula unit ($M_{\text{net}}$) can be empirically written as\cite{10, 13}:

$$M_{\text{net}} = 3M_{\text{Fe}}(d) - [2M_{\text{Fe}}(a) + 3M_{\text{Gd}}(c)]$$ (1)

At $T = T_{\text{comp}}$, it is expected that $[3M_{\text{Fe}}(d)] = [2M_{\text{Fe}}(a) + 3M_{\text{Gd}}(c)]$. Here, the enhanced PM moment of Gd$^{3+}$ refers to the weak exchange-coupled magnetic moment of Gd$^{3+}$ ions with Fe$^{3+}$ ions at the ‘a’ site. Two important observations, such as decrease in $T_{\text{comp}}$ and increase in peak magnetization value, can be ascribed to the Sm$^{3+}$-substituted ions having a smaller moment (0.71 $\mu_B$) at Gd$^{3+}$ site (7 $\mu_B$). Such substitution gives rise to the reduction in the second term within the square bracket in equation (1). So, it leads to the shifting of $T_{\text{comp}}$ towards low temperature and the enhanced peak magnetization. The secondary increase in magnetization for $T < T_{\text{comp}}$ is associated with the flipping of the magnetic spin of each sublattice due to the relatively small anisotropic constant in these samples.

Figure 1. (a) XRD patterns of Sm-GIG samples with $x = 0$ to 3.0, (b) Rietveld refined pattern for $x = 2.0$ sample and (c) the variation of $a$ and $V$ with Sm-concentration.
We have also performed the \( M-T \) measurement under field-cooled (FC) condition for \( H_{FC} = 200 \text{ Oe} \) in the temperature range of 25 K to 300 K, as shown in figure 5. For \( x = 0, 0.5 \) and 1.0 samples, no appreciable change in magnetization is observed under FC condition, as the temperature is lowered, barring some irreversibility for \( T < 100 \text{ K} \). However, for \( x = 2.0 \) sample, a novel negative magnetization is observed (figure 5(e)) for the first time in this series as the temperature is lowered below \( T_{comp} \). This can be understood in terms of relatively large magnetic anisotropy introduced by \( \text{Sm}^{3+} \) ions. According to Pearson [45], \( \text{Sm}_3\text{Fe}_5\text{O}_{12} \) exhibits larger magnetic anisotropy at lower temperature. No magnetic compensation and hence no negative magnetization is observed for \( x = 3.0 \) sample due to significantly smaller value of moment within the square bracket in equation (1) such that it cannot compensate the tetrahedral sublattice moment \([3M_{c}(d)]\). One cannot rule out the shifting of \( T_{comp} \) below the measured temperature limit of 25 K. Generally, the negative magnetization is quantitatively estimated from the ratio of minimum \( (M_{min} \text{ negative}) \) and maximum \( (M_{max} \text{ positive}) \) values of magnetization, i.e., \( \left( \frac{M_{min}}{M_{max}} \right) \)

and it is found to be 0.7. The value of \( \left( \frac{M_{min}}{M_{max}} \right) \) is known to be in the range of \( 2 \) to \( 9 \) for rare earth orthochromites [46–48] and it lies in the range of \( 0.1 \) to \( 5 \) in some spinels and intermetallic alloys [17, 23, 24, 49, 50]. The relative irreversible magnetization, \( \frac{\Delta M}{M_{ZFC}} = \frac{M_{FC} - M_{ZFC}}{M_{ZFC}} \), was estimated and it is found to \( -11 \) at 25 K for \( H = 200 \text{ Oe} \) as shown in the inset of figure 5(e).
Figure 3. FESEM micrographs and EDS spectra for $x = 0.5$ (a), (c) and $x = 2.0$ (b), (d) samples of Sm-GIG.

Figure 4. XPS spectra for $x = 1.0$ (a), (c) and $x = 2.0$ (b), (d) showing the oxidation state of Gd, Sm and Fe ion.
In order to further confirm that the negative magnetization is not due to any experimental artifact, we have performed the $M-T$ measurements for both $H_{FC} = \pm 200$ Oe and $-200$ Oe using physical properties measurement system (PPMS, Quantum Design (Dynacool)) in the temperature range of $10 \text{ K to 300 K}$ as shown in figure 6(a) for $x = 2.0$ sample. We can evidently see magnetization reversals in both cases with the mirror image of $M-T$ plots for $H_{FC} = \pm 200$ Oe, and it confirms the presence of negative magnetization in $x = 2.0$ sample. We have also measured the FC $M-T$ data by varying $H_{FC}$ from 100 Oe to 600 Oe as depicted in figure 6(b). The $T_{comp}$ is found to shift towards lower temperature with an increase in $H_{FC}$, and they are 70 K, 68 K, 65 K, 51 K for $H_{FC} = 100, 200, 300$ and 400 Oe respectively. For $H_{FC} \geq 500$ Oe the magnetization passes through a magnetic compensation followed by a secondary rise in magnetization for $T < T_{comp}$ similar to other samples in this series, i.e., without undergoing negative magnetization. So, under this condition, the system overcomes the anisotropy energy and flip the sublattice magnetic spin.

Figure 7(a) depicts magnetic hysteresis loops ($M-H$) recorded at room temperature (RT) for Sm-GIG samples. All Sm-substituted samples exhibit magnetic saturation as expected in a typical ferrimagnetic material.
Figure 6: FC $M-T$ plots of $x = 2.0$ sample for (a) $H_{FC} = \pm 200$ Oe and (b) for different $H_{FC}$ values.

Figure 7: (a), (b) $M-H$ loops, (c), (d) observed initial magnetization data (open symbol) along with the LAS fitted data (solid line) for Sm-GIG samples. (e), (f) Variation of $M_s$ and $H_c$ as a function of Sm-concentration at 303 K and 30 K, respectively.
The $M-H$ loop measured at a temperature close to $T_{\text{comp}}$ resulted in quite a small magnetization value with a considerable linear contribution for $x = 0$ sample [inset of figure 7(a)]. The saturation magnetization ($M_s$) was obtained by using the law of approach to saturation (LAS) model fitted to the initial magnetization curve (figure 7(c)), $M = M_s \left( 1 - \frac{H}{105\mu_B M_s} \right) + cH$[51]. Here $K_1$ is the effective anisotropy constant, and the term $cH$ represents the higher field forced magnetization. The $M_s$ value at RT increases from 0.19 emu g$^{-1}$ ($x = 0$) to 19.54 emu g$^{-1}$ ($x = 3.0$). The net magnetic moment in Sm-GIG is basically attributed to the three different magnetic sublattices, viz., $\text{Gd}^{3+}/\text{Sm}^{3+}$ ($c$), $\text{Fe}^{3+}$ ($a$) and $\text{Fe}^{3+}$ ($d$) ions. The total magnetic moment is represented as: $3M_{gig}(d) - \left[ 2M_{gig}(a) + (3 - x)M_{cig}(c) + xM_{cig}(c) \right]$. $\text{Sm}^{3+}$ ($0.71 \mu_B$) ions having smaller magnetic moment substituting the $\text{Gd}^{3+}$ ions at the $c$ site gives rise to an increase in net magnetization value at RT, as per the above empirical relation. It is noticed that the estimated value of $K_1$ increases from $1.39 \pm 0.03 \times 10^3$ Jm$^{-3}$ ($x = 0$) to $1.65 \pm 0.05 \times 10^3$ Jm$^{-3}$ ($x = 3.0$), which also approves the explanation given for the negative magnetization in $x = 2.0$ sample. However, these $K_1$ values are quite small compared to conventional ferromagnets and hexaferrites[52, 53]. These obtained values suggest that Sm-substituted samples are magnetically soft. The coercivity of $x = 0$ sample is $330 \pm 10$ Oe; while for other samples, they are in the range of 14 to 23 Oe. Since, the $T_{\text{comp}}$ for $x = 0$ sample is in the vicinity of RT, it can lead to the relatively large value of $H_c$, $M_s$, and $H_s$ values as a function of Sm-concentration ($x$) are shown in figure 7(e).

The $M-H$ loops recorded at 30 K (figure 7(b)) show quite a different trend compared to those of RT. The magnetization rises gradually with increase in the magnetic field due to considerable domain anisotropy at low temperature. The obtained $M_s$ value as per the fitting using the LAS model (figure 7(d)), decreases from 69.11 emu g$^{-1}$ ($x = 0$) to 9.29 emu g$^{-1}$ ($x = 2.0$). This can be understood by carefully studying the $M-T$ plots. For $x = 0$ sample, the chosen temperature of 30 K is far below the $T_{\text{comp}}$ and the secondary rise in magnetization due to spin flipping is completely set in. On the other hand, for $x = 2.0$ sample, 30 K is close to its magnetic compensation, so $M_s$ is quite low. $M_s$ and $H_s$ values at 30 K as a function of Sm-concentration are shown in figure 7(f), where the minimum $M_s$ and the maximum $H_s$ are found for $x = 2.0$ sample due to the magnetic compensation close to 30 K in this sample.

### 3.3. Complex impedance analysis

RT data of real and imaginary ($Z'$ and $Z''$) components of impedance as a function of frequency ($f$) are shown in figures 8(a) and (b), respectively. Relatively sharp fall in $Z'$ value is observed for all samples as the frequency is increased up to 10$^3$ Hz and beyond that, it displays plateau-like behavior. $Z''$ is observed to decrease linearly up to 10$^3$ Hz. Such a fall in $Z'$ and the linear behavior in $Z''$ in the low frequency region are mainly attributed to space charge polarization. The frequency independent behavior of $Z'$ at higher frequency is due to the release of space charge polarization[25]. At a given frequency $Z'$ increases with Sm-concentration.

Similar impedance spectra were measured by heating the sample from 303 K to 623 K as illustrated in figures 8(c)–(e) for $x = 0$ to 3.0 samples. For $x = 0$ sample, a broad peak in the low frequency region, i.e., at $f_{\text{max}} = 300$ Hz is observed at 473 K. This peak shifts towards higher $f_{\text{max}}$ with rise in temperature, which is the manifestation of thermally activated charge carriers. These relaxation peaks in the low frequency region with large relaxation time varying from $5 \times 10^{-8}$s at 473 K to $3 \times 10^{-6}$s at 623 K are attributed to relaxation across grain boundaries (GB) [38]. Similar behavior is observed in Sm-substituted samples, but at lower $f_{\text{max}}$ compared to that of $x = 0$ sample at a given temperature as can be seen in figures 8(c)–(e). For example, at 623 K, $f_{\text{max}}$ values for $x = 0$, 1.0 and 3.0 samples are found to be 60 kHz, 10 kHz and 1 kHz, respectively. Such reduction in $f_{\text{max}}$ value in Sm-substituted samples is consistent with their larger grains having fewer grain boundaries.

The relaxation time $\tau = (1/2\pi f_{\text{max}})$ obtained from the above impedance spectra was plotted with inverse temperature ($10^3/T$) (figure 8(f)). They all exhibit a linear behavior and follow the Arrhenius law,

$$\tau(T) = \tau_0 \exp \left( \frac{E_a}{k_B T} \right)$$

with a change of slope in the temperature range of 560 K to 570 K for various samples. In $x = 0$ sample, the change of slope occurs around $T \approx 560$ K, which happens to be the FIM $T_c$ as discussed in section (3.2), and it highlights the existence of magneto-electric coupling. The activation energy ($E_a$) values obtained by fitting the data to Arrhenius relation in both paramagnetic (PM: $T > T_c$) and ferrimagnetic (FIM: $T < T_c$) regions are given in table 1. They are found to be in the range of 0.41 eV to 0.71 eV in the FIM region and 0.91 eV to 1.19 eV in the PM region. These $E_a$ values in the FIM region are comparable with singly ionized oxygen vacancies, while the values in the PM regions are comparable with doubly ionized oxygen vacancies[54, 55].

The complex impedance plane plots ($Z''$ versus $Z'$: Nyquist plots) for different Sm-GIG samples are shown in figures 9(a)–(c). We have analyzed the semi-circular arc using ZSimpwin 3.21 software in the temperature range from 523 K to 623 K. The radius of semi-circular arc decreases with rise in temperature indicating the negative temperature coefficient of impedance. The semi-circular arcs are found to be suppressed and asymmetric with its centre falling below the $Z'$ axis and it implies the non-Debye type relaxation. The Nyquist plots were fitted
Figure 8. Frequency variation of (a) $Z'$ and (b) $Z''$ at RT, (c)–(e) $Z''$ versus frequency for Sm-GIG samples in wide temperature range (303 K to 623 K), (f) Arrhenius plots of relaxation time due to GB contribution.

Table 1. The estimated values of activation energy ($E_a$) as per the analysis of Arrhenius plots of relaxation time obtained from the impedance spectra.

| $x$ | 0     | 0.5   | 1.0   | 2.0   | 3.0   |
|-----|-------|-------|-------|-------|-------|
| FIM (eV) | $0.41 \pm 0.02$ | $0.58 \pm 0.04$ | $0.71 \pm 0.03$ | —     | —     |
| PM (eV)  | $0.91 \pm 0.06$ | $1.04 \pm 0.12$ | $1.09 \pm 0.10$ | $1.13 \pm 0.12$ | $1.19 \pm 0.15$ |
Figure 9. (a)–(c) Nyquist Plots in the temperature range of 623 K ≤ T ≤ 523 K typically for x = 0, 0.5 and 2.0 samples, (d) the variation of \( R_{\text{GB}} \) with Sm-concentration at different temperature and (e) the equivalent modelled circuit.

(shown as solid lines in figure 9) by choosing a model circuit shown in figure 9(e). Here, \( R_G \) and \( R_{\text{GB}} \) refer to the grains and grain boundaries resistance, while \( Q_{\text{GB}} \) accounts for capacitance due to constant phase element having impedance \( Z_{\text{CPE}} = \frac{1}{j\omega}^{m} \) and \( C_{\text{GB}} \) represents the capacitance across GB [37]. The exponent \( (m) \) associated with GB are lying in the range of 0.4 to 0.8. The plot of obtained value of \( R_{\text{GB}} \) as a function of Sm-concentration at different temperature are shown in figure 9 (d). It can be seen that the value of \( R_{\text{GB}} \) increases with Sm-concentration and it may be due to the decrease in the number of charge carriers across GB. However, it decreases with increase in temperature and it suggests the negative temperature coefficient of resistance (NTCR) [37].

4. Conclusion

Sm-substituted polycrystalline gadolinium iron garnet \((\text{Gd}_{1-x}\text{Sm}_x\text{Fe}_5\text{O}_{12})\) with compositions \( x = 0, 0.5, 1.0, 2.0 \) and 3.0 were prepared in pure-phase form by solid-state chemical reaction method. The substitution of larger Sm\(^{3+}\) ions at Gd\(^{3+}\) site gives rise to considerable increase in lattice constant, i.e., from 12.4624 Å \((x = 0)\) to 12.5211 Å \((x = 3.0)\). Sm-substitution leads to stronger Fe\(^{3+}\)(\(a\)) – O\(^{2-}\) – Fe\(^{3+}\)(\(d\)) super-exchange
interaction and larger ferrimagnetic $T_C$, i.e., from 567 K ($x = 0$) to 575 K ($x = 3.0$). In addition, these samples exhibit magnetic compensation with decrease in $T_{\text{comp}}$ value, i.e., from 286 K ($x = 0$) to 70 K ($x = 2.0$). In addition to magnetic compensation, an interesting negative magnetization is introduced in $x = 2.0$ sample due to the enhanced magnetic anisotropy as a result of Sm-substitution. We have also demonstrated an improvement in saturation magnetization at room temperature upon selective substitution of Sm at Gd site. It is also explained with the help of an empirical relation, where Sm-substitution resulted in the reduction in net down spin moment with respect to the positive ferrimagnetic moment of Fe$^{3+}$ ions. The impedance spectra were analyzed in detail using Nyquist plots as well as the temperature dependence of relaxation frequency based on Arrhenius law. They show the deviation of relaxation dynamics from the ideal Debye type relaxation. The activation energy for charge carriers varies from 0.41 eV to 0.71 eV in the FIM region and 0.91 eV to 1.19 eV in the PM region.

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