Temperature and frequency dependent dielectric relaxation of Ni–Fe–Oxide nanocomposites

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Abstract
Nickel-iron Oxides powder with different molar ratios of Ni:Fe are successfully synthesized by easy facile glycol mediated sol-gel auto-combustion synthesis process. Influence of compositional molar percentage variation on structural, dielectric and charge transport mechanism has been studied. The change of average crystallite size from 26 nm to 8 nm of these nickel iron powder samples has been observed with the change of Ni:Fe molar ratios. The dielectric constant and loss factor of all these materials show strong temperature dependence at all frequencies. The nanocomposites exhibit high dielectric constant and relatively low dielectric loss which is the key factor for many practical applications. The ac conductivity of this material increases with increasing frequency irrespective of the compositional variation. An anomalous behavior related to the relaxation mechanism is observed for these materials which also suggest that the materials follow the non-Debye type dielectric relaxation. The complex impedance plots (Z'' vs Z') i.e. the cole-cole plots demonstrate the contribution of grain, grain boundary and conducting nature of these nickel iron oxides. The overall dielectric property and ac conductivity infer the potential application of this nickel iron oxide in energy storage and entrenched electronics devices.

1. Introduction

Recently nickel ferrite material has attracted enormous attention of many theoretical and experimental research works with the focus on its remarkable properties such as mechanical hardness, low cost, excellent magnetic and dielectric properties, electrochemical energy storage and conversation properties such as Hydrogen evolution reaction (HER), Oxygen evolution reaction (OER) [1, 2]. However, mixed metal oxides (binary or ternary) with high dielectric constant draw more consideration in many advanced integrated circuit over monoxides [3, 4]. The significant magnetic and dielectric properties of such mixed oxides depend on the nature of ions and distribution of charges among the sites. The dielectric properties of the nickel ferrite also strongly depend on synthesis procedure, compositional ratios, shape, size, purity, sintering temperature/duration, heating and cooling rate etc. The temperature and frequency dependent dielectric study of this nickel ferrite can provide important information about the dielectric polarizations and dielectric relaxation of this material [5]. Different physical (pulse laser deposition, vapor phase transparent process, chemical vapor deposition etc) and chemical (co-precipitation, complexometric method, microwave, sol-gel process, hydrometallurgical process etc) synthesis processes are employed for the preparation of nickel iron oxide nanocomposites. The desired control of particle size and shape is a great challenge for co-precipitation method and other physical and chemical processes are quite expensive or inefficient for the industry. But, among various synthesis processes, the sol-gel method is found to be one of the most important and suitable methods for the preparation of nickel iron oxide.
nanoparticles with their simplicity, controlled compositional ratios, homogeneous composition and higher purity [6–9].

There are several reports available in the literature on the structural, optical, magnetic and electrical properties of nickel ferrite. Senthilkumar et al investigated the electrical properties of NiFe$_2$O$_4$ synthesized by the molten salt technique [10]. Maji et al reported dielectric properties of PMMA-NiFe$_2$O$_4$ nanocomposite [5]. Sun et al showed Influence of Cu$^{2+}$ doping on dielectric and magnetic properties of NiFe$_2$O$_4$ [7]. Ponpandian et al studied the dielectric behaviour and electrical conductivity NiFe$_2$O$_4$ [11]. Devmunde et al reported electrical, and dielectric properties of Cd$^{2+}$ substituted nickel ferrite nanoparticles [12]. However, to the best of our knowledge there are few reports available in literature on the influence of compositional molar percentage variation on dielectric properties of Ni–Fe–Oxide. The demands for high-temperature dielectric materials with excellent energy storage capability are also serious to meet the growing demand of electrical energy storage and power conditioning from several emerging applications such as solar converters, hybrid electric vehicles, wind generators, underground oil industries and aerospace systems [13, 14]. This has motivated us to carry out the study of frequency and temperature dependent electrical conductivity, dielectric properties of Ni–Fe–Oxide, which is still a least explored area in modern research. In this work, we report Ni–Fe–Oxide nanopowders with different molar ratios of Ni:Fe (1:1, 1:2, 1:3 and 1:4) synthesized by a facile ethylene glycol mediated sol-gel auto-combustion method. The crystallinity and morphology of Ni–Fe–Oxide samples have been characterized by x-ray diffractometer (XRD) and field emission scanning electron microscopy (FESEM). The temperature and frequency dependent dielectric properties, conductivity and complex impedance properties have been studied extensively. The effect of compositional variation, the mechanism of conduction, the contribution of grain and grain boundary, the variation of dielectric constant and dielectric loss with temperature and frequency have been studied. The dielectric relaxation has also been analyzed using electrical modulus spectroscopy to investigate the relaxation mechanism.

2. Experimental

2.1. Chemicals

Ferric nitrate [(Fe(NO$_3$)$_3$]$\cdot$9H$_2$O, Merck Chemical, 99%], nickel nitrate [(Ni(NO$_3$)$_2$]$\cdot$6H$_2$O, Merck Chemical, 99.9%], ethylene glycol [(CH$_2$OH)$_2$, Merck Chemical, 97%] and Polyvinylpyrrolidone (PVP) [(C$_6$H$_9$NO)$\cdot$FW = 40,000, Sigma Aldrich, 97%] were used to synthesize the material. All the chemicals here were of analytical grade and used without further purification.

2.2. Synthesis of Ni–Fe–Oxide by sol-gel auto-combustion technique

In this distinct sol-gel synthesis approach, stoichiometric amount of 2 mM ferric nitrate (Fe(NO$_3$)$_3$)$\cdot$9H$_2$O, 1 mM nickel nitrate (Ni(NO$_3$)$_2$)$\cdot$6H$_2$O and 0.1 g PVP were dissolved in 50 ml ethylene glycol at room temperature under vigorous magnetic stirring for 30 min. Next, the sol was heated at 90 $^\circ$C to form a wet gel. Here, (Ni(NO$_3$)$_2$)$\cdot$6H$_2$O and (Fe(NO$_3$)$_2$)$\cdot$9H$_2$O were used as cation precursors of Ni and Fe. The gel at that time dried at 150 $^\circ$C for 4 h self-ignites to form Ni–Fe oxide powder and next heated at 400 $^\circ$C for 24 h. This sol-gel auto-combustion technique can be deliberated as a thermally induced redox reaction of the sol. In this synthesis ethylene glycol works as a reducing agent while the nitrate ion acts as an oxidant. The nitrate ion offers an in situ oxidizing atmosphere for the disintegration of the organic component. The final powder was cooled at room temperature and used for further characterizations. In this same synthesis process we have varied the molar ratios of Fe composition to obtain four different samples (Ni:Fe = 1:1, 1:2, 1:3 and 1:4).

2.3. Characterizations

The phase composition of the prepared Ni–Fe–Oxide samples were determined with a Rigaku miniflex-600 bench top x-ray diffractometer (XRD) using CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å) in the 2θ range from 20° to 80°. The morphology of the synthesized powder samples was recorded on a FEI INSPECT F 50 field emission scanning electron microscopy (FESEM) using secondary electron (SE) mode. The chemical information and the bond formation between different atoms of the prepared samples were obtained by Fourier transform Infrared (FT-IR) spectra (Perkin-Elmer 843) using the KBr pellets within the range 400–4000 cm$^{-1}$. The dielectric and complex impedance of these samples were measured by inserting 8.0 mm diameter pellets of thickness 0.44, 0.55, 0.53 and 0.51 mm of NiFe = 1:1, 1:2, 1:3 and 1:4, respectively between two 8.0 mm diameter Cu pellet electrodes. The pellets were made using hydraulic press under 50 ton pressure. The two probe method was employed to investigate the temperature (523 K–683 K) and frequency (5 kHz–5 MHz) dependent dielectric relaxation behavior of the synthesized Ni–Fe–Oxide nanocomposites using a computer controlled Hioki LCR Q (HIOKIIM3536) instrument.
3. Results and discussion

3.1. XRD analysis

Figure 1(a) represents the powder XRD patterns of as synthesized Ni–Fe–Oxide nanocomposites with different molar ratio of Ni:Fe = 1:1, 1:2, 1:3 and 1:4, respectively. The Bragg diffraction peak positions and broadening of these XRD patterns have been identified and compared with respect to a standard cubic phase spinel type NiFe2O4 XRD pattern (JCPDS PDF card No. 074-2081) with Fd-3m space group. The XRD patterns exhibit broad diffraction peaks at 2θ (degree) = 24.34, 30.54, 36.05, 37.72, 43.40, 49.60, 54.15, 57.63, 62.90 and 74.40 which correspond to (111), (220), (311), (222), (400), (411), (422), (511), (440) and (533) planes respectively. A small shift of diffraction angle towards lower and higher diffraction angle is also observed. The diffraction peak broadening with increase of Fe molar ratio may be due to the grain refinement while the shift of the peak position could be due to the increase of atomic level average microstrain (ε) caused by change of crystallite size (D) with molar ratios. The average crystallite size (D) in nm and microstrain (ε) have been calculated from the Bragg reflection peaks using Williamson-Hall equation (equation (1))

\[
\frac{\beta \cos \theta}{\lambda} = \frac{K D}{\sin \theta} + \frac{4\varepsilon \sin \theta}{\lambda} \tag{1}
\]

where D is the average crystallite size (nm), λ is the x-ray wavelength (1.5418 Å), θ is the Bragg angle (degree), β is the full width half maxima (FWHM) or line broadening (rad) and ε is considered as average microstrain [3, 15–17]. Here the value K (Scherrer constant) is considered to be equal to 1, which is suggested by Laue [18].

The average crystallite size and microstrain have been calculated from the Williamson-Hall plot figure 1(b) and a decrease of average crystallite size from 26.1 nm to 8.5 nm is observed with increase of Fe molar ratio. The substantial increase of average microstrain (ε = 0.521 × 10⁻³, 2.57 × 10⁻³, 3.39 × 10⁻³ and 3.42 × 10⁻³)
with the decrease of average crystallite size is shown in figure 1 (b) (inset). The presence of microstrain in these nanocomposites signifies the distribution of lattice constant which may be due to crystal defects (point defects, small dislocation loops etc). Such types of defects are usually introduced during crystal growth due to grain boundary triple junction, sinter stresses, stacking faults etc. These changes of microstrain, crystallite size significantly affect the diffraction peak by changing peak intensity, peak position and peak width in different ways [3, 16, 19].

3.2. Morphological analysis
The FESEM images (figure 2) of Ni–Fe–Oxides show porous and homogeneous distribution of spherical particles. Figure 2(a) shows the rough agglomerated large spherical particles whereas figures 2(b)–(d) shows spherical morphology of the nanocomposite. The decrease of nanoparticles size with increase of Fe-molar ratios is also observed. The formation of different morphology of the material for Ni:Fe = 1:3 from other three samples is observed which may be due to the strong dipole interaction between the magnetic nanoparticles. The particle size distribution curves (figure 3) have been obtained from the FESEM images by measuring the average size of 100 nanoparticles using Image J software. The histogram for each particle distribution curve represents the average particle size of the as synthesized Ni–Fe–Oxide nanocomposites with different molar ratios of Ni:Fe. The average particle size obtained from this distribution curves are 32.3 nm, 22.4 nm, 17.3 and 15.5 nm for Ni:Fe = 1:1, 1:2, 1:3 and 1:4, respectively. These particles sizes are very similar to those obtained from XRD patterns and follow the same trends i.e. the decrease in particle size with increase of Fe molar ratio.

3.3. FT-IR spectra analysis
The FT–IR spectra (supporting information figure S1 is available online at stacks.iop.org/MRX/6/1250h4/mmedia) of Ni–Fe–Oxides show same nature for all the samples. The broad absorption band at around 3135 cm⁻¹ and 1620 cm⁻¹ can be assigned to the stretching vibration of –OH group due to physically absorbed water molecules in the air [3, 6, 20]. The sharp absorption peak centered at 2336.5 cm⁻¹ is observed mainly due to the absorption of CO₂ from atmosphere. The significant broad band in the range of 875 to 400 cm⁻¹ is contributed from the formation of metal-oxide bands. The main bands centered at 813, 545 and 416 cm⁻¹ are observed correspond to the stretching vibration of Fe–OH, Fe–O and Ni–O at tetrahedral- and octahedral-site,
respectively [6, 21, 22]. The appearance of peaks around 1402 and 1051 cm\(^{-1}\) may be due to the presence of stretching vibrations of the anti-symmetric NO\(_3\)\(^-\) group and C–O group, respectively during ethylene glycol mediated synthesis of Ni–Fe–Oxide nanocomposites [2, 23–25].

3.4. Complex impedance studies

The frequency and temperature dependent imaginary part of impedance (\(Z''(\omega)\)) vs real part of impedance (\(Z'(\omega)\)) (where, \(\omega = 2\pi f\)) in the form of Cole-Cole plots (figure 4) of Ni–Fe–Oxide nanocomposites show two overlapping semi-circles and the center of which exist below the real axis. For a dielectric material, the grain, grain boundary and electrode–dielectric material interface contribute significantly to the total impedance of the dielectric material. The contributions of these three parameters are observed via the presence of three semicircles in the Cole-Cole plot. The semicircle at high frequency region signifies the influence of grain, the semicircle at low frequency corresponds to grain boundary contributions and the semicircle in very low frequency region indicates the electrode–dielectric material interface contribution, respectively [3, 4, 26]. No contribution of electrode–dielectric material interface is observed in these Ni–Fe–Oxide nanocomposites in ultralow frequency region, thus the contribution of third semicircle has been neglected. But in this case, it also becomes too difficult to distinguish the influence of grain and grain boundary due to existence of closely overlapped semicircles. The Cole-Cole plots for all Ni–Fe–Oxide nanocomposites (figure 4) demonstrated a single depressed semicircle signifying the overall contribution due to grain and grain boundary [3, 4]. The center of the semicircle is found to be depressed due to the non-Debye relaxation charge transport mechanism. It has been observed that with increase of temperature the diameter of the semicircle decreases for all samples, which indicates the increase of conductivity. The experimental data of Cole-Cole plot can be modeled using Maxwell-Wagner equivalent circuit model containing of two parallel combinations of ‘RC’ elements in series, as shown in figure 4(a) (inset). The first semicircle (\(R_g || C_g\)) represents the contribution of grain resistance (\(R_g\)) and grain capacitance (\(C_g\)), while the second semicircle (\(R_{gb} || C_{gb}\)) represents the effect of grain boundary resistance (\(R_{gb}\)) and grain capacitance (\(C_{gb}\)) [3, 4]. Here, the contribution of electrode polarization due to the Schottky barriers between semiconducting Ni–Fe–Oxide nanocomposites and cupper electrode (non-Ohmic electrode effect) has not been

![Figure 3. Particles size distribution of Ni–Fe–Oxide nanocomposites for (a) Ni:Fe = 1:1, (b) Ni:Fe = 1:2, (c) Ni:Fe = 1:3 and (d) Ni:Fe = 1:4.](image-url)
observed in the ultralow frequency region [10, 27]. The equations (2a)–(2b) correspond to the total impedance $Z'(\omega)$ of the material. It can be represented by the equivalent circuit as shown in figure 4 (inset) [3, 28, 29]

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) \quad (2a)$$

Or,

$$Z^*(\omega) = \frac{1}{R^{-1}_s + j\omega C_s} + \frac{1}{R^{-1}_{gb} + j\omega C_{gb}} \quad (2b)$$

Where,

$$Z'(\omega) = \frac{R_s}{[1 + (\omega R_s C_s)^2]} + \frac{R_{gb}}{[1 + (\omega R_{gb} C_{gb})^2]} \quad (3)$$

$$Z''(\omega) = \frac{\omega C_s R^2_s}{[1 + (\omega R_s C_s)^2]} + \frac{\omega C_{gb} R^2_{gb}}{[1 + (\omega R_{gb} C_{gb})^2]} \quad (4)$$

The fitted Cole-Cole plots using equation (2b) for all samples at a fixed temperature (603 K) (supporting information figure S2 is available online at stacks.iop.org/MRX/6/1250h4/mmedia) clearly shows that among all samples with different molar ratios of Ni:Fe, the sample Ni:Fe = 1:2 exhibits minimum impedance value, while the impedance increase with increase of Fe molar ratios for the other three samples. The minimum value of impedance for Ni:Fe = 1:2 is may be due to the formation of stable and ordered structure of NiFe$_2$O$_4$. The different charge transfer parameters for all samples at a fixed temperature (603 K) have been represented in table 1.

The frequency dependent $Z'(\omega)$ curves (figure 5) at different temperatures for all Ni–Fe–Oxide nanocomposites show a sigmoidal type i.e. S-shaped variation of $Z'(\omega)$ with increasing frequency. At low frequency region the $Z'(\omega)$ become higher and decrease sharply with increasing frequency. The decrease of $Z'(\omega)$ with frequency may be recognized to the increase of ac conductivity [30, 31]. The decrease of $Z'(\omega)$ with increasing temperature at low frequency region also exposes the presence of negative temperature coefficient of
resistance (NTCR) in Ni–Fe–Oxide nanocomposites. This decrease of impedance with increasing temperatures is generally observed in semiconducting material leading to the enhancement of ac conductivity \[3, 32\]. Large polarization effect is one of the main reasons for higher value of $Z'(\omega)$ in low frequency and low temperature region. Due to applied alternating field, the charge carrier becomes active and as a result the dipole orientation, space charge formation and charge displacement contribute significantly. Generally, at low temperature the conductivity is low due to activation of less number of thermally activated charge carriers. But as the temperature increases, the number of thermally activated charge carriers increase which enhances the ability of hopping across the barrier potential. The giant dielectric properties of these nanocomposites are interpreted as an internal barrier layer capacitor (IBLC) effect due to the electrical heterogeneous nature of these nanocomposites. Usually, the semiconducting grains are separated by grain boundary and grain boundary considerably contributes to the total impedance of the material. Thus, the total impedance as well as grain boundary contribution become less at higher frequency and temperature leading to increase of ac conductivity due to increase of thermally activated charge carriers \[28, 30, 31, 33, 34\].

The frequency dependent $Z''(\omega)$ plots at various temperatures of Ni–Fe–Oxides (figure 6) show low value of $Z'(\omega)$ at both lower and higher frequency regions and becomes maximum at intermediate frequencies, known as relaxation frequency, $f_m$. This $Z''(\omega)$ also provides us the essential information about the inter-particles interaction such as contribution of grain and grain boundaries. In $Z''(\omega)$ spectra, it has been observed that the

**Figure 5.** Frequency dependence $Z'(\omega)$ at different temperatures of Ni–Fe–Oxide nanocomposites for (a) Ni:Fe = 1:1, (b) Ni:Fe = 1:2, (c) Ni:Fe = 1:3 and (d) Ni:Fe = 1:4.

**Table 1.** Different charge transport parameters of the Ni–Fe–Oxides samples at 603 K.

| Sl. no. | Ni:Fe ratio | $R_g$ (Ω) | $C_g$ (pF) | $R_{gb}$ (Ω) | $C_{gb}$ (pF) | $\chi^2$ (goodness of fit) |
|---------|-------------|-----------|-------------|--------------|--------------|-----------------------------|
| 1.      | 1:1         | 135.1     | 32.2        | 176.0        | 326.0        | 0.01059                     |
| 2.      | 1:2         | 741.1     | 224.0       | 134.2        | 28.6         | 0.01063                     |
| 3.      | 1:3         | 3259.0    | 242.0       | 138.6        | 16.4         | 0.04395                     |
| 4.      | 1:4         | 128.5     | 28.25       | 22452.0      | 228.0        | 0.17300                     |
peak position shifts to a higher frequency as the temperature increase, which proposes the variation of relaxation time ($\tau$) with temperature and conduction mechanism is mainly due to thermally activated charge carriers [35]. The shift of peak frequency to higher frequency also suggests the non-Debye type of relaxation behavior in the materials. The activation energy of the materials for all molar ratios has been calculated using Arrhenius relation, $\tau_m = \tau_0 \exp \left[ -E_a/kT \right]$ (where $E_a$, $k$ and $T$ are activation energy (eV), Boltzmann constant ($1.38 \times 10^{-23}$ J/K) and absolute temperature (K)) and from the least square fitting of data $\ln \tau_m$ vs $1000/T$ plot (figure 7). The calculated activation energies are 0.250 eV, 0.193 eV, 0.290 eV and 0.285 eV, respectively and it has also been observed that the material with molar ratio Ni:Fe = 1:2 offers minimum activation energy [36, 37].

3.5. Dielectric relaxation studies

The complex dielectric function of a dielectric material can be written as equation (5),

$$\varepsilon'(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

(5)

Which can be also be obtained from the impedance studies using the expression,

$$\varepsilon'(\omega) = \frac{1}{j\omega C_{0}Z''} = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

(6)

where $C_0 = \varepsilon_0 A/d$, is the free space capacitance ($\varepsilon_0$), A and d are free space permittivity, area of the electrode and thickness of the pellet, respectively. The real part of dielectric constant ($\varepsilon'(\omega)$) and imaginary part of dielectric constant or dielectric loss factor ($\varepsilon''(\omega)$) can be calculated as equations (7) and (8),

$$\varepsilon'(\omega) = \frac{Z''(\omega)}{\omega C_0(Z''^2 + Z''^2)}$$

(7)

$$\varepsilon''(\omega) = \frac{Z'(\omega)}{\omega C_0(Z''^2 + Z''^2)}$$

(8)

The frequency dependent $\varepsilon'(\omega)$ at various temperatures for Ni–Fe–Oxide nanocomposites with different molar ratios of Ni:Fe (figure 8) shows that $\varepsilon'(\omega)$ decreases gradually at the low frequency region and becomes almost
saturated with increase of frequency [3, 29, 38]. The increasing tendency of \( \varepsilon'(\omega) \) with increasing temperature in low frequency region is also observed for all compositions, which is mainly due to the increase of thermally activated charge conduction process and some ordering inside the nanoparticles along with formation of an electric dipole moment in the entire volume of the material [39]. As temperature increases the orientation of these dipole are assisted, increasing the dielectric constant. Generally, there are four types of polarizations such
as ionic, electronic, orientation and space charge polarization present in the materials, which contribute significantly to the dielectric properties of the materials. Such types of polarizations also strongly depend on the purity and perfection of the synthesized dielectric materials. At low frequencies, the dipolar and interfacial or space charge polarizations play significant role and both these polarizations intensely depend on the temperature. But at high frequency region the ionic and electronic polarizations are known to play dominant role and their temperature dependence is irrelevant. The increase of $\varepsilon'(\omega)$ with increasing temperature at low frequency region is not so prominent for Ni:Fe = 1:3 and 1:4 (figures 8(c), (d)) compared to other two nanocomposites materials which may be due the relatively less contribution of dipolar and interfacial polarizations. The dispersion of $\varepsilon'(\omega)$ at low frequency can also be explained according to Maxwell-Wagner interfacial polarization and it is in well agreement with Koops’s phenomenological theory. According to this theory the dispersion of $\varepsilon'(\omega)$ arises due to the inhomogeneous double layer dielectric structure. At low frequency region the maximum dispersion of $\varepsilon'(\omega)$ is observed and then it decreases with increase in frequency [3, 40–42]. Such types of dispersion generally occur due to electron exchange between Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ (Fe$^{3+} \leftrightarrow$ Fe$^{2+} + e^-$) and hole exchange between Ni$^{2+} \leftrightarrow$ Ni$^{3+}$ (Ni$^{3+} \leftrightarrow$ Ni$^{2+} + e^-$) which cannot follow the frequency of the applied signal [10, 43]. At low frequency it is found that the dipoles follow the applied field but, as the frequency increases the dipoles are unable to follow the external field. Therefore, the transport of charge carriers becomes restricted towards the grain boundary and reduces the number of polarizations near grain boundary [3, 44, 45]. From figure 8 it can also be seen that $\varepsilon'(\omega)$ decreases with increase in Fe-molar ratio from 1:1 to 1:4. It may be due to the addition of Ni elements with Fe, reduce the number of cationic charge carriers which are able to move around the adjacent energy level in presence of applied external electric field. The substitution of Fe by Ni cation has also been found to affect the mobility of Fe ions which slabs the diffusion of Ni ions and as a result the composite becomes more resistive with decreasing Fe-molar ratio. But when we increase the Fe-molar ratio the composites become most conductive and the $\varepsilon'(\omega)$ decrease.

The frequency and temperature variation of $\varepsilon''(\omega)$ (figure 9) show $\varepsilon''(\omega)$ decreases with increasing frequency for all Ni:Fe molar ratios at all temperatures. Generally the polarization mechanism is mainly accompanying with the accumulation of charge at the interface between the inter-domain regions. According to Koops’s theory
a dielectric material is usually made up of well conducting layer of grains separated by poorly conducting layers of grain boundaries. It is also known that the presence of impurities and imperfections in the material creates a potential barriers for the charge transport [4, 27, 43, 46]. Thus, when an alternating voltage is applied to the material, a huge amount of space charge polarization is generated near the grain boundaries. This polarization mechanism consists of the exchange of electrons between the ions of the same elements. Such elements exist in multivalent states and are randomly distributed over crystallographic sites. As discussed earlier, for this case the exchange of electrons take place between the same Fe-ions. During this exchange process the electrons have to move through the grains and grain boundaries of this material. As the grain boundary of this dielectric material is poorly conducting relative to the grain, the electrons accumulate at the grain boundary and induced large number of space charge polarizations. Koops’s theory also proposed that at low frequency region grain boundaries are more effective and grains are effective at high frequency. Thus, due to the dominant effect of poorly conducting grain boundaries at low frequency region, more energy is required for hopping mechanism of electrons between the grain boundaries and thus the high dielectric loss is observed for Ni–Fe–Oxides nanocomposites. On the other hand, at high frequency the conducting grains come into action and the hopping electrons also cannot follow the high frequency electric field, as a result small amount of energy is required for electron transfer between the ions of same element [47]. Hence, the small dielectric loss is observed at high frequency region for all samples [4, 30, 48]. It has been also observed that among all Ni–Fe–Oxide nanocomposites the Ni:Fe = 1:2 composites exhibits higher dielectric loss at low frequency region, while dielectric loss is decreased with increase of Fe- molar ratio. Generally, the polarization time for electronic and ionic displacement polarization is very short (~10^{-11}) s. On the other hand, the relaxation polarization time, including interface, dipolar, space charge thermal ion relaxation polarization, is relatively longer (~microsecond to few second). When the frequency of the applied electric field is low (f < 1 kHz or t > 10^{-3} s), almost all types of polarization contribute significantly as the polarization times for all may be smaller than the time period of the applied electric field. Thus the larger ε″(ω) is observed at lower frequency region. In contrast, when the applied frequency increased (~10^5 Hz), only the displacement polarization such as electronic and ionic displacement polarization can contribute and other polarizations cannot follow the applied electric field. Thus the ε"(ω) value decreases at the higher frequency region.

3.6. Electrical modulus studies

To further investigate the relaxation mechanism in the high temperature and frequency region the study on electrical modulus has also been carried out. The most important advantage of electric modulus studies is that the electrical relaxation due to electrode polarization effect can be better understood. In some cases, for high electrical conductive material, loss peaks are not observed in its ε″(ω) spectrum, thus this is one of the most appropriate ways to interpret the relaxation mechanism of a dielectric material. On the other hand, sometimes it also becomes very challenging to evaluate the response properties of the dielectric material due to the presence long range conductivity or dipole relaxation. For such case, the impedance study (Z′′, Z″) becomes promising and consequently the electrical modulus (M′, M″), dielectric properties (ε′, ε″) becomes more effective for short range relaxation mechanism [10, 27, 46]. The complex electrical modulus (M′) of the material can be expressed as equation (9)

\[ M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = \frac{1}{\varepsilon'(\omega) - j\varepsilon''(\omega)} = M'(\omega) + jM''(\omega) \]  

(9)

The variation of real part of M′(ω) as function of frequency and temperature for all Ni–Fe–Oxide nanocomposites (supporting information figure S3 is available online at stacks.iop.org/MRX/6/1250h4/mmedia) shows M′(ω) close to Zero at low frequency region due to presence of small electronic polarization and reaching a higher value due to the short-range conduction process. The dispersion is also observed for all samples at the mid frequency region due to lack of restoring force leading the mobility of the induced charge carrier under applied electric field.

The variation of imaginary part of M″(ω) as function of frequency and temperature for all Ni–Fe–Oxide nanocomposites (supporting information figure S4 is available online at stacks.iop.org/MRX/6/1250h4/mmedia) that the M′′(ω) reaches maximum value at particular frequency f_m (relaxation frequency) and the peak shifts towards higher frequency as temperature increases for all compositions. The corresponding relaxation time has been calculated using the relation ω_mτ_m = 1, which reveals the condition for transition from long range to short range conduction mechanism. As at low frequency the charge carriers are able to move long distance easily, but at higher frequency side of the peak position the charge transport are to some extent constrained to the potential barriers [35, 49–51]. The activation energy for all samples also calculated from peak value of M′′(ω) spectra using Arrhenius relation, \[ \tau_m = \tau_0 \exp \left[ \frac{-E_a}{kT} \right] \]  

The obtained activation energy from slope of the least square fitting of ln τ_m vs 1000/T plots (supporting information figure S5 is available online at stacks.iop.org/MRX/6/1250h4/mmedia) are 0.302 eV, 0.216 eV, 0.323 eV and 0.307 eV, respectively, which are approximately close to the activation energy calculated from Z′′ spectra using Arrhenius relation,

\[ Z''(\omega) = \frac{1}{\varepsilon''(\omega)} = \frac{1}{\varepsilon''(\omega) - j\varepsilon'''(\omega)} = Z''(\omega) + jZ'''(\omega) \]  

(10)
spectra. This also confirms that the charge conduction mechanism in Ni–Fe–Oxide nanomaterials is mainly due to hopping of thermally activated charge carriers.

### 3.7. Electrical conductivity
To get the conductivity, we firstly calculated the loss tangent (\(\tan(\delta)\)) using the following equation (10)

\[
\tan(\delta) = \frac{\varepsilon''(\omega)}{\varepsilon'\varepsilon_0}\tan \delta
\]  

(10)

Then finding the ac conductivity is pretty straightforward using the equation mentioned below,

\[
\sigma_{ac} = \omega\varepsilon\varepsilon_0 \tan \delta
\]

where \(\varepsilon_0\) corresponds to the permittivity of free space.

The frequency and temperature dependent electrical conductivity \(\sigma_{ac}\) plot of all Ni–Fe–Oxide nanocomposites (figure 10) shows the frequency independent behavior at low frequency region and frequency dependent conductivity at higher frequency region. Low frequency electrical conductivity is known as d.c. conductivity \(\sigma_{dc}\) and increase of conductivity at higher frequency known as a.c. conductivity \(\sigma_{ac}\). Thus, the electrical conductivity of the material obeys Jonscher’s Power Law of equation (11), [4, 10, 27]

\[
\sigma(\omega) = \sigma_{dc} + \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n
\]

(11)

where \(A\) is a constant which governs the strength of polarizability and \(n\) is known as exponent factor \((0 < n < 1)\), which represents the degree of interaction between the mobile ions and lattice. Due to hopping of thermally activated charge carriers the increase of \(\sigma_{dc}\) with increasing temperature is observed. It has also been confirmed that the mobility of charge carriers increases with temperature. The \(\sigma_{ac}(\omega)\) term explains the electrical conductivity due to electron hopping and it is more effective than \(\sigma_{dc}\). In the high frequency region, it has been observed that \(\sigma(\omega)\) increases with frequency which may be due to removal of space charge polarization. In this case, the \(\sigma_{dc}\) values at different temperatures have been calculated by non-linear curve fitting of \(\sigma(\omega)\) using Jonscher’s Power Law of equation (10) (figure 10). The activation energy \(E_a\) for all Ni–Fe–Oxide nanocomposites.

![Figure 10. Frequency dependence \(\ln(\sigma_{ac})\) at different temperatures of Ni–Fe–Oxide nanocomposites for (a) Ni:Fe = 1:1, (b) Ni:Fe = 1:2, (c) Ni:Fe = 1:3 and (d) Ni:Fe = 1:4.](image-url)
nanocomposites have further been determined from the least square fitting data of $\sigma_{dc}$ vs 1000/T plots (supporting information figure S6 is available online at stacks.iop.org/MRX/6/1250h4/mmedia) using Arrhenius relation $\sigma_{dc} = \sigma_0 \exp \left[ -E_a/kT \right]$, where $\sigma_0$ is known as pre-exponential factor. The activation energy ($E_a$) values for all nanocomposites with Ni:Fe = 1:1, 1:2, 1:3 and 1:4 are 0.240, 0.209, 0.327 and 0.331 eV, respectively which are also almost same as the values obtained from $Z''(\omega)$ and $M''(\omega)$ spectra. Nearly same values of activation energies for conductivity relaxation and dc conduction for all these Ni–Fe–Oxide nanocomposites again clearly suggests that the mechanism of dielectric polarization and electrical conduction is same for these materials [48, 52]. In this case the n values have also been obtained by non-linear fitting of the conduction curve at various temperature ranges (523 K–683 K) and the variation of n values with temperatures has been represented in table 2. It has also been observed that n values increase with increase of temperature which clearly explain that the conduction mechanism is mainly due to strong dipole-dipole interaction and due to small polaron assisted tunneling mechanism [27, 46, 49, 52, 53].

4. Conclusions

In this work, we have successfully synthesized Ni–Fe–Oxide nanocomposites with different molar ratios of Ni:Fe (1:1, 1:2, 1:3 and 1:4) using facile sol-gel auto-combustion method. The XRD study followed by Williamson–Hall plots and FESEM images with particle size distribution curve confirm that average crystallite size of the nanoparticles decrease with the increase of Fe-molar ratio from approximate 33 nm to 15 nm. The $\varepsilon''(\omega)$ and $\varepsilon''(\omega)$ decreases with increase of frequency and increases with increase of temperature. The presence of relaxation peak in the $Z''(\omega)$ and $M''(\omega)$ spectra is observed due to matching of hopping frequency of electrons (Fe$^{3+} \leftrightarrow$ Fe$^{4+}$) with applied frequency. The shift of peak position to the higher frequency proposes the non-Debye type of relaxation behavior in this material. The conductivity curve shows a constant plateau region ($\sigma_{dc}$) in the low frequency region and shows dispersion in the high frequency region. The decrease of impedance with increasing temperature and linear variation of conductivity clearly suggest the semiconducting nature of Ni–Fe–Oxide nanocomposites material. Approximately same values of activation energy conductivity relaxation and dc conduction for these nanocomposites suggest that the mechanism of dielectric relaxation and electrical conduction is same.

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Conflicts of interest

The authors declare no competing financial interest.

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Table 2. Obtained values of n for Ni–Fe–Oxide nanocomposites with different Ni:Fe molar ratios.

| Sl. | Ni:Fe | 523 K | 563 K | 603 K | 643 K | 683 K |
|-----|-------|-------|-------|-------|-------|-------|
| 1   | 1:1   | 0.7055| 0.7188| 0.7269| 0.7539| 0.7787|
| 2   | 1:2   | 0.6763| 0.6943| 0.7138| 0.7312| 0.7449|
| 3   | 1:3   | 0.6903| 0.7070| 0.7108| 0.7148| 0.7298|
| 4   | 1:4   | 0.7321| 0.7391| 0.7548| 0.7625| 0.7882|
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