Dielectric Properties

4.1 Introduction

The dielectric properties of materials depend upon their chemical composition, structure and particle size, etc. and various external factors such as temperature, pressure, humidity, intensity and frequency of the applied electric field. Therefore, it is very essential to characterize the materials for their better understanding and applications. The characterization of dielectric materials has received a considerable scientific interest because of their enormous applications in electronic devices such as resonators, actuators, multilayer capacitors, electrical insulations etc. The spontaneous dipole moments of some oxides lie in the asymmetric configuration of polar molecules. When an external electric field is applied to the dielectrics, dipoles reorient in a particular direction, and exhibit alignment of polar charges. The ability of the dielectric material to reorient and neutralize charges on the electrodes can be measured experimentally, and it is expressed in terms of a transfer function referred to as the relative permittivity or dielectric permittivity (dielectric constant). The dielectric permittivity of most dielectric materials is frequency dependent. In the presence of an applied electric field, the dipole moment inside the material oscillates with the direction of the electric field [208]. According to Debye model, the expression for complex permittivity is given by,

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)}$$  \hspace{1cm} (4.1)

Where, $\varepsilon_s$ and $\varepsilon_\infty$ are the value of permittivity at low and high frequency limit respectively, $\tau$ is the relaxation time and $\omega$ is the angular frequency. However, not all dielectrics follow the perfect Debye model. Cole- Cole [181] made an extension of the ideal Debye model for real systems having interfacing dipoles.

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha}$$  \hspace{1cm} (4.2)

Where $(\varepsilon_s - \varepsilon_\infty)$ is the dielectric strength and $\alpha$ represents a distribution of the relaxation time $(\tau)$. This expression further needs modification when a significant amount of dc conductivity $(\sigma_{dc})$ is present in the dielectric medium. The modified equation of dielectric response is expressed as
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\[ \varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_{3} - \varepsilon_{\infty}}{1 + (i\omega\tau)^{\alpha}} - \frac{i\sigma_{dc}}{\omega} \] (4.3)

For ferroelectric materials, the dielectric constant increases up to the transition temperature and then decreases obeying the Curie-Weiss law.

In this chapter, detailed studies of dielectric properties as a function of frequency and temperature have been discussed to get a better understanding of the polarization behavior of all the studied materials.

4.2. Frequency and temperature dependence of dielectric constant and tangent loss

The relative permittivity or dielectric constant (\(\varepsilon_r\)) is directly related to the electronic, atomic and dipolar polarizations of the materials. Under the impact of an ac field, the association of dielectric constant with the polarization of the material is prominent. From the nature of the variation of dielectric constant with frequency, it is possible to find out the contribution of the particular polarizations present in a given frequency range [208-209]. Typically, in the audible range of frequency, all types of polarizations are present. Space charge polarization is a purely surface phenomenon and depends upon the purity and perfection of the materials. At radio frequencies (~\(10^6\)Hz), the space charge effect may not have time to build up in most ionic conducting materials [210]. The dipolar polarization effect is exhibited in the materials below \(10^{10}\) Hz. In the low-frequency region, the presence of dipolar polarization is very much important for applications with suitable capacitive and insulating properties of the materials. Therefore, the electronic polarization persists above a frequency of \(10^{13}\)Hz, atomic polarization above \(10^{10}\)Hz, while the dispersion for dipolar polarization may lie anywhere within a wide frequency range (\(10^2-10^{10}\)Hz), depending on the materials and its temperature. However, the value of dielectric permittivity depends on other factors such as voids, grain boundaries and dipolar interactions, etc., which are present in the samples. On the other hand, dielectric loss or tangent loss represents the amount of energy spent by the applied field in dipolar alignment [7]. The size of grains also affects the dielectric loss.

In normal ferroelectrics, relative dielectric constant increases with rise in temperature up to a certain transition temperature (\(T_c\)) and then it decreases.
4.2.1. Dielectric properties of mechanically alloyed NiFe₂O₄ (NFO)

![Graphs showing frequency dependence of εᵣ and tan δ for NFO with different milling time (30, 60 and 90h) at selected temperatures.]

Fig. 4.1 (a): Frequency dependence of εᵣ (left hand side) and tan δ (right hand side) of NFO with different milling time (30, 60 and 90h) at selected temperatures.

Fig. 4.1(a) represents the frequency dependence of relative permittivity (left hand side of Fig 4.1(a)) and the tangent loss (right hand side of Fig. 4.1(a)) spectrum of NFO nanoceramic synthesized by mechanical alloying with different milling time (30, 60 and 90h) at selected temperature ranging from room temperature (25°C) to 300°C using the experimental method as discussed in chapter-2. The value of εᵣ and tanδ decreases smoothly with increasing frequency for all the samples. At low frequencies, the dielectric constant has high value,
whereas at high frequencies, it is low. The large dispersion is occurring in the low-frequency region. It is due to a Maxwell–Wagner type of interfacial polarization, which agreed well with Koop’s phenomenological theory. The increase in the value of $\varepsilon_r$ was attributed to a better electric flux caused by the reduced grain size with increasing the milling time which is consistent with observed micrograph of the material. This same trend is found to be parallel with the loss spectrum. From fig. 4.1(a), it is clear that for 60 h of milled sample both the dielectric parameters are found to be higher than those of 90h of milled sample. So it may be concluded that at a particular milling time (which is related to the particle size), dielectric parameters don’t follow the same rule (i.e., with a decrease in particle size the enhancement in dielectric parameters no longer bound to do so). So, 60 h of milling, which is related to the critical particle size, is responsible for the reduction of dielectric constant with an increase in milling time from 60 h to 90 h. This result can be correlated with the HRTEM micrograph also.

Fig. 4.1 (b) shows the temperature dependence of relative dielectric constant ($\varepsilon_r$) (left hand side of the Fig. 4.1(b)) and loss tangent ($\tan\delta$) (right hand side of Fig. 4.1 (b)) of different milled samples of NFO at different frequencies. Both the dielectric parameters ($\varepsilon_r$ and $\tan\delta$) decrease with increase in frequency, which is again a general feature of dielectric materials. It is a well-known fact that at low frequency, all the different types of polarizations (interfacial, dipole, atomic, ionic, electronic, etc.,) exist in the dielectrics. The existence of these polarizations vanishes slowly on increasing the frequency, as a result, dielectric constant decreases. There are some other reasons also for higher values of dielectric constant at low frequency. According to Maxwell–Wagner interfacial polarization law [211], the dispersion or higher value of dielectric constant is observed at low frequency, which is in good agreement with Koop’s phenomenological theory [212]. This theory explains that the dispersion is a result of the inhomogeneous nature of a dielectric structure composed of two layers [212]. The first layer is of large ferrite grains of highly conducting material that is separated by the second thin layer of relatively poor conducting substance (grain boundary). The grain boundaries are more effective at lower frequencies while the grains are found to be more effective at higher frequencies. In ferrites materials, as electrons being the majority charge carriers, the hopping mechanism of electrons takes place between Fe$^{3+}$ ions and Fe$^{2+}$ ions present at different crystallographic sites. The smallest value of $\varepsilon_r$ at higher frequencies may be due to the fact that the electron hopping between Fe$^{3+}$ ions and Fe$^{2+}$ ions at both octahedral
and tetrahedral sites cannot follow the alteration of ac electric field at these frequencies. Therefore, electrons have to pass through the well conducting grains and the poorly conducting grain boundaries. Since grain boundaries offer high resistance, the electrons get crowded there, and thus producing an enhanced space charge polarization. As a result, the material has larger \( \varepsilon_r \) value in the low-frequency range. With increasing frequency, the direction of motion of electrons changes rapidly. This hinders the movement of electrons inside the dielectric materials, and thereby reducing accumulation of charges at grain boundaries. Thus, decrease of space charge polarization and relative permittivity are observed. Further, \( \varepsilon_r \) increases gradually with increasing temperature with a same trend as observed in the variation of \( \tan \delta \) (as in \( \varepsilon_r \)) with temperature graph. The rate of increase in \( \tan \delta \) in the material at low temperatures is slow, whereas at higher temperatures the increase is relatively sharper. This sharp increase in the value of \( \tan \delta \) at higher temperatures is due to scattering of thermally activated charge carriers and presence of some unknown defects (including oxygen vacancies) in the materials. At higher temperatures, the domination of conductivity is responsible for rise in \( \tan \delta \) (right hand side of the fig. 4.1(b)). As the milling time goes on increasing, the dielectric constant also goes on increasing in the low-temperature and frequency region. The same trend is observed in the high- temperature and high-frequency region. For example, the dielectric constant at 500°C is 402 (for 30 h), 598 (for 60 h) and 627 (for 90 h) at 1MHz. As the composition, milling configuration and annealing temperature for all the three samples are same with the difference in milling time; the decrease in particle size is observed which is responsible for the enhancement of dielectric constant. It is observed that on an increase milling time, there is a remarkable change in the loss spectrum of different samples. An anomaly in both the relative dielectric constant \( (\varepsilon_r) \) and \( \tan \delta \) at about 300°C, and dielectric peak shifts towards the lower temperature side on the increasing frequency were observed.
Fig. 4.1 (b) Temperature dependence of relative dielectric constant ($\varepsilon_r$) (left hand side) and loss tangent ($\tan\delta$) (right hand side) of different milled samples of NFO at selected frequencies.
4.2.2. Dielectric properties of mechanically alloyed CoFe$_2$O$_4$ (CFO)

Fig. 4.2 (a): Frequency dependence of $\varepsilon_r$ (left hand side) and $\tan \delta$ (right hand side) of CFO with different milling time (30, 60 and 90h) at few selected temperatures.

Fig.4.2 (a) shows the Frequency dependence of $\varepsilon_r$ (left hand side) and $\tan \delta$ (right hand side) of CFO with at selected temperature starting from room temperature to 300°C. As discussed in the section 4.2.1, the dielectric properties i.e., the variation of dielectric parameters with frequency and can be modeled to the theory of Maxwell–Wagner interfacial polarization [211]; the dispersion or higher value of dielectric constant is observed at low frequency, and is in good agreement with Koop’s phenomenological theory [211]. In CoFe$_2$O$_4$ the small value of $\varepsilon_r$
at higher frequencies because of the fact that the electron hopping between Fe$^{3+}$ ions and Fe$^{2+}$ ions at both octahedral and tetrahedral sites cannot follow the alteration of applied ac electric field at these frequencies and hence, electrons have to pass through the well conducting grains and the poorly conducting grain boundaries whose explanation has already been discussed in the previous section. Fig. 4.2(b) shows the temperature dependence of relative dielectric constant ($\varepsilon_r$) (left hand side) and tan$\delta$ (right hand side) of different-time milled samples at the selected frequency. From fig. 4.2(b)(right side) it is confirmed that the loss possesses the similar behavior to that of the dielectric constant. As ferrite samples are lossy, that is why they have high value of dissipation factor in low frequency. Another reason is that the conductivity found to be dominating at high temperature which results in the enhancement of tan$\delta$. The dielectric loss factor or dissipation factor is the one of the most important part of the total core loss in the ferrite. With the increase in milling time the dielectric constants also goes on increasing in the low-temperature and the lower frequency region. The same trend is observed in the high-temperature and high-frequency region. Since the composition, milling configuration and annealing temperature for all the three samples are same with the difference in milling time; the decrease in particle size is found to be responsible for the enhancement of dielectric constant which is confirmed from the comparisons of dielectric constant at 1MHz. It is observed that with increase in milling time, there is a remarkable change in the loss spectrum of different samples. It is seen that there is an anomaly in both the relative dielectric constant ($\varepsilon_r$) and tan$\delta$ at or about 300°C, and dielectric peak shifts towards the lower temperature side on the increasing frequency, and hence peak shifts toward higher temperature side (on the increase in milling time) in all the samples. Similarly, in the temperature dependence loss factor one thing is clear that an anomaly peak found to be above 300°C and which shifts towards higher temperature side with increase in frequency in each milling time plot.
Fig. 4.2 (b): Temperature dependence of $\varepsilon_r$ (left hand side) and $\tan \delta$ (right hand side) of CFO with different milling time (30, 60 and 90 h) at selected frequencies.
4.2.3. Dielectric properties of mechanically alloyed MnFe$_2$O$_4$ (MFO)

Fig. 4.3 (a): Frequency dependence of $\varepsilon_r$ (left hand side) and tan $\delta$ (right hand side) of MFO with different milling time (30, 60 and 90h) at selected temperatures.
Fig. 4.3 (b): Temperature dependence of $\varepsilon_r$ (left hand side) and $\tan \delta$ (right hand side) of MFO with different milling time (30, 60 and 90 h) at few selected frequencies
Fig. 4.3 (a) shows the variation of relative dielectric constant ($\varepsilon_r$) (left hand side of fig 4.3(a)) and $\tan \delta$ (right hand side of fig 4.3(a)) of the different duration milled samples of MFO with frequency at selected temperature. The dielectric response with frequency shows the general trends of oxide materials [32]. Due to the presence of all type of polarization in low frequency region the value of dielectric constant quite high at low frequency range. This behavior is in accordance with Maxwell–Wagner interfacial polarization and Koop's phenomenology theory [212]. As discussed in section 4.2.1 the same explanation may be applied to this material also. From the figure it is confirmed that at high temperature say it to be $>250^\circ$C there is the increase in tangent loss in the material, and it increases with increase in milling time. This is due to the increase in disorderness in the materials with increase in milling. At low temperature the tangent loss value is low, consistent, and reasonable. At high temperature the thermally activated charge carriers formed, and conductivity begins to dominate, so the value of $\tan \delta$ quite high in the low frequency domain.

Fig. 4.3(b) shows the temperature dependence of relative dielectric (left hand side of fig 4.3(b)) constant and tangent loss (right hand side of fig. 4.3(b)) at some selected frequencies. The value of $\varepsilon_r$ increases gradually with increasing temperature with a same trend as that of $\tan \delta$. The rate of increase in $\tan \delta$ in the material at low temperatures is slow, whereas at higher temperatures the increase is sharper. This sharp increase in the value of $\tan \delta$ at higher temperatures is due to scattering of thermally activated charge carriers and presence of some unknown defects including oxygen vacancies in the material. At higher temperatures, the conductivity begins to dominate, which in turn, is responsible for rise in $\tan \delta$. On increasing milling time, the dielectric constant increases in the low temperature-frequency region. The same trend is observed in the high temperature and frequency region. Since, all the physical parameters and processing condition of all the three samples are same, but with differences in milling time; hence, the decrease in particle size is responsible for the enhancement of dielectric constant. It is also observed that milling time changes the loss spectrum of the samples significantly. There is an anomaly in both $\varepsilon_r$ and $\tan \delta$ at about 300$^\circ$C. The dielectric peak shifts towards the low-temperature side on increasing frequency, and thus peak shifts toward higher temperature side on increasing milling time in all the samples.
4.3. Dielectric properties of polymer–nanocomposite: The frequency and temperature dependence of polymer nano-composites are described below.

4.3.1 Dielectric properties of Polyvinilidene-difluoride (PVDF)

Fig. 4.4(a) Frequency dependence of $\varepsilon_r$ (left hand side of figure) and $\tan\delta$ (right hand side of figure) of pure PVDF

Fig 4.4(a) shows the frequency dependence of dielectric constant (left hand side of figure) and $\tan\delta$ (right hand side of figure) at selected temperature from room temperature to 125°C with an interval of 25°C. Both the dielectric parameters show a similar trend (i.e., decrease in dielectric constant and $\tan\delta$ with increase in frequency) which is a normal behavior of ferroelectric polymer. The value of dielectric constant is found to be 9.6 at room temperature at 1kHz which is consistent with the reported one [153]. The loss tangent of PVDF is also found to be very small [215-218]. Fig 4.4(b) shows the temperature dependence of dielectric constant (left hand side of figure) and $\tan\delta$ (right hand side of the figure) at selected frequencies from room temperature to 125°C. From the figure it is confirmed that the dielectric constant and loss tangent increase with increase in temperature. At low temperature, the segmental motion of the chain is practically frozen which reduce the dielectric constant. As temperature increases, the intermolecular forces between the polymer chains is broken which enhances the thermal agitation. So higher temperatures facilitate easier movement of different dipole, and hence these dipoles are able to follow the change in frequency more
aptly. Another reason for the increase in dielectric constant is that the polymer matrix expands with temperature, which results in increase in interfacial polarization [217-219].

![Graph](image)

**Fig. 4.4(b) Temperature dependence of ε_r (left hand side of figure) and tanδ (right hand side of figure) of pure PVDF**

### 4.3.2 Dielectric properties of (1-x) PVDF-x NFO (x=0.05, 0.1, 0.15)

The frequency dependency of dielectric constant (left hand side of fig 4.5(a)) and dielectric loss(right hand side of fig. 4.5(a)) of (1-x) PVDF-x NFO(x=0.05,0.1,0.15) nano-composite with the different volume fraction of the spinel nanoferrite in the low-frequency range (1kHz to 1MHz) at selected temperature (room temperature to 125°C) is shown in fig. 4.5(a). The dielectric constant shows a decrease with the increase in frequency in the frequency range of 1 kHz to 1MHz. In the earlier discussion on the dielectric response of NFO nanoceramic with frequency, it can be co-related (i.e., the decrease is mainly because of the reduction in the dielectric constant of NFO nano-ceramics), to the Maxwell–Wagner-Sillar (MWS) interfacial polarization and space charge polarization. In high-frequency range, NFO nanoceramics exhibit a large dielectric relaxation and reduced dielectric constant. In addition, the MWS interfacial polarization and space charge polarization mainly work in the low-frequency range.
Dielectric Properties because of their long relaxation time. Moreover, the dielectric constant of pure PVDF is low (~9.6 at 1kHz). The dielectric constant of the composite gradually increases with the content of the nano-particle, which means, it can be tuned by changing the filler content, and thus value is quite encouraging for capacitive energy device fabrication. The maximum value of dielectric constant at room temperature and at 1kHz is achieved in case of x=0.10 of the nano-composite series of (1-x)PVDF-x NFO and it is about 340, which is very much higher than that of the virgin PVDF. The dielectric constant increases with the filler concentration from x=0.05 to x=0.10 and then decreases at x=0.15. The dielectric constant of a composite is well described by the effective medium theory, where the depolarization factor is strongly dependent on the aspect ratio of the fillers in the composite [215]. Therefore, the excellent improvement in the dielectric performance of the composite can be attributed to nanoceramic with large aspect ratios, which are more effective in enhancing the dielectric constant of composites at lower concentration than particles [216].

The loss tangent of the composite films slowly decreases from low frequency, which is attributed to MWS interfacial polarization, and then it decreases from $10^3$ Hz to $10^6$ Hz which is attributed to the $\alpha_a$ relaxation, which is associated with the glass transition of the pure PVDF polymer. In addition, the value of dielectric loss is also considerably lower than that of percolative composite [217-218]. Similar to the dielectric constant, the loss tangent is also increased with increase in filler concentration.

Fig.4.5(b) shows the temperature dependence of the dielectric constant ($\varepsilon_r$) (left hand side of fig.4.5(b)) and tangent loss (right hand side of fig.4.5(b)) of (1-x)PVDF-x NFO (x=0.05, 0.1, 0.15) at selected frequencies (25, 100, 500 and 1000kHz). The figure shows that the dielectric constant increases with increase in temperature. At low temperatures, the segmental motion of chain is practically frozen which reduce the dielectric constant. As temperature increases, the intermolecular forces between the polymer chains is broken which enhances the thermal agitation. So higher temperature facilitates easier movement of different dipoles, and hence these dipoles are able to follow the change in frequency more aptly. Another reason for the increase in dielectric constant is that the polymer matrix expands with temperature and which results in increased interfacial polarization [219]. These results indicate that introduced ceramic filler have a positive influence on the structure of the polymeric matrix and contribute to the dielectric response of the composite. The value of the dielectric constant does not vary
substantially with temperature, but it is found to vary very much with the composition. It is found that the value of dielectric constant is the highest for $x=0.10$ of (1-$x$)PVDF- $x$ NFO and it varies within 305 to 335 and the loss is found to be very low.

Fig. 4.5 (a) Frequency dependence of dielectric and loss tangent of (1-$x$) PVDF-$x$ NFO
($x=0.05, 0.1, 0.15$) at selected temperature
There is a slight abnormal increase in both dielectric parameters in the low-temperature region, i.e., up to 40°C from room temperature, which suggest the influence of atmospheric humidity on the composite. But with the increase in temperature from 45°C onwards the slight increasing trend in both dielectric parameters observed in each composite, however, it seems to be independent of temperature at high temperature. For the all composite the value of $\varepsilon_r$ initially decreases and then remains almost constant with temperature. Because of the constrained polymer chain obstructs the formation of electrical polarization, for the reason the value of $\varepsilon_r$ is less. The value of $\varepsilon_r$ for all composites is significantly higher than that of PVDF. It is because the dielectric constant of the ferrite nanoparticles ceramic is significantly higher than that of polymer.
Fig. 4.5 (b) Temperature dependent dielectric constant (left hand side) and loss tangent (right hand side) of (1-x) PVDF-x NFO (x=0.05, 0.1, 0.15) at selected frequencies.

The nature of tanδ follows the similar pattern as that of $\varepsilon_r$. For PVDF the increased in tanδ is gradual but for the composite there is a sharp rise above 70°C for both x=0.10 and 0.15 of (1-x) PVDF- x NFO. This may be due to the scattering of thermally activated charge carrier or some unknown defects [220]. The increment of dielectric loss with temperature indicates the increase in conductivity of the polymer matrix. At high temperatures, the contribution of ferroelectric domain walls to tanδ is less, which causes the rise in the value of the tanδ. The
higher value of tan\(\delta\) at low frequencies and at high temperature may be due to the enhanced space charge relaxation [221]. It is found that the dielectric loss of PVDF is less compared to ceramic-polymer composites which are due to the higher loss of a ferrite nanoparticle as compared to that of the PVDF matrix.

4.3.3 Dielectric properties of (1-x) PVDF-x CFO (x=0.05, 0.1, 0.15)

Fig 4.6(a) represents the frequency dependence of dielectric constant (left side of the figure) and dielectric loss (right side of the figure) of (1-x)PVDF-xCFO (x=0.05,0.1,0.15) nanocomposites in the frequency range 1kHz to 1MHz at selected temperature. The dielectric constant decreases with the increase in frequency. In pretend to our earlier discussion in the dielectric response of CFO nanoceramic with frequency, it can be concluded that the decrease in dielectric parameters is mainly due to the reduction in the dielectric constant of CFO nanoceramics, and is in accordance with Maxwell–Wagner-Sillar (MWS) interfacial polarization and space charge polarization. In addition to the MWS interfacial polarization, space charge polarization mainly works in the low-frequency range because of its long relaxation time. Moreover, the dielectric constant of pure PVDF is low (~9.6 at 1kHz). The dielectric constant of the composite gradually increases with the content of the nanoparticle, which means, it can be tuned by changing the filler content and the value is quite encouraging for capacitive energy device fabrication. The maximum value of dielectric constant at room temperature and at 1kHz is achieved in case of x=0.15 of the nano-composite series of (1-x) PVDF-xCFO, and it is about 400, which is very much higher than that of the virgin PVDF. The dielectric constant of a composite is well described by the effective medium theory, where the depolarization factor is strongly dependent on the aspect ratio of the fillers in the composite [215].
Fig. 4.6 (a) Frequency dependent dielectric constant (left hand side) and loss tangent (right hand side) of (1-x) PVDF-x CFO (x=0.05, 0.1, 0.15) at selected temperature

Therefore, the excellent improvement in the dielectric performance of the composite can be attributed to nano-ceramic with large aspect ratios, which are more effective in enhancing the dielectric constant of composites at lower concentration than particles [216].
The dielectric loss of the composite films gently decreases from low frequency, which is attributed to the MWS interfacial polarization. And then it decreases from $10^3$ Hz to $10^6$ Hz noted, were attributed to the $\alpha_a$ relaxation, which is associated with the glass transition of the pure PVDF polymer [217-218]. Like the dielectric constant, the loss tangent also increases with increase in filler concentration.

The temperature dependence of the dielectric constant ($\varepsilon_r$) of (1-x) PVDF-x CFO (x=0.05, 0.1, 0.15) at selected frequencies (25, 100, 500 and 1000 kHz) is shown in Fig.4.6 (b). At low temperature, the segmental motion of chain is practically frozen which reduces the dielectric constant, and it is evidenced from the figure (whose effect is up to 50°C) for the filler concentration of x=0.05 and 0.15 and not clear for x=0.15. As temperature increases, the intermolecular forces between the polymer chains is broken that enhances the thermal agitation. So higher temperature facilitates easier movement of different dipoles, and hence these dipoles are able to follow the change in frequency more aptly. Another reason for the increase in dielectric constant is that the polymer matrix expands with temperature, which results in increased interfacial polarization [219]. These results indicate that introduced ceramic filler have a positive influence on the structure of the polymeric matrix and contribute to the dielectric response of the composite. The value of the dielectric constant does not vary substantially with temperature, but it is found to vary very much with the composition. It is found that the value of dielectric constant is the highest for x=0.15 of (1-x)PVDF- xCFO, and it is vary within 78 to 86 in the room temperature and the loss is found to be very low. There is a slight abnormal increase in both dielectric parameters in the low-temperature region i.e., up to 40°C from room temperature, which suggests the influence of atmospheric humidity on the composite. But with the increase in temperature from 45°C onwards, the slight increasing trend in both dielectric parameters is observed in each composite. However, it seems to be independent of temperature at higher temperatures. For all composites, the value of $\varepsilon_r$ initially decreases and then remains almost constant with temperature. Because of the constrained polymer chain obstructs the formation of electrical polarization, for the reason the value of $\varepsilon_r$ is less. The value of $\varepsilon_r$ for all composites is significantly higher than that of PVDF. It is because the dielectric constant of the ferrite nanoparticle ceramic is significantly higher than that of polymer.
The increase in dielectric constant with the increase in filler percentage could be explained by following two reasons. The first one was the introduction of high dielectric constant ferrite particle leading to the average electric field enhancement in the matrix, and the more the ferrite content was introduced, the higher the dielectric constant would be obtained. The second thing was the large amount of charges accumulated at the interfaces of the two phases due to the difference between the ferrite particle and PVDF matrix forming the interfacial polarization. With the increase in ferrite concentration, the amount of interfacial charges increases, as a result, the enhancement of interfacial polarization density is observed, which increases the dielectric constant of the whole materials [222].

Fig. 4.6 (b) the temperature dependence dielectric and loss tangent of (1-x) PVDF-x CFO (x=0.05, 0.1, 0.15) at selected frequencies
4.3.4 Dielectric properties of (1-x) PVDF-x MFO (x=0.05, 0.1, 0.15)

Fig. 4.7 (a) Frequency dependent dielectric constant (left hand side) and loss tangent (right hand side) of (1-x) PVDF-x MFO (x=0.05, 0.1, 0.15) at selected temperature.

Fig 4.7(a) represents the frequency dependence of dielectric constant (left hand side) and dielectric loss (right hand side) of (1-x) PVDF-x MFO (x=0.05, 0.1, 0.15) nanocomposites in the frequency range of 1kHz to 1MHz at selected temperature. From the figure, it is found that for all composition the dielectric constant decreases rapidly in the lower frequency domain, and then become more or less constant at higher frequencies representing the dielectric
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dispersion. The decrease in dielectric parameters is mainly due to the reduction in the dielectric constant of MFO nanoceramics and in accordance with Maxwell–Wagnor-Sillar (MWS) interfacial polarization and space charge polarization. In addition to the MWS interfacial polarization and space charge polarization mainly works in the low-frequency range because of their long relaxation time, because the grain boundaries are more effective at lower frequencies while grains are found to be effective at higher frequencies. As grain boundaries offer high resistance, the electrons get crowded there, and thus space charge polarization enhances and also the dielectric constant. The dielectric constant of the composite gradually decreases with the increase in filler content of the nanoparticle, which means; there is a critical filler content limit beyond which the dielectric constant decreases with increase in filler concentration. In the present case, it is found to be $x=0.05$. Though the dielectric constant is found to be decreased with increase in filler concentration still the dielectric constant is quite encouraging for device fabrication. The loss tangent increases with increase in filler concentration.

To illustrate the thermal stability of the polymer nano-composite, the temperature dependence of dielectric behavior (left hand side of fig.4.7(b)) and tangent loss of (right hand side of fig.4.7(b)) of (1-$x$) PVDF-$x$ MFO ($x=0.05, 0.1, 0.15$) were investigated and depicted in fig.4.7(b). From the above figure it is obvious that over the whole measured temperature range, the addition of the nano filler into the polymer matrix results an increase in the dielectric constant of the composites as compared to the pure PVDF but decreases with increase in filler content. Another distinctive feature is that the broad dielectric constant peak moves to a high temperature as the frequency increases, typical for relaxor ferroelectrics, which corresponds to the dipolar freezing transition in which different components of the polarization response will freeze at different temperature. Furthermore, the dielectric constant and loss of pure PVDF polymer and the composites exhibit a sharp increase at $10^4$ Hz and above $50^\circ$C, where the space charge contribution (conduction) causes a large increase in both dielectric parameters with temperature. These phenomena are attributed to an interfacial polarization, known as the Maxwell-Wagnor-Sillars (MWS) effect. Because of the discrepancies of dielectric properties (conductivity, dielectric constant) of the two phases, leading to the appearance of an interfacial polarization, which can significantly enhance the dielectric constant of the nanocomposite in the low-frequency range [222]. The increase in dielectric constant of the filler concentration of $x=0.05$ and $0.10$ above the temperature $60^\circ$C
could be related to the $\alpha_a$-relaxation, as these values became higher as they approaches towards the melting point. Though all the parameters of measurement kept in pace as like the measurement for $x=0.05$ and $0.10$ but some anomalous results are found in case of $x=0.15$. As per the general rule of temperature dependence of the dielectric constant, it doesn’t follow the similar trend rather it decreases with increase in temperature. The loss tangent spectrum for $x=0.15$ also follows the same rule.

Fig. 4.7 (b) the temperature dependence dielectric constant (left hand side) and loss tangent (right hand side) of $(1-x)$ PVDF-x MFO ($x=0.05, 0.1, 0.15$) at selected frequencies.
4.4 Summary

Based on dielectric measurement and analysis we conclude that:

- The dielectric constant of the spinel ferrite (i.e., NFO, CFO and MFO) is strongly dependent on milling time or particle size of the materials.
- The value of $\tan\delta$ changes with particle size. In case of NFO and MFO, reduction in particle size leads to the decrease in $\tan\delta$, but in case of CFO, it found to be opposite.
- The value of $\varepsilon_r$ for pure PVDF is less than that of ceramic – polymer composite because the constrained polymer chain which obstructs the formation of electrical polarization. Low dielectric loss is observed in PVDF as compared to the ceramic – polymer composite.
- The value of dielectric constant of polymer-ceramic composite depends on the concentration of filler. From the dielectric spectrum of polymer-ceramic composite it is concluded that there is a critical limit for filler for which the dielectric is maximized and beyond it decreases with increase in filler concentration.