

Investigation on dielectric performance and charge transport mechanism in synthesized PVDF films embedded with BaTiO₃ nanofillers for energy harvesting applications

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Composites of Polyvinylidene fluoride (PVDF) with different percentages of Barium Titanate (BaTiO₃) has been synthesized by solution casting method. This study explores the influence of BaTiO₃ particles on dielectric properties of PVDF composite films at elevated temperatures. The relative dielectric permittivity increases upto 90 with the increase in the BaTiO₃ particle concentration with good stability of dielectric loss and enhances ac conductivity upto three order of magnitude as compare to pure PVDF. The current-voltage characteristic plots of PVDF-BaTiO₃ composite films show the dependence of current on electric field, temperature and filler concentration with better understanding of role played by charge carriers in conduction mechanism. The current-voltage characteristic plots show two conduction regions: one is ohmic conduction at low field and another is non ohmic conduction at higher field which is better interpreted in the light of Richardson and Frenkel models. These characteristics of composite film open the window to develop flexible material for high energy storing devices.

(Received May 3, 2021; accepted November 24, 2021)

Keywords: PVDF, Barium Titanate, Dielectric permittivity, Conductivity, Charge carriers, Ionic hopping, Schottky and Frenkel plots

1. Introduction

Recently, polymeric material with efficient dielectric permittivity have drawn much attention due to their various applications especially in energy storing devices, miniaturized electronic devices [1-3]. Ferroelectric polymer polyvinylidene fluoride PVDF has become an interesting research material in the recent decades due to its excellent piezoelectric property, good flexibility and large mechanical strength [4-5]. The presence of fluorine in this polymer chain offers high thermal and chemical stability. These advantages leads to use PVDF as potential material for numerous applications [6]. However poor crystallinity (less than 50%) and relatively low dielectric constant limits its applications in the electronic industry [7]. Thus optimal properties can be achieved by incorporating filler or ceramic composite into the polymer matrix, which enhances dielectric constant. Improvement of low dielectric constant will expand its range of applications in electronics such as piezosensors, hydrophones, transducers and high charge storage capacitors [8-9]. Dash et al. uses multiferriocs as dopant increase the dielectric constant of PVDF [10]. Wang et al. synthesized PVDF based nanocomposite with Fe_3No_4 / MWNCT as filler for capacitor applications [11]. Recently, Yang et al. synthesized PVDF nanocomposite with carbon nanotubes to enhance dielectric properties [12]. He et al. synthesized an excellent dielectric composite of PVDF efoliated with graphite nanoplates [13].

In present investigation BaTiO₃ ceramic is embedded with PVDF polymer to explore the possibility of obtaining high dielectric permittivity. Apart from the dielectric properties, addition of BaTiO₃ influences the charge transport mechanism within the polymer. A good amount of work has been reported on the conduction mechanism of PVDF but the mechanism of charge transportation is not well understood with the blending of BaTiO₃ particles. Therefore the apt understanding of conduction mechanism within the polymeric blend invoked the interest for advancement in future realistic applications. In our previous work, we synthesize PVDF-BaTiO₃ composite films via sol gel casting technique and investigate the change in a crystalline structure, phases, morphology with the objective to nucleate the β -phase [14]. Our XRD and FTIR results show that BaTiO₃ particles favors the alignment of diploes of polymer chain leads to enhance the degree of crystallinity from 49% (for pristine PVDF) to 60 % in composite films. FESEM images reveal that $BaTiO_3$ particles were homogeneously distributed within the polymer matrix with little porosity.

In this present work PVDF-BaTiO₃ composite films is fabricated with the aim of improving dielectric properties. We analyse the dielectric permittivity, losses and conductivity at different frequencies (100Hz-5 MHz) and temperature (50-150°C) along with the effect of filler concentration in order to make this composite material suitable for electronic applications. We also measure the dependence of current on electric field, temperature and filler concentration by studying current-voltage characteristic plot and analyse the charge transport

mechanism by interpreting Ionic hopping conduction mechanism and Schottky-Frenkel conduction models.

2. Experimental details

Materials used for synthesis i.e. Polyvinylidene fluoride (PVDF) having MW \approx 534,000 and Barium Titanate with particle size $<$ 100 nm were purchased from Sigma–Aldrich, India. Dimethylformamide (DMF) was purchased from Rankem Chemicals, India used as solvent. PVDF-BaTiO₃ composite films is synthesized by sol-gel casting technique which has been mentioned in detail in

our previous article [14]. Thereafter the obtained film is coated with Al layers by vacuum thermal evaporation coating on both the sides within the area of 1 cm². The dielectric study of composite films were carried out using Hioki LCR 3532-50 meter over the frequency range of 100 Hz-5 MHz as the function of temperature from 50°C - 150°C. Keithley Semiconductor Characterization Unit (SCS-4200) were used for the Current-Voltage measurements. The configuration of the experimental arrangement for the dielectric and current-voltage measurements is shown in the Fig. 1.

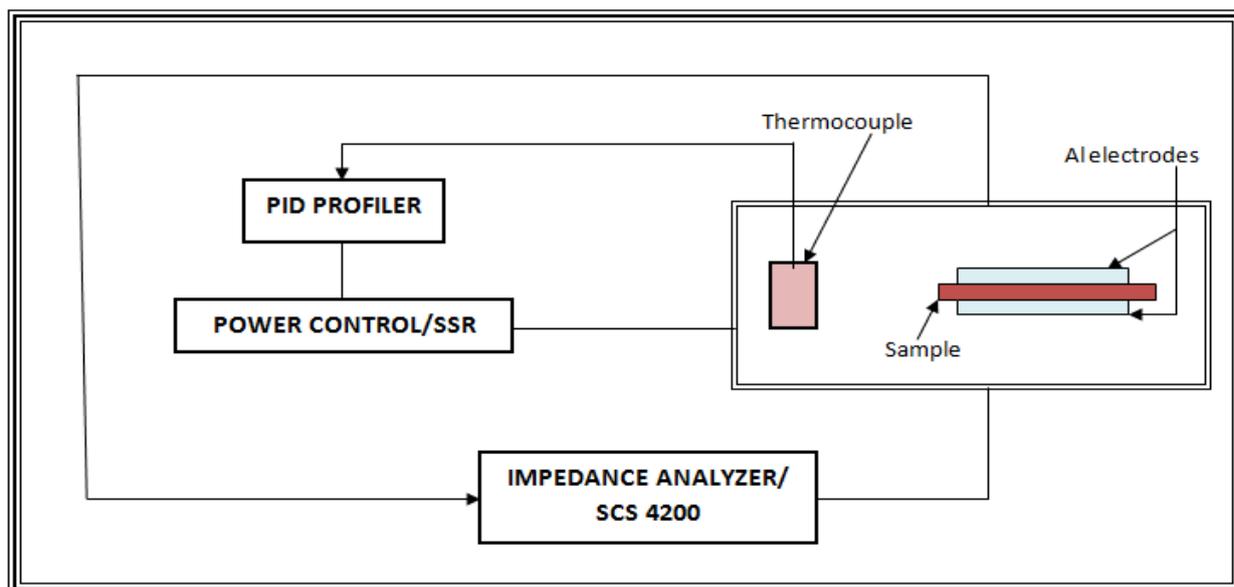


Fig. 1. The experimental arrangement for the dielectric and current-voltage measurements (color online)

3. Results and discussions

3.1. Dielectric analysis

Generally dielectric performance is dependent on three major factors i.e. applied frequency, annealing temperature and concentration of the dopant. The dielectric performance is determined by the distribution of charge carriers and also by thermal motion of its polar groups. The polarization of a dielectric is contributed by the ionic, electronic and dipole polarizations [15-16]. The relative dielectric permittivity (ϵ') calculated from the capacitance (C_p) measured by LCR meter with a parallel equivalent circuit and AC conductivity of the samples are calculated from the data of the dielectric permittivity (ϵ') and tangent loss factor ($\tan\delta$) by using the following equations [16-17]:

$$\epsilon' = \frac{C_p \times d}{A \epsilon_0} \quad (1)$$

$$\sigma_{ac}(\omega) = 2\pi f \epsilon' \epsilon_0 \tan\delta \quad (2)$$

where d , A and f are thickness (cm), area (cm²) and frequency (Hz) of the samples respectively. ϵ' is permittivity of the sample and ϵ_0 permittivity of free-space having value 8.85×10^{-12} farad/m.

3.1.1. Analysis of Dielectric Permittivity and losses

Frequency dependent analysis of dielectric permittivity for PVDF-BaTiO₃ composite films at different temperature is presented in Fig. 2. It is observed that dielectric permittivity of PVDF is substantial higher at low frequency than high frequency at constant temperature. This is due to the presence of dipoles within matrix and their ability to orient under the applied electric field [16-18]. At lower frequencies, the free dipoles in the PVDF chains have enough time to orient themselves according to the applied electric field which contributes towards polarization. At higher frequencies, dipoles donot get enough time to orient themselves at the same pace with frequency of alternating field resulting in decrease of relative permittivity values [10,18].

Fig. 2 shows the enhancement in the permittivity values of composite films with the increase in the filler concentration. At the frequency of 20 Hz, the highest dielectric permittivity value of 90 is achieved for 1 wt% of BaTiO₃ nanofiller. This enhancement in dielectric permittivity may be due to the Maxwell-Wagner-Sillars (MWS) interfacial polarization effect. BaTiO₃ particles exhibits the interface polarization which leads to high dielectric values. This is because of more uniform distribution of nano filler which gives effective interaction between filler particles and the PVDF matrix resulting in high dielectric values. At higher frequencies, the gradual decrease in dielectric permittivity is due to the decreasing effect of interfacial polarization.

It is also observed from Fig. 2 that the dielectric values enhances with the increase in temperature. This is due to annealing effect in which the molecular motion aligns the dipole in same direction. At higher temperatures, dipole units were unfrozen which attributes to increase in dielectric permittivity. Maximum relative permittivity was found to be 90 at 20 Hz annealed at 150°C which is 10 times more than that of pure PVDF.

High values of dielectric permittivity suggest that PVDF films embedded with BaTiO₃ might be anticipated for energy storage applications.

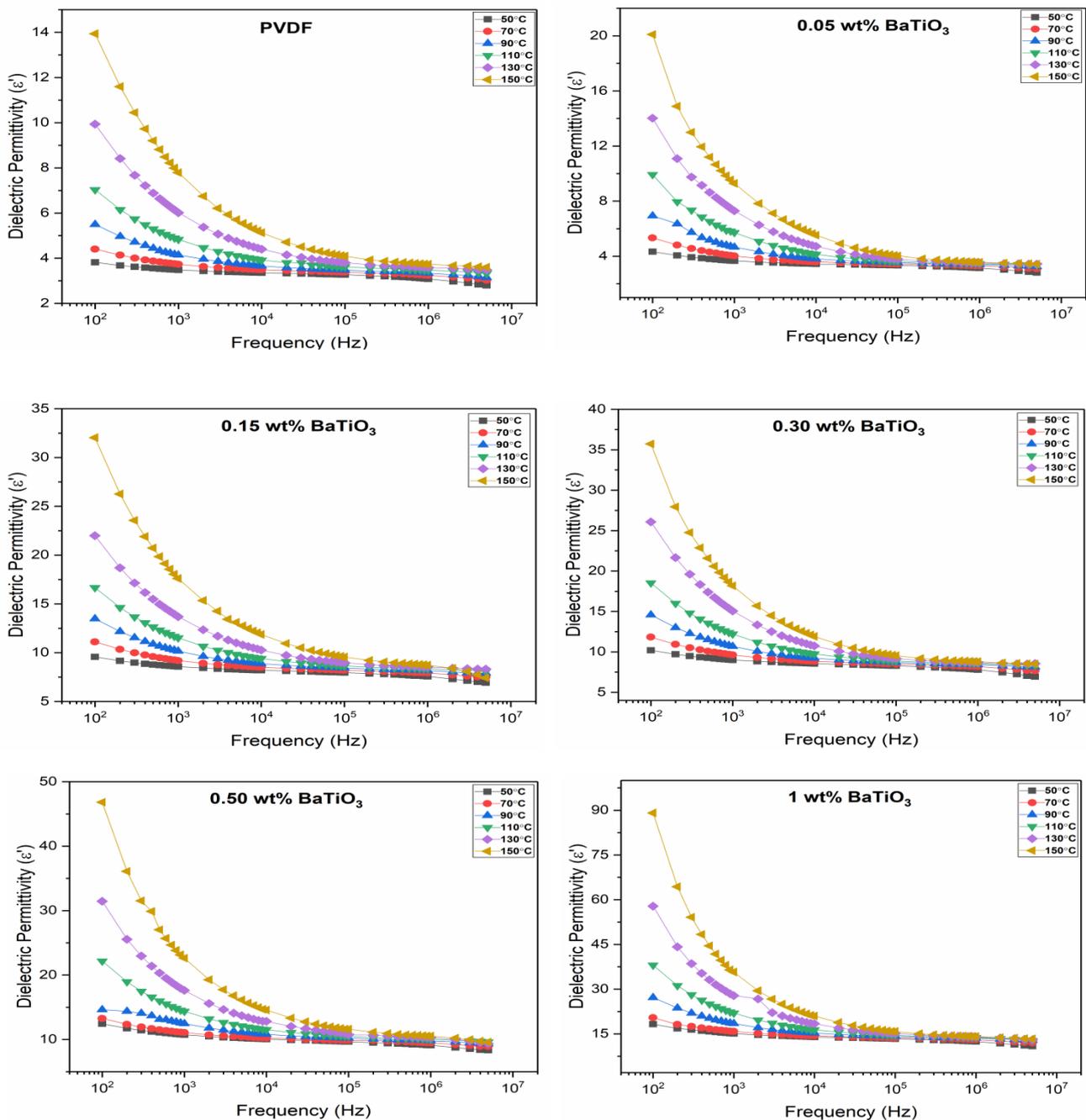


Fig. 2. Frequency dependent analysis of dielectric permittivity for PVDF-BaTiO₃ composite films (color online)

Dielectric losses is explained in terms of $\tan \delta$ which is calculated using equation given below [18,19]:

$$\tan \delta = \varepsilon''/\varepsilon' \quad (3)$$

Frequency dependent analysis of dielectric losses for PVDF-BaTiO₃ composite films decreases with the rising frequency are presented in Fig. 3. It is observed that losses are maximum at lower frequencies whereas losses remain almost constant at higher frequencies for all temperature. This is explained by the interfacial polarization between PVDF and BaTiO₃ interface. At low frequencies, charge

carriers take longer time to reach at the PVDF-BaTiO₃ interfaces, creates the interfacial polarization and produces maximum dielectric loss. At lower frequencies, dielectric losses increases at slower pace with the increase in temperature where as at higher frequencies, losses has almost same values at all temperatures. Dielectric losses also increases with the filler concentration. This is due to the barium and titanate ions which are well aligned with the CH₂ and CF₂ contributes the increase in leakage current which in turn enhances ε'' and $\tan \delta$.

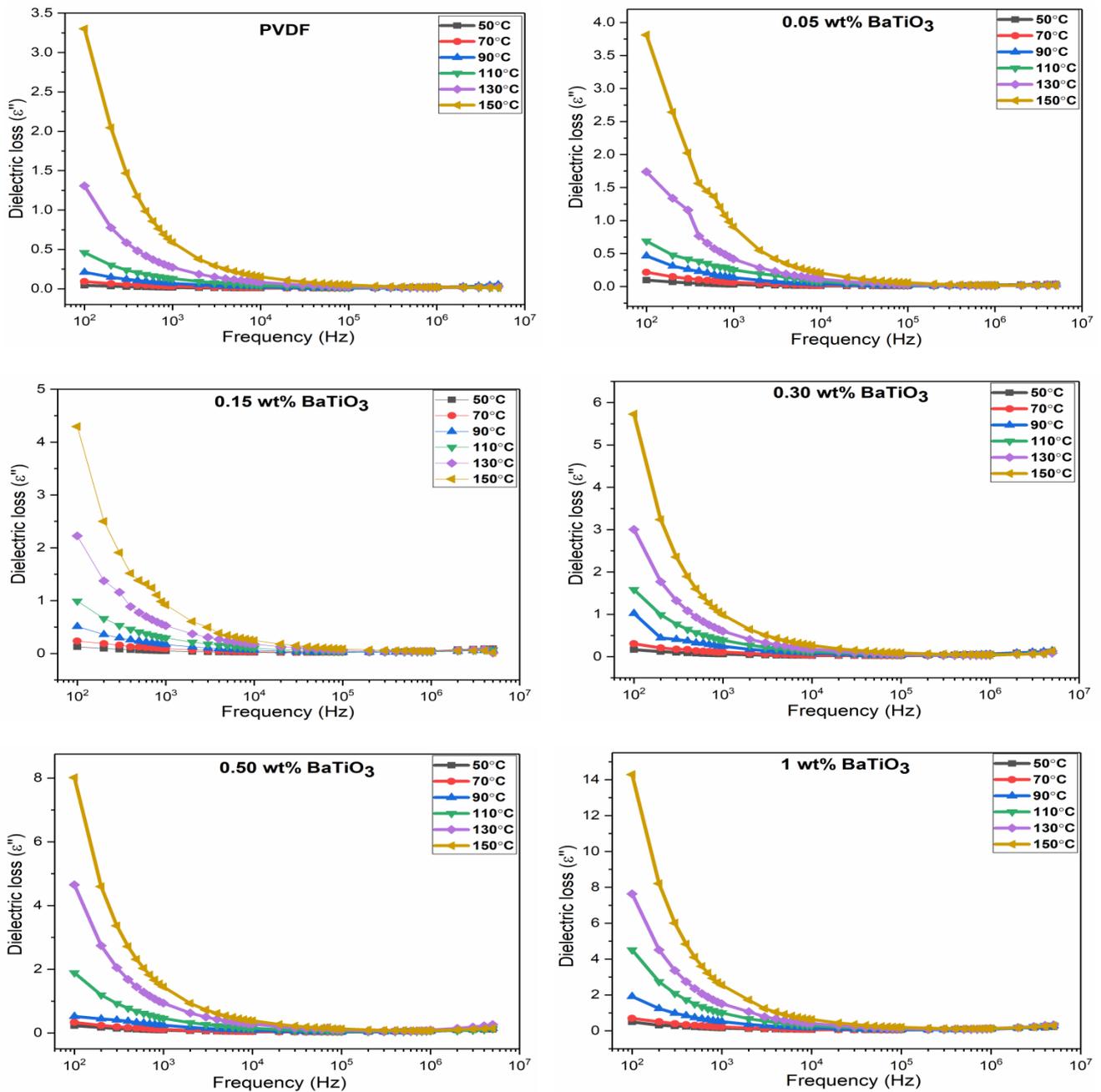


Fig. 3. Frequency dependent analysis of dielectric losses for PVDF-BaTiO₃ composite films (color online)

3.1.2. Analysis of AC conductivity

Frequency dependent analysis of AC conductivity for PVDF-BaTiO₃ composite films at different temperature is presented in Fig. 4. In case of pristine PVDF, AC conductivity was influenced by presence of loosely ions bound to the molecules and its polar property [16,17]. In PVDF, negatively charged fluorine (F) is responsible for net dipole moment which contributes to polarization. Addition of BaTiO₃ filler enhances the β -phase which forces H and F atoms to be more aligned in order to give net dipole moment and enhancing the overall conductivity.

AC conductivity has temperature dependency which is described by Jonscher power law [19]:

$$\sigma(\omega) = A (\omega)^S \quad (4)$$

where A is constant and S is function of temperature lies between 0 and 1.

As the temperature is elevated the charge carriers are thermally activated and the free volume increases and more vacant sites are created for the motion of ions, which in turn enhanced the conductivity. It is concluded from the above study that AC conductivity increases with increase in frequency, temperature and filler concentration.

In summary, it can be concluded that inclusion of BaTiO₃ particles favors the alignment of dipoles of polymer chain resulting in achieving the maximum dielectric constant with less losses. The above conclusion is in line with the results concluded from the XRD and FTIR investigation [14].

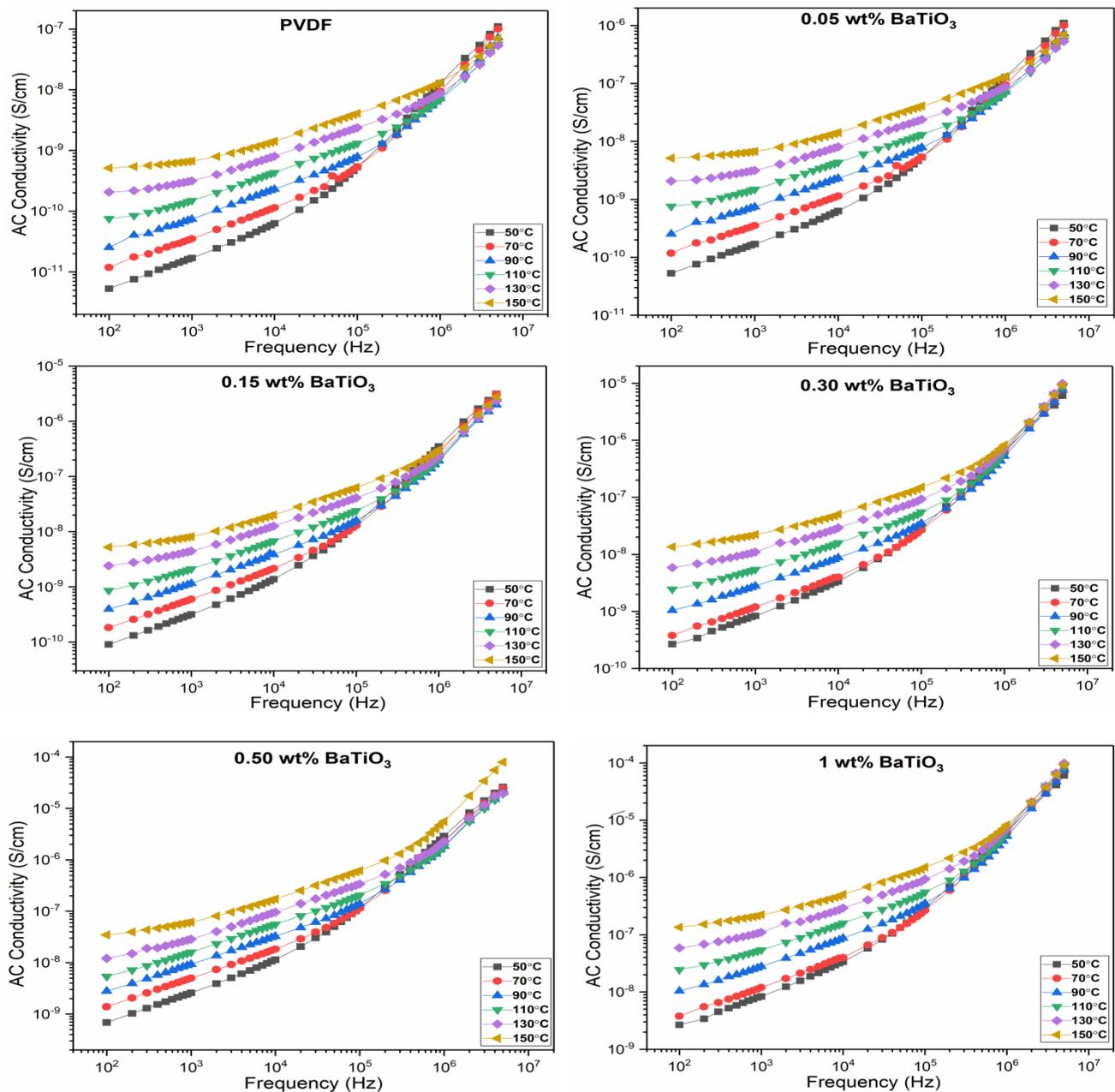


Fig. 4. Frequency dependent analysis of AC conductivity for PVDF-BaTiO₃ composite films (color online)

3.2. Analysis of Electrical properties (current-voltage measurements)

The temperature dependence Current-Voltage measurements for PVDF-BaTiO₃ composite films are shown in Fig. 5. These current-voltage characteristic plots show the steady state dc conduction current for electric field at various operating temperature ranges 50-150 °C. At low temperature, PVDF reveals the negligible current flow which may be due to the presence of intrinsic free charge carriers. At the higher temperature sharp peak was observed which is defined as β -peak [20]. This β -peak indicates the predominant switching current arises in PVDF due to the polarization at higher temperature known as dipolar relaxation. Inclusion of BaTiO₃ particles enhances the existing injected carriers which may be due

to the orientation of PVDF dipoles. This orientation of dipoles induces ferroelectric polarization in the direction of applied field and improves the electrical current. This increase in the current value correlates well with our previous FESEM result in which homogeneous distributed BaTiO₃ particles with porous surface favors the enhancement in electrical conductivity.

A current-voltage characteristic plot for PVDF-BaTiO₃ composite films initially shows linear behavior at low electric field followed by non-linear behavior at high electric field. Non linearity dominates in composite films at higher temperature. With the elevation of operating temperature, the thermal ionization of the trapping centers increases which lowers the barrier for the electrons/ions to be transported and make the conduction non linear.

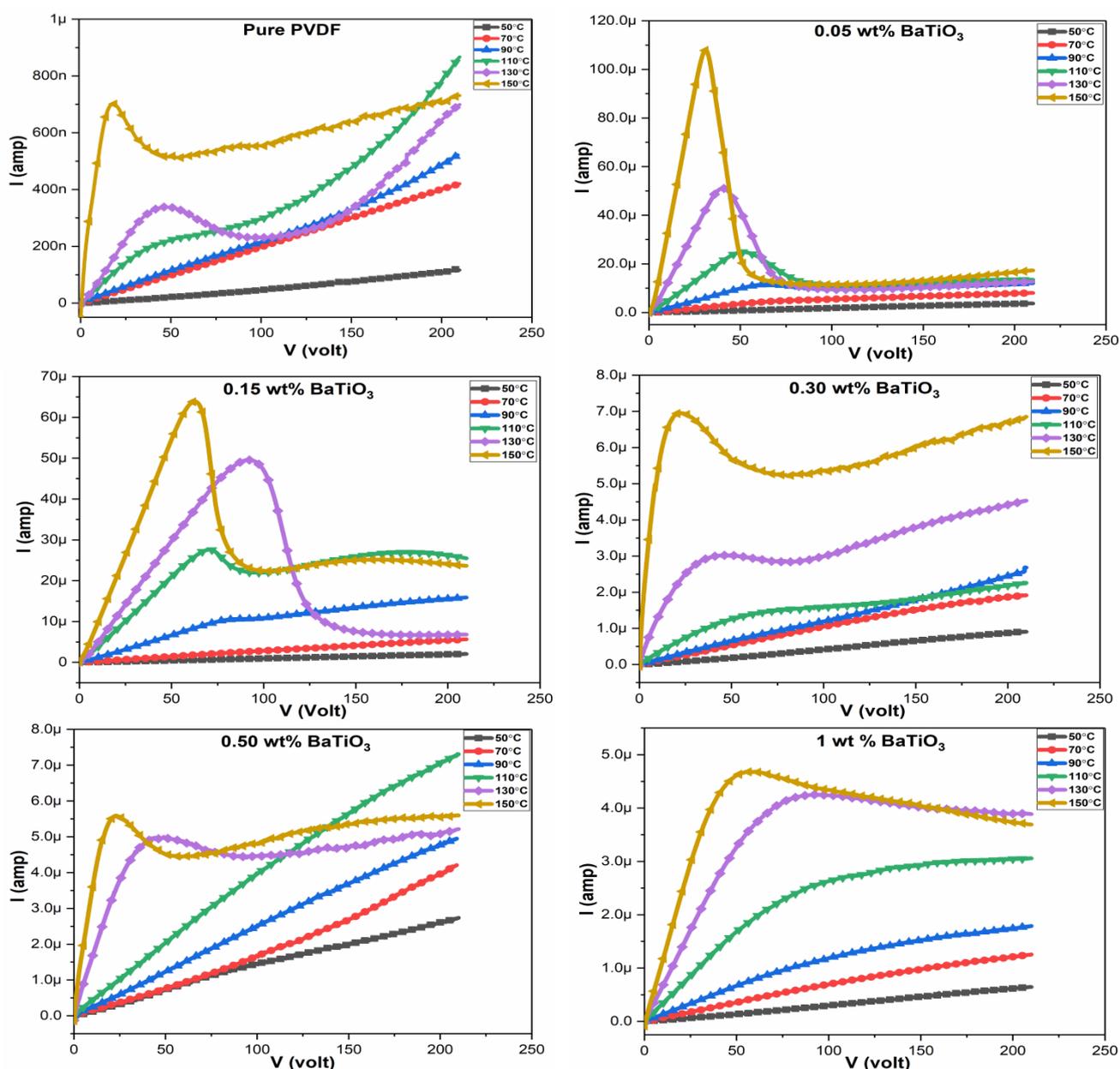


Fig. 5. Current-Voltage characteristic plot for PVDF-BaTiO₃ composite films (color online)

The conduction stays linear until the free carriers that are injected counterbalance the thermally generated carriers. Thus it is worth to believe that non linear behavior at higher field region may be due to the other conduction processes mainly Ionic hopping, Richardson-Schottky (RS) and Poole-Frenkel (PF) type conduction [21-22].

To understand ionic hopping conduction mechanism in the composite films, temperature dependent dc charge transport has been further evaluated in terms of current (I) is shown in expression below [22-23]:

$$I = 2 sqnav \exp\left(\frac{qEa}{2kT} - \frac{U}{kT}\right) \quad (5)$$

where s , q , n , a , v , E , U , k and T are electrode area, charge, ionic concentration, ionic distance, electron escape attempt frequency, electric field, barrier height, Boltzmann constant and temperature respectively.

The non-linearity exists at higher field strengths i.e. $(qEa/2kT \gg U/kT)$ thus equation 5 can be rewrite as

$$I = I_0 \exp\left(\frac{qEa}{2kT}\right) \quad (6)$$

where $I_0 = 2 sqnav$

Table 1. Calculated ionic distance 'a' for PVDF-BaTiO₃ composite films

Ionic distance 'a' (Å)						
Temperature	50°C	70°C	90°C	110°C	130°C	150°C
Pure PVDF	5.9	5.59	5.72	5.00	3.4	1.07
0.05 wt% BaTiO ₃	5.53	5.56	4.58	3.23	1.70	0.5
0.15 wt% BaTiO ₃	5.51	4.24	2.85	0.82	1.62	2.27
0.30 wt% BaTiO ₃	5.72	5.18	5.62	3.44	2.4	0.67
0.50 wt% BaTiO ₃	5.08	6.18	5.82	5.66	1.72	1.12
1 wt% BaTiO ₃	5.66	5.21	4.79	4.06	3.05	1.68

Fig. 6 shows the ionic distance plot in the form of log I versus E at different operating temperatures. The slope of straight line of plot log I versus E graph gives the ionic distance 'a'. The calculated ionic distance evaluated from the log I versus E characteristic plot is given in Table 1. For the PVDF films, calculated ionic distance 'a' decreases from 5.9 to 1.07Å⁰ with the increase in temperature. This may be due to the additional linkages at higher temperature which results in the modification of intermediate energy states. The variation in ionic distance with temperature has also reported by other authors but no one can give the exact reason for this variation [22-23]. From the Table 1, it is observed that for low concentration of BaTiO₃ particles, the ionic distance 'a' decreases for the whole temperature range whereas for higher concentration

of BaTiO₃ particles, the ionic distance 'a' shows irregular pattern. At higher concentration, there is an indication of some resonance type of phenomena in the interfacial polarization. This may be mainly due to dissociation of dipoles of PVDF with the incorporation of BaTiO₃ particles which significantly improves the free charge carriers.

However, the magnitude of ionic distance 'a' lies in the range of 1-7Å, which favors the ionic conduction as possible type of charge transport mechanism in PVDF-BaTiO₃ composite films. Thus this would be fair to clarify the presence of ion conductivity as a result of passage of carrier ions.

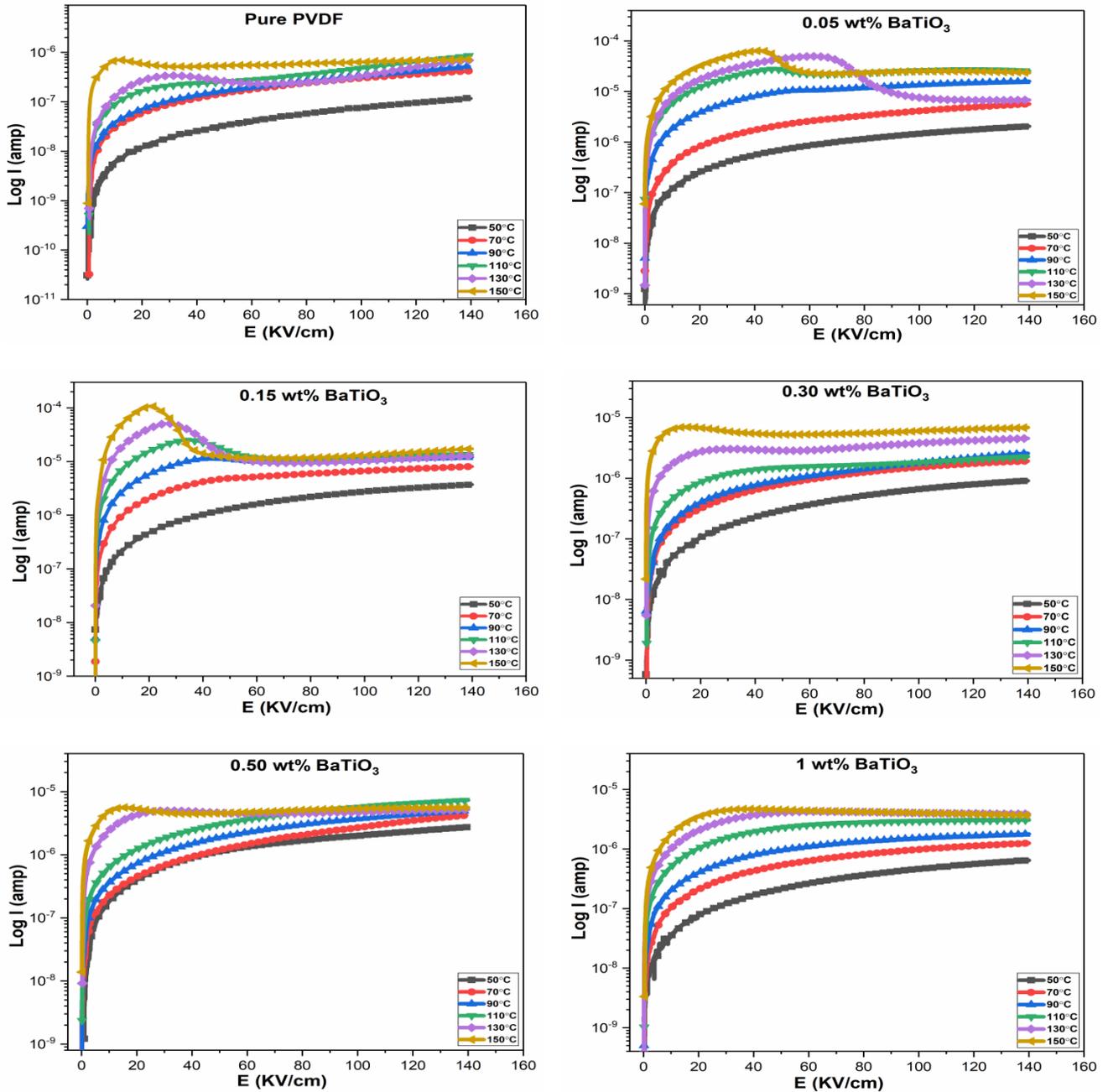


Fig. 6. Ionic distance plots ($\log I-E$) for PVDF-BaTiO₃ composite films (color online)

In order to analyse the present results in relation to other conduction processes mainly Schottky or Frenkel type, their current densities are expressed respectively as [22-23]

$$I = AT^2 \exp\left(\frac{\beta_S E^2 - \phi}{kT}\right) \quad (7)$$

$$I = BE^{\frac{1}{2}} \exp\left(\frac{\beta_F E^2 - \phi}{kT}\right) \quad (8)$$

where E is electric field, ϕ is work function, A and B are constant terms. β_S and β_F represents Schottky and Frenkel coefficients respectively given as,

$$\beta_S = \left(\frac{e^3}{4\pi K \epsilon_0}\right)^{\frac{1}{2}} \text{ and } \beta_F = 2\beta_S \quad (9)$$

where e , ϵ_0 and K represents electronic charge, vacuum permittivity and high frequency dielectric constant respectively.

The conduction in Schottky mechanism is barrier limited which involves thermionic emission resulting in lowering potential barrier whereas Frenkel mechanism is bulk limited involves the current is assisted due to the thermal excitation of electrons from traps into the conduction band [24].

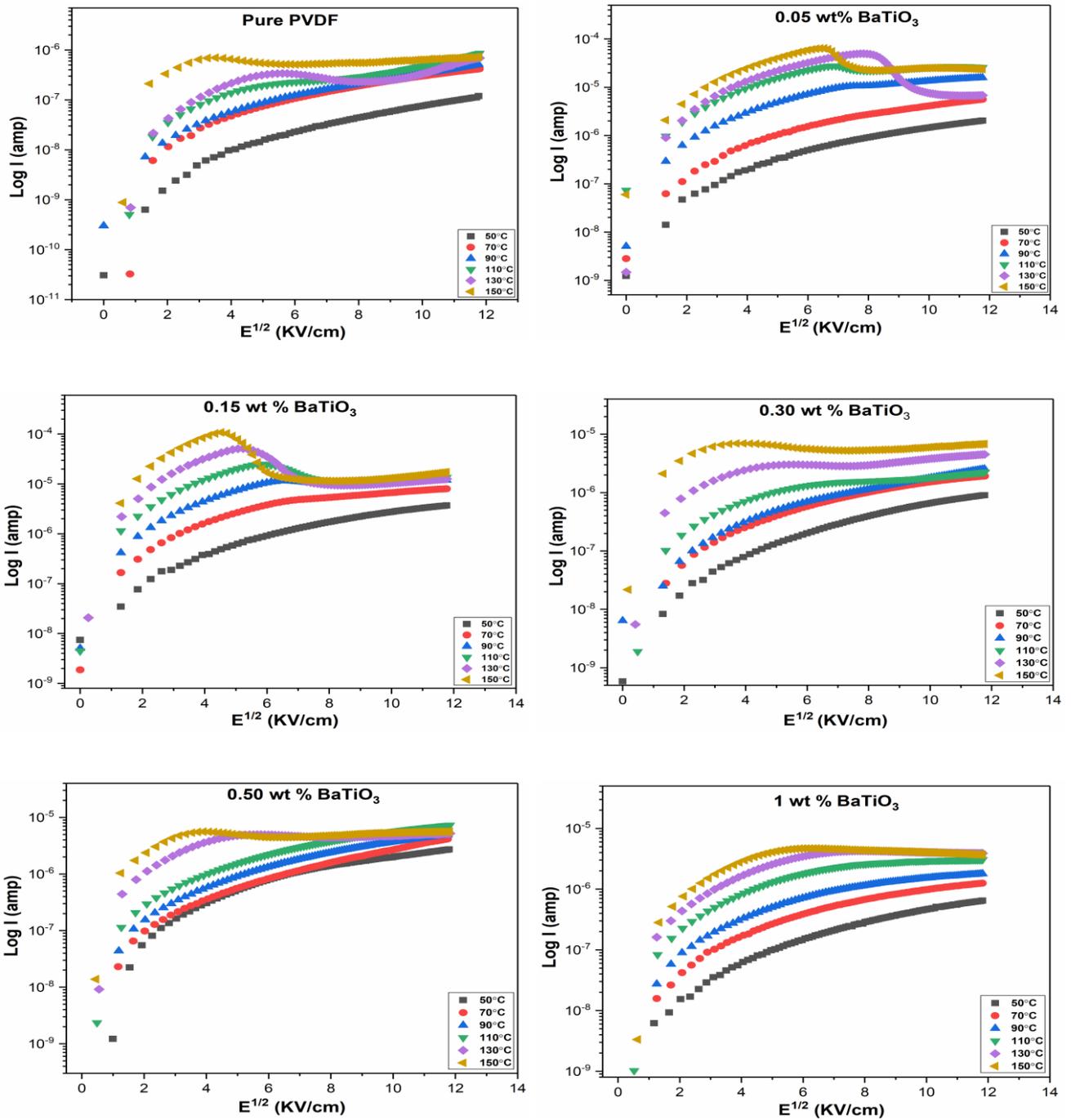


Fig. 7. Richardson Schottky plots ($\log I$ versus $E^{1/2}$) for PVDF-BaTiO₃ composite films (color online)

The data used in Fig. 6 have been replotted in the form of $\log I$ versus $E^{1/2}$ known as Schottky plots represented in Fig. 7. The slope of Schottky plots gives the experimental values β (β_{exp}). The theoretical values of β (β_{th}) can be obtained from equation (9). To examine the

best fitted conduction mechanism to above results, compare the experimental values β (β_{exp}) with the theoretical values β (β_{th}) as shown in Table 2.

Table 2. Experimental and theoretical values Schottky Coefficient (β_s) for PVDF-BaTiO₃ composite films

Schottky Coefficient (β_s) ($J m^{1/2} V^{-1/2}$) $\times 10^{-24}$												
Temperature	50°C		70°C		90°C		110°C		130°C		150°C	
	β_{exp}	β_{th}										
Pure PVDF	7.39	3.03	6.93	2.86	7.13	2.52	6.23	2.25	4.28	1.92	1.38	1.62
0.05 wt% BaTiO ₃	7.06	2.96	7.13	2.54	6.02	2.18	4.51	1.89	4.68	1.59	1.40	1.35
0.15 wt% BaTiO ₃	6.97	1.92	5.59	1.75	4.02	1.59	1.60	1.47	1.46	1.29	2.55	1.06
0.30 wt% BaTiO ₃	7.21	1.90	6.62	1.72	7.09	1.57	4.57	1.38	3.14	1.18	0.92	1.01
0.50 wt% BaTiO ₃	6.54	1.68	7.70	1.62	7.36	1.56	7.19	1.26	2.52	1.07	1.56	0.88
1 wt% BaTiO ₃	7.12	1.43	6.67	1.36	6.22	1.13	5.45	0.96	4.37	0.79	2.70	0.64

From the Table 2 it is concluded that for pristine PVDF samples, β_{exp} values are almost twice to β_{th} values or slightly greater over the whole temperature range upto 130°C whereas at high temperature of 150°C $\beta_{exp} \approx \beta_{th}$ values. This implies strong possibility of Poole Frenkel conduction mechanism in PVDF samples for full experimental temperature range with the exception at higher temperatures which shows the possibility of Richardson Schottky conduction mechanism. For low concentration of BaTiO₃, we observed β_{exp} is slightly greater than twice of β_{th} value which also suggests the possibility of Frenkel conduction mechanism whereas for higher concentration of BaTiO₃, an definitive statement on the possibility of conduction process cannot be made since β_{exp} values are neither similar to β_{th} values nor double of that. It can be concluded that charge transport mechanism in PVDF-BaTiO₃ composite films is mainly governed by Poole Frenkel.

4. Conclusions

In summary, PVDF composite films embedded with BaTiO₃ has been prepared by using a solution casting method to develop dielectric flexible thin films. It is concluded from our study that dielectric permittivity of nanocomposite films depends on filler concentration as well as on annealing temperature. The inclusion of BaTiO₃ filler to polymer matrix enhances the dielectric permittivity upto ten fold larger than PVDF and improves the conductivity more than three order of magnitude. The analysis of current-voltage-temperature characteristics gives the better understanding of the existence of trap carriers and position of carriers in the conduction system. For pure PVDF, the conduction mechanism is mainly observed by Frenkel mechanism where as at higher temperature it obeys Richardson Schottky mechanism. On blending with BaTiO₃, charge transport mechanism appears to be Frenkel for lower concentration with the dominance of ionic hopping conduction at higher concentration. It is expected that PVDF nanocomposites film with suitable weight percentage of BaTiO₃ shows the desirable dielectric properties for its potential application in energy storage devices and harvesting applications.

Acknowledgments

We are grateful to UGC, Government of India, for financial assistance.

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