

# Synthesis and Electrical Properties of Anhydrous GdCl<sub>3</sub> Doped PVA Polymer Electrolyte Films

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GdCl<sub>3</sub> doped PVA polymer electrolyte films were prepared using solvent casting method. XRD pattern confirms the increase in amorphous phase of PVA with the GdCl<sub>3</sub>. UV-Vis optical absorption spectra reveal the decrease in absorption coefficient, direct band gap energy and indirect band energy with increasing of GdCl<sub>3</sub> content. The dielectric constant at low frequency side increases with increase in GdCl<sub>3</sub> salt and temperature due to the space charge polarization. The AC conductivity plot obeys the Jonscher power law and the maximum ac conductivity is found to be  $2.06 \times 10^{-4}$  S/cm. The complex impedance plot show a depressed semicircular arc and the maximum ionic conductivity is found to be  $6.12 \times 10^{-5}$  S/cm for 15 mol% GdCl<sub>3</sub> doped PVA. The electric modulus plots show the non-Debye type relaxation of the samples. The present report strongly recommends the GdCl<sub>3</sub> doped PVA polymer electrolyte film as the worthy candidate for the electrochemical device fabrication.

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**Keywords:** Polymer electrolyte, thick films, solvent casting technique, ionic conductivity

## 1. INTRODUCTION

Metal salts doped polymer electrolytes have been widely reported by many research groups recently due to their potential applications in batteries, sensors, fuel cells, supercapacitors, etc [1-6]. Among the polymer electrolytes, polyvinyl alcohol (PVA) based electrolytes have received much attention not only for ionic conductivity but also for their excellent film forming nature, high mechanical strength and thermal stability. PVA is a semicrystalline polymer having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. It has carbon chain backbone with hydroxyl groups attached to methane carbons/these OH groups can be a source of hydrogen bonding and hence assist the formation of polymer complexes. The semicrystalline structure of PVA showed an important feature rather than of amorphous one. This is because semicrystalline PVA leads to the formation of both crystalline and amorphous regions. The crystalline nature of PVA limits its potential applications in the fabrication of electrochemical devices due to the

occurrence of ionic conduction only in amorphous phase. For this purpose, PVA has been doped with different types of metal ions such as Li, Ag, Na, Cu, Ni, Pb, Co, Mg, Sm, Eu, La, Ce and Ti [7-17]. Recently, Gd doped CeO<sub>2</sub>, Gd doped Li<sub>1.3</sub>Li<sub>1.3</sub>Al<sub>0.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>)<sub>3</sub>, Gd doped BaZrO<sub>3</sub>, Gd doped SrZrO<sub>3</sub>, Gd doped BaCeO<sub>3</sub> and Gd doped SrCeO<sub>3</sub> have been reported as the electrolytes [18-20]. These reports have supported that the ionic conductivity of electrolytes can be greatly enhanced with the addition of Gd<sup>3+</sup> ions. They have exhibited the highest ionic conductivity at moderate temperatures and are known as the potential candidates in the applications of solid oxide fuel cells. Therefore, it can be expected that the doping of Gd<sup>3+</sup> ions into PVA polymer would increase the room temperature ionic conductivity of PVA films. In this view point, a systematic study of electrical properties of GdCl<sub>3</sub> doped PVA polymer electrolyte films have been reported in detail.

## 2. EXPERIMENTAL WORK

### 2.1. Preparation of GdCl<sub>3</sub> doped PVA polymer electrolyte films

Polymer electrolyte films containing PVA polymer with molecular weight of 14000 g mol<sup>-1</sup> (Kemphasol, India) and anhydrous GdCl<sub>3</sub> metal salt (Sigma Aldrich, India) have prepared by solvent casting technique using double distilled water as a solvent. PVA aqueous solution was prepared by dissolving 1 g of PVA in double distilled water. The aqueous solution of 5 mol% GdCl<sub>3</sub> salt dissolved in double distilled water was added to the PVA solution. The resultant solution was stirred continuously for 4 h using a magnetic stirrer at room temperature. Then the homogenous mixture solution was cast onto glass petri-dishes and allowed to evaporate slowly at room temperature. After evaporation, the film of 5 mol% GdCl<sub>3</sub> doped PVA was peeled off from the glass petri dishes. Similarly, 10 and 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte films were prepared and also PVA film was separately prepared without the addition of GdCl<sub>3</sub> for comparison. Finally, the films were dried at vacuum oven for 30 min.

### 2.2. Characterization

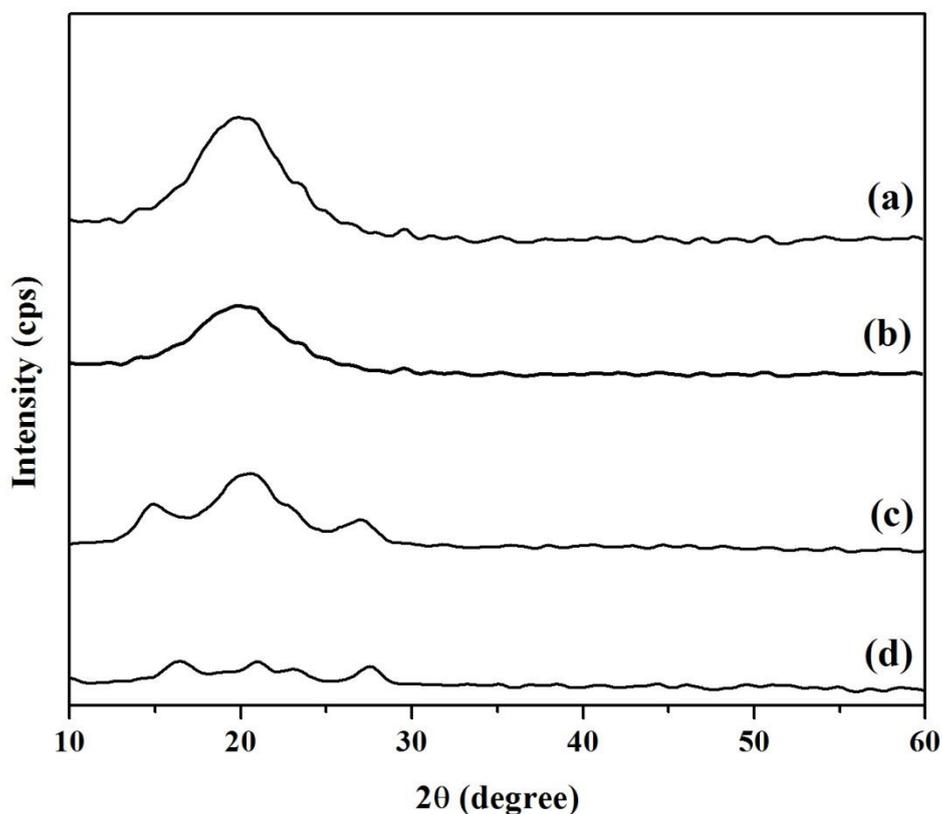
X-ray diffraction (XRD) studies of the films was carried out using the Rigaku Miniflex-II desktop X-ray diffractometer using CuK $\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ) in the range of 10-60°. Optical absorption spectra of the films were recorded using the Perkin-Elmer LAMBDA 35 UV-VIS-NIR spectrometer in the wavelength region 200-800 nm. The dielectric, AC conductivity, impedance and electric modulus measurements of the films were carried out using the N4L Phase Sensitive Multimeter interfaced with Impedance Analyzer with a cell with stainless steel electrodes in the temperature range of 303-423 K over a frequency range of 100 Hz-1 MHz.

## 3. RESULTS AND DISCUSSION

### 3.1. XRD studies

Fig. 1 shows the XRD patterns of PVA, 5 and 10 and 15 mol% GdCl<sub>3</sub> doped PVA films. XRD pattern of pure PVA film shows the diffraction peak at 19.4° which represents the semi-crystalline

nature of PVA [21]. XRD patterns of  $\text{GdCl}_3$  doped PVA films show that the intensity of the diffraction peak decreases with increase in the concentration of  $\text{GdCl}_3$  dopant due to fact that the  $\text{GdCl}_3$  salt interacts with the PVA polymer.

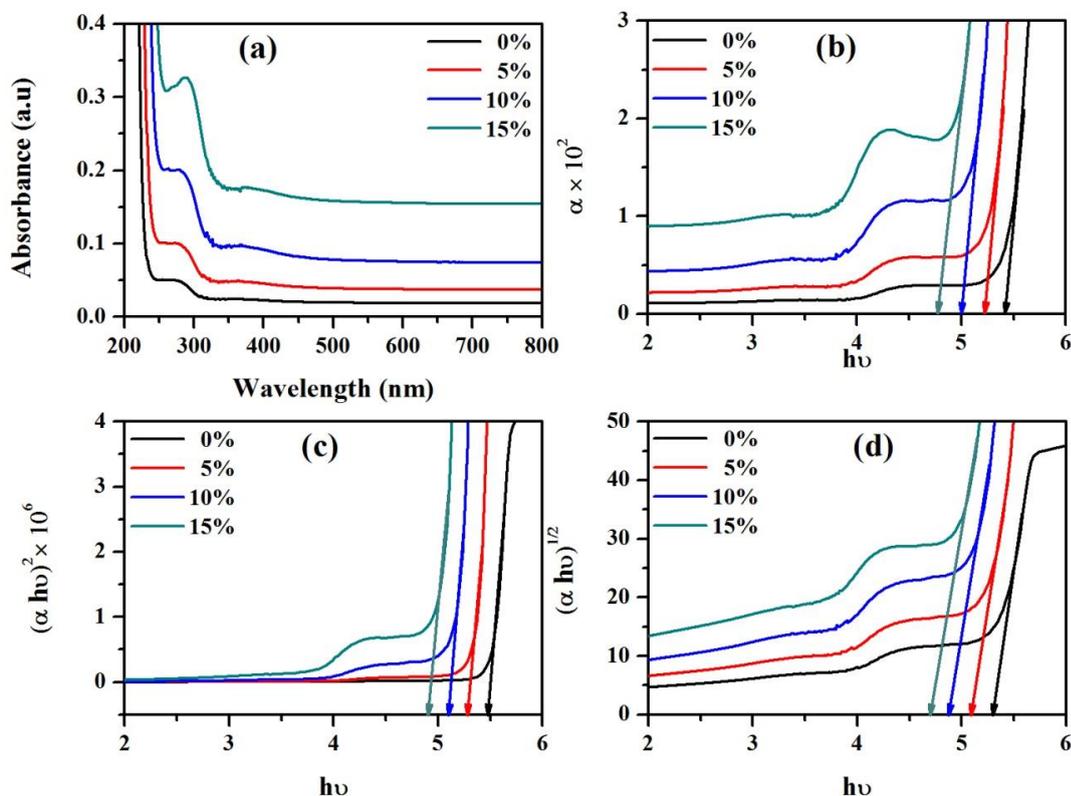


**Figure 1.** XRD patterns of (a) PVA, (b) 5 mol%, (c) 10 mol% and (d) 15 mol%  $\text{GdCl}_3$  doped PVA polymer electrolyte films.

During the interaction between them, the attractive forces between the neighboring molecules in the polymer decreases which could be a reason for decreasing the intensity of diffraction peaks of PVA polymer films doped with  $\text{GdCl}_3$  salt. Hodge et al. have reported that the intensity of XRD peaks decreases with increasing the amount of dopant concentration and there by enhances the degree of the amorphousness of the samples [22]. Similar results have been observed in the present study. In the XRD pattern of 15 mol%  $\text{GdCl}_3$  doped PVA films, the sharp peaks were not observed and they are completely vanished. It confirms the complete dissolution of  $\text{GdCl}_3$  salt into PVA polymer and shows the dominant role of amorphous phase in the polymer-salt complexes which also allows the diffusion of more ions for enhancing ionic conductivity.

3.2. Optical absorption studies

Fig. 2a shows the optical absorption spectra of PVA, 5, 10 and 15 mol% GdCl<sub>3</sub> doped PVA films. No absorption peak was found in the optical absorption spectrum of PVA whereas in the optical absorption spectrum of GdCl<sub>3</sub> doped PVA films, a wide absorption peak was found at 281 nm.



**Figure 2.** (a) Optical absorption spectra, (b)  $\alpha$  vs  $h\nu$  plot, (c)  $(\alpha h\nu)^2$  vs  $h\nu$  and (d)  $(\alpha h\nu)^{1/2}$  vs  $h\nu$  plot of different concentrations of GdCl<sub>3</sub> doped PVA polymer electrolyte film.

When an amount of GdCl<sub>3</sub> dopant is increased in PVA polymer, the absorption peak is shifted towards the longer wavelength due to the strong interaction between GdCl<sub>3</sub> dopant and PVA. This result is well agreed with result of XRD. Both XRD and optical absorption studies confirm the formation of polymer-salt complexes. The absorption coefficient ( $\alpha$ ) of all the films can be estimated using the following relation:

$$\alpha = \frac{2.303}{xA} \tag{1}$$

where A and x are the absorbance and thickness of the film. Furthermore, the absorption coefficient has the following expression based on incident photon energy.

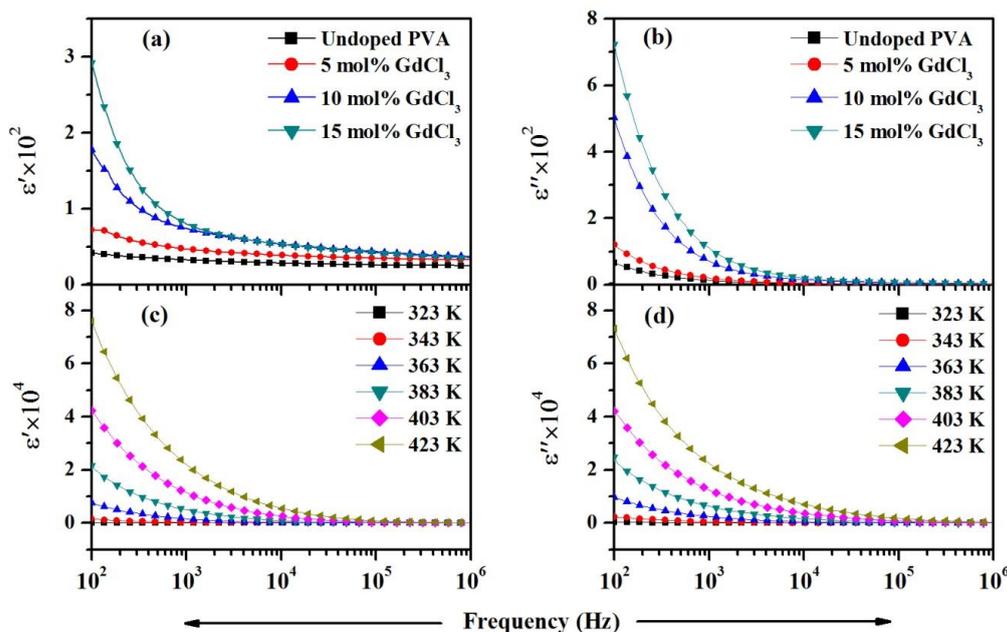
$$(\alpha h\nu) = \beta(h\nu - E_g)^n \tag{2}$$

where  $E_g$  is the optical energy band gap,  $\beta$  is a constant,  $\nu$  is the frequency of incident light and  $h$  is the Planck's constant. An exponent ( $n$ ) is value that represents the electronic transitions and has values of 2 and 1/2 for direct and indirect electronic transitions [12]. A plot of  $\alpha$  vs  $h\nu$ ,  $(\alpha h\nu)^2$  vs  $h\nu$  and  $(\alpha h\nu)^{1/2}$  vs  $h\nu$  is shown in Figs 2(b-d). The absorption coefficient, direct band gap energy and

indirect band gap energy values were estimated using the intercept on the X-axis by fitting a best straight line on the linear portion of the curve to zero absorption value. The absorption coefficient was obtained from the plot of  $\alpha$  vs  $h\nu$ . For PVA film, the absorption coefficient is 5.41 eV whereas the absorption coefficient of 5, 10 and 15 mol%  $\text{GdCl}_3$  doped PVA polymer electrolyte films is 5.21, 5.0 and 4.7 eV respectively. The direct band gap energy was obtained from the plot of  $(\alpha h\nu)^2$  vs  $h\nu$ . For PVA film, the direct band gap energy is 5.47 eV whereas the direct band gap energy of 5, 10 and 15 mol%  $\text{GdCl}_3$  doped PVA polymer electrolyte films is 5.28, 5.1 and 4.88 eV respectively. The indirect band gap energy was obtained from the plot of  $\alpha$  vs  $h\nu$ . For PVA film, the indirect band gap energy is 5.29 eV whereas the direct band gap energy of 5,10 and 15 mol%  $\text{GdCl}_3$  doped PVA polymer electrolyte films is 5.1, 4.88 and 4.69 eV respectively. The decrease in absorption coefficient, direct band gap energy and indirect band gap energy with increase in the concentration of  $\text{GdCl}_3$  dopant is attributed to the presence of defects in the films. These defects form the localized electronic states in the gap between the valence band and conduction band and they reduce the band gap energy when the amount of  $\text{GdCl}_3$  salt is increased in PVA [23].

### 3.3. Dielectric studies

Fig. 3 shows a plot of (a) real ( $\epsilon'$ ) and (b) imaginary ( $\epsilon''$ ) parts of dielectric constant as a function of frequency for PVA, 5, 10 and 15 mol%  $\text{GdCl}_3$  doped PVA films.

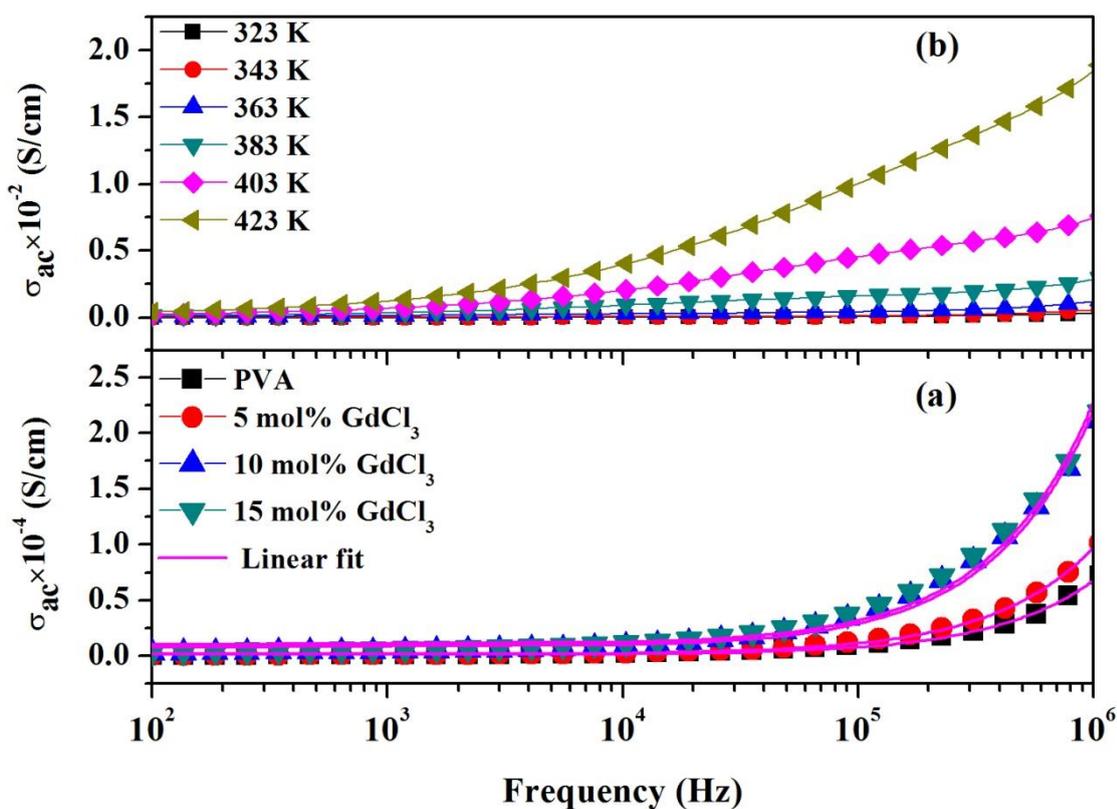


**Figure 3.** (a)  $\epsilon'$  and (b)  $\epsilon''$  plots for different concentrations of  $\text{GdCl}_3$  doped PVA polymer electrolyte films. (c)  $\epsilon'$  and (d)  $\epsilon''$  plots for 15 mol%  $\text{GdCl}_3$  doped PVA polymer electrolyte film at different temperatures.

The dielectric constant decreases rapidly with increasing frequency and reaches a constant value at high frequency. At low frequency side, the electric dipoles can easily be able to orient themselves along the direction of an applied electric field whereas at high frequency side, the electric dipoles cannot be able to orient themselves easily along the direction of an applied electric field [8]. On the other hand, the dielectric constant at low frequency side increases with the addition of GdCl<sub>3</sub> dopant and the maximum value was obtained for 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte film. Fig. 3 shows the dielectric plot of (c)  $\epsilon'$  and (d)  $\epsilon''$  as a function of frequency for 15 mol% GdCl<sub>3</sub> doped PVA films at different temperatures. The value of  $\epsilon'$  and  $\epsilon''$  increases with increasing temperature, facilitating the orientation of electric dipoles and thereby increasing the dielectric constant [7,12].

### 3.4. AC conductivity

Fig. 4a shows the room temperature AC conductivity of PVA and GdCl<sub>3</sub> doped PVA films. The conductivity increases with increase of frequency and concentration of GdCl<sub>3</sub> salt in PVA film due to the shift in transition region from the low frequency side to high frequency side and the reduction of glass transition temperature of PVA films with the addition of GdCl<sub>3</sub>.



**Figure 4.** (a) AC conductivity of PVA polymer electrolyte films doped with different concentrations of GdCl<sub>3</sub> and (b) AC conductivity of 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte film at different temperatures.

The 15 mol% GdCl<sub>3</sub> doped PVA electrolyte film exhibits the highest AC conductivity which is attributed to the enhancement of the motion of Gd<sup>3+</sup> ions by restricting the motion of Cl<sup>3-</sup> ions. AC conductivity plot of all the films exhibits the two characters: a) frequency independent conductivity at low frequency side and b) frequency dependent conductivity at high frequency. The first character is contributed by free charges available in the composite system and is also associated with the dc conductivity. The second character is due to the contribution of trapped charges at higher frequency side [7, 8]. Hence, the AC conductivity of PVA doped with various concentrations of GdCl<sub>3</sub> salt obeys the Jonscher power law in the form of:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \quad (3)$$

Where  $\sigma_{dc}$  is the frequency independent conductivity and also called dc conductivity, A is the coefficient of exponential term and n is the frequency exponent which lies between 0.5 and 1 for an ideal electrolyte [24]. The value of n can be obtained by fitting the eq (3) to the experimental data and is found to be 0.89 for PVA film while this value is 0.82, 0.76 and 0.71 for 5, 10 and 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte film respectively. Similar behavior can be observed in AC conductivity plot (Fig. 4b) of 15 mol% GdCl<sub>3</sub> doped PVA electrolyte film at different temperatures. The conductivity increases with increasing temperature which is due to the movements of thermally activated charge carriers. When the temperature increases, the polymer backbone and side chains are thermally vibrated. The increase of thermal vibrations reduces the strength of hydrogen bonds which become very weak in the molecules. Due to the weak hydrogen bonds between the molecules, it creates the free volume which favors the ions to hop from one polymer segment to another and thereby enhances the conductivity [11].

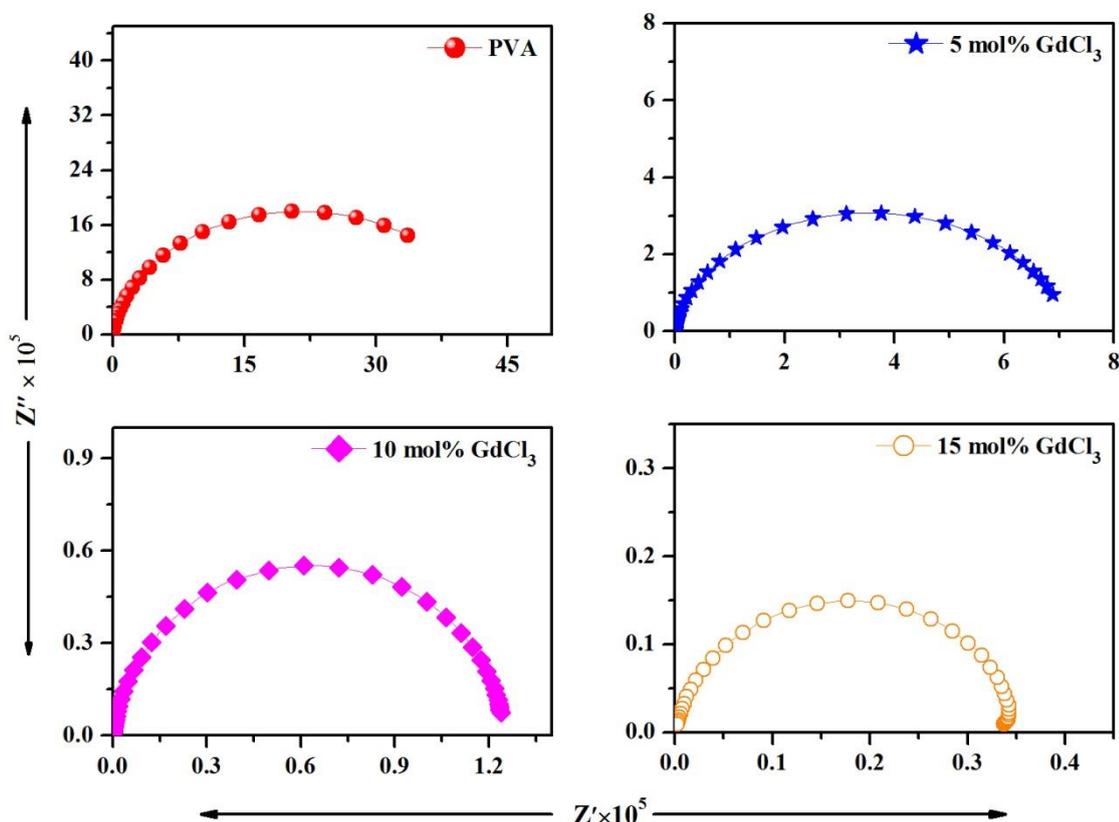
### 3.5. Impedance analysis

Fig. 5 shows the complex impedance plot of PVA, 5, 10 and 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte films. The plot of all the films shows a semicircular arc at high frequency due to the parallel combination of bulk resistance and inclined spike at low frequency due to bulk capacitance. The bulk resistance is caused by the migrations of ions whereas the bulk capacitance is caused by the immobilized polymer chains. The presence of the depressed semicircle reveals the bulk property of the materials. The ionic conductivity ( $\sigma$ ) of the films was calculated by the following equation:

$$\sigma_{dc} = \frac{L}{R_b A} \quad (4)$$

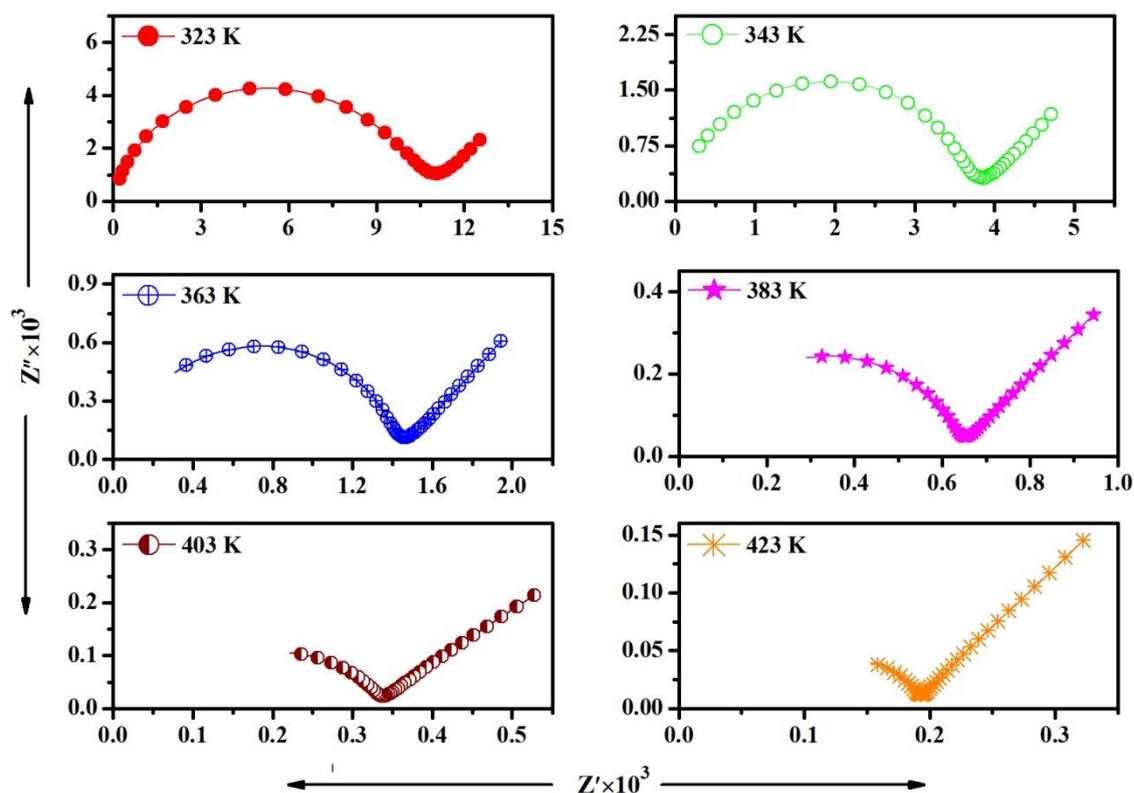
where L is the film thickness, A is the area of the film and R<sub>b</sub> is the bulk resistance. The intercept of the semicircular arc with the real axis (Z') at the low frequency side of the impedance plot gives the value of bulk resistance [23]. It can be seen from the Fig. 5 that the value of bulk resistance decreases with increasing of GdCl<sub>3</sub> dopant concentration. It can be understood from the eq (4) that the ionic conductivity is inversely proportional to the bulk resistance. Hence, the ionic conductivity is increased by the increasing amount of Gd<sup>3+</sup> ions into PVA. This might be attributed to the reduction in degree of crystallinity of the polymer electrolyte films. The improved amorphous phase in the films

allows the high dispersion of ions to hop from one polymer segment to another and thereby enhancing the ionic conductivity [25]. The estimated ionic conductivity is found to be  $5.06 \times 10^{-7}$ ,  $2.78 \times 10^{-6}$ ,  $1.71 \times 10^{-5}$  and  $6.12 \times 10^{-5}$  S/cm for PVA, 5, 10 and 15 mol%  $\text{GdCl}_3$  doped PVA films respectively. It can be concluded that the ionic conductivity depends on the concentration of  $\text{GdCl}_3$  dopant.



**Figure 5.** Complex impedance plot of PVA polymer electrolyte films doped with different concentrations of  $\text{GdCl}_3$ .

The 15 mol%  $\text{GdCl}_3$  doped PVA film exhibits the maximum ionic conductivity compared with other electrolyte films [2,6-8,10,12,23]. Fig. 6 shows a complex impedance plot of 15 mol%  $\text{GdCl}_3$  doped PVA films at different temperatures. As the temperature increases, the bulk resistance also decreases. So the ionic conductivity was abruptly increased with increasing temperature. This is due to the fact that the ions were gained sufficient energy to overcome the potential barriers formed between the polymer segments and thus increasing the volume of the free space in the polymer chains, facilitating the motion of ions in the polymer segments. Therefore, the volume of the free space causes the mobility of the ions to increase around the polymer chain and the segmental motion of polymer chain causes the conductivity to increase [23-25]. As discussed in the section of XRD pattern, the 15 mol%  $\text{GdCl}_3$  doped PVA film shows only the amorphous phase, in the entire diffraction angle, which also additionally provides a large volume of free space with increasing temperature. Therefore, the ions can be easily hopped from one polymer segment to another.

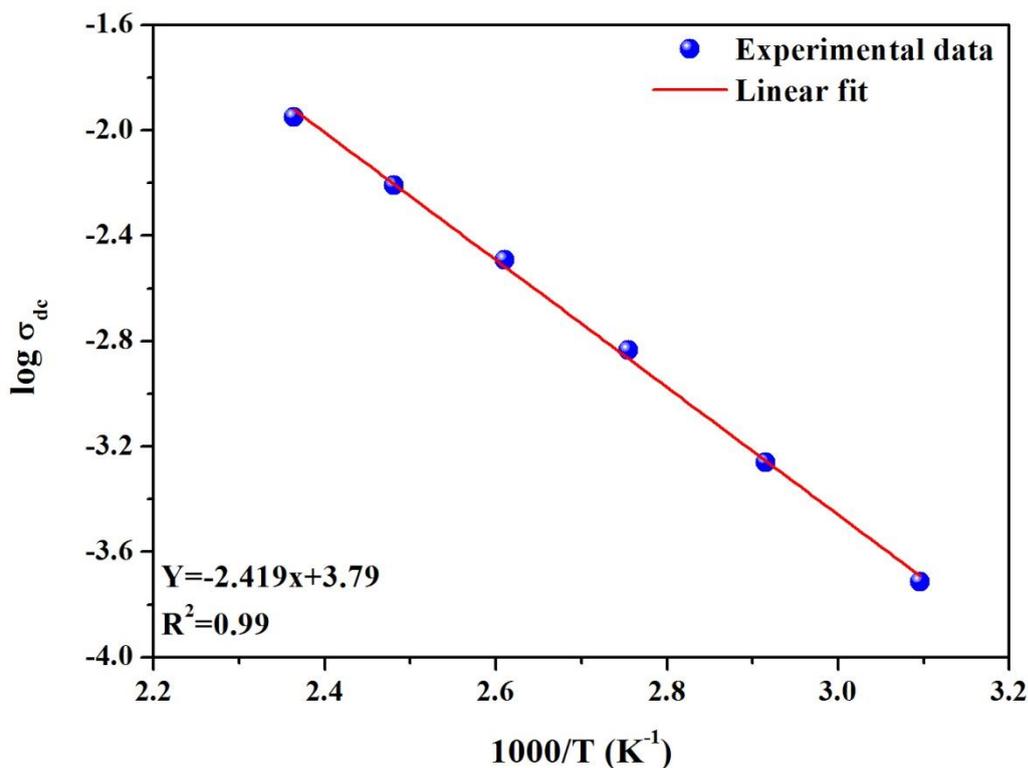


**Figure 6.** Complex impedance plot of 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte film at different temperatures.

Then the ionic conductivity of the 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte film is increased with increasing temperature. Fig. 7 shows a plot of log  $\sigma_{dc}$  vs inverse temperature (1000/T) for 15 mol% GdCl<sub>3</sub> doped PVA polymer electrolyte film. The variation of log  $\sigma_{dc}$  with temperature obeys an Arrhenius-type thermally activated process and it is represented as given below

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \tag{5}$$

where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature [23]. The activation energy value was calculated by linear fitting of the above equation to the experimental data. The value of  $E_a$  is found to be 0.115 eV which is the smallest value with the comparison of the value of other existing polymer electrolytes [12, 23]. The lowest activation energy makes the ions to very easily hop from one coordinate site to another through the conduction process. Thus the Gd<sup>3+</sup> ions with this small activation energy can be detached from it bond and then coordinated onto to the end chain of PVA polymer. This process would make the ions to enhance the conduction activity inside the polymer electrolyte films, which later increased the ionic conductivity in the system.



**Figure 7.** Plot of  $\log \sigma_{dc}$  vs  $1000/T$  for determining  $E_a$  of 15 mol%  $GdCl_3$  doped PVA polymer electrolyte film.

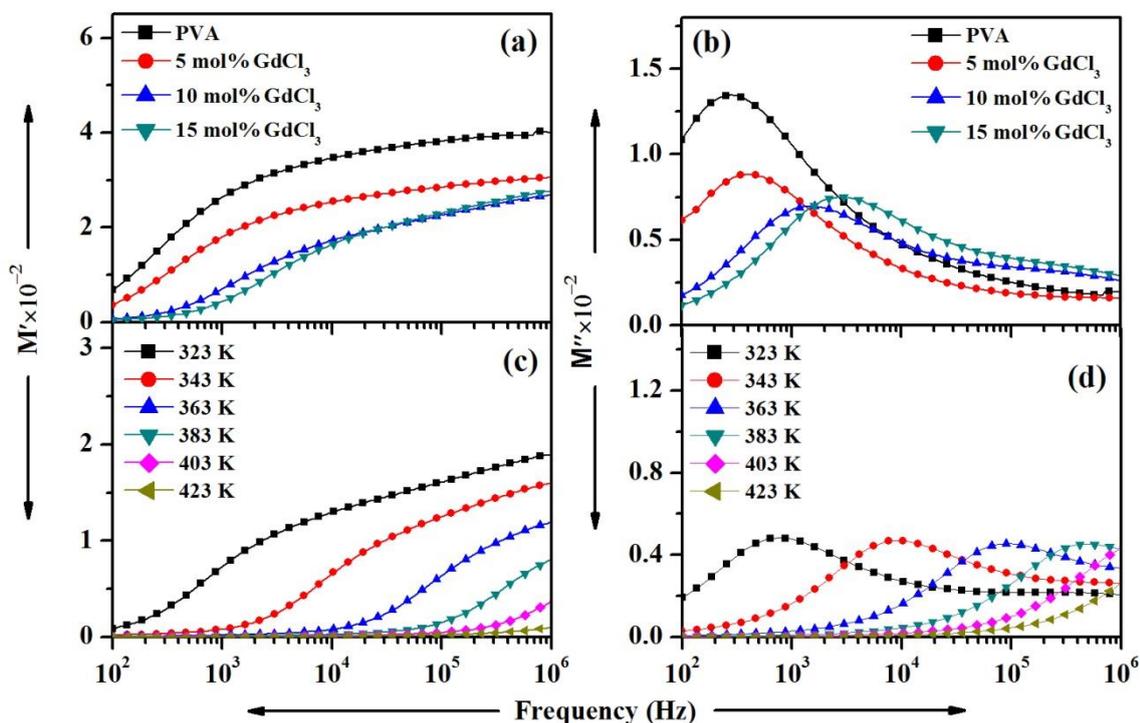
### 3.6. Modulus formalism

Fig. 8 shows the (a) real ( $M'$ ) and (b) imaginary ( $M''$ ) parts of electric modulus plot for PVA, 5, 10 and 15 mol%  $GdCl_3$  doped PVA films. The value of  $M'$  decreases with decrease in frequency and gives a long tail at lower frequency side. This behavior is attributed to the removal of electrode polarization. The presence of long tail at lower frequency side represents the large capacitance values associated with the electrodes [10]. The plot of  $M''$  shows an asymmetric peak whose position is shifted towards higher frequencies with increase in the concentration of  $GdCl_3$  salt. This behavior is attributed to the decrease in the relaxation time with increasing of conductivity. The relaxation time was estimated using following relation [26]

$$2\pi f_{max} = \frac{1}{\tau_{\sigma}} \tag{6}$$

where  $\tau_{\sigma}$  is the conductivity relaxation time and  $f_{max}$  is the frequency maximum on  $M''$ . The calculated  $\tau_{\sigma}$  value is found to be  $5.83 \times 10^{-4}$ ,  $4.13 \times 10^{-4}$ ,  $1.15 \times 10^{-4}$  and  $5.21 \times 10^{-5}$  s for PVA, 5, 10 and 15 mol%  $GdCl_3$  doped PVA polymer electrolyte films. It can be observed that the conductivity relaxation time decreases with increase in  $GdCl_3$  dopant concentration. Similar trends can be observed

in the Figs. 8 (c and d) which show a plot of  $M'$  and  $M''$  for 15 mol%  $GdCl_3$  doped PVA polymer electrolyte film at different temperatures.

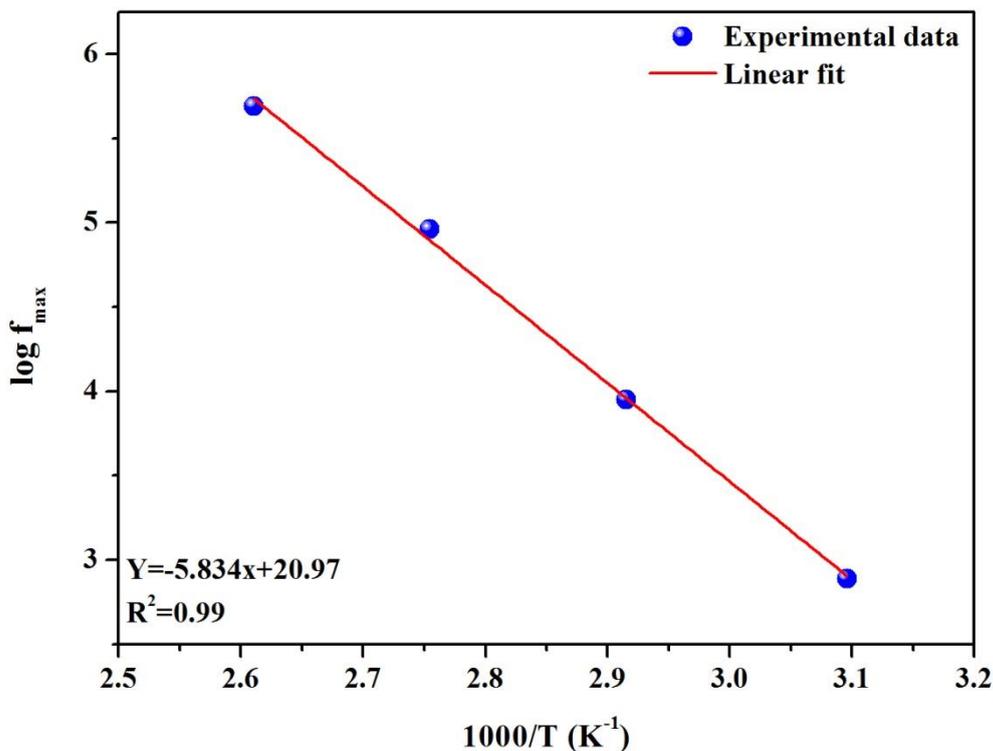


**Figure 8.** (a)  $M'$  and (b)  $M''$  plots for different concentrations of  $GdCl_3$  doped PVA polymer electrolyte films. (c)  $M'$  and (d)  $M''$  plots for 15 mol%  $GdCl_3$  doped PVA polymer electrolyte film at different temperatures.

This behavior suggests that the relaxation is thermally activated process. The conductivity relaxation time decreases with rising in temperature due to the fast motion of  $Gd^{3+}$  ions. Hence, the peak observed in the plot of  $M''$  as the function of temperature shifts towards to high frequency side. The position of each peak represents the relaxation peak and has been taken as frequency maximum ( $f_{max}$ ) [7]. The migration energy ( $E_m$ ) can be estimated by plotting a graph between  $\log f_{max}$  and inverse temperature ( $1000/T \text{ K}^{-1}$ ) as shown in Fig. 9 using the following equation:

$$\omega_m = \omega_0 \exp\left(\frac{-E_m}{k_B T}\right) \quad (7)$$

where  $\omega_0$  is the coefficient of exponential term,  $k_B$  is the Boltzman constant and  $T$  is the absolute temperature [12]. The migration energy was calculated by least square fitting of the experimental data and is found to be 0.119 eV, which is agreed well with the activation energy estimated from the plot of  $\log \sigma_{dc}$  vs  $1000/T \text{ (K}^{-1}\text{)}$ . This agreement confirms the non-Debye behavior of polymer electrolyte system.



**Figure 9.** Plot of  $\log f_{\max}$  vs  $1000/T$  for determining  $E_m$  of 15 mol%  $GdCl_3$  doped PVA polymer electrolyte film.

#### 4. CONCLUSIONS

Polymer electrolyte films containing PVA doped with  $GdCl_3$  salt as the dopant at different concentrations have been prepared by simple solvent casting technique. XRD pattern revealed the amorphous phase of polymer electrolyte films. UV-Visible optical absorption spectra showed the presence of defects in the polymer electrolyte system formed by the content of  $GdCl_3$  which leads to the decrease in optical band gap energy with increase in the concentration of  $GdCl_3$  salt. The dielectric plot exhibited an increase in dielectric constant at low frequency with  $GdCl_3$  dopant and increase in temperature. The ac conductivity plot obeyed the universal power law. The ionic conductivity of the samples was estimated from the impedance plot and is increased with the  $GdCl_3$  concentration. The maximum ionic conductivity is found to be  $6.12 \times 10^{-5}$  S/cm for 15 mol%  $GdCl_3$  doped PVA film. The electric modulus plot confirmed that the present material is highly capacitive and the non-Debye type relaxation is present in the samples. The activation energy estimated from dc conductivity plot is almost equal to the migration energy estimated from the electric modulus plot. The highest ionic conductivity and other supporting results obtained in this report suggest that the  $GdCl_3$  doped PVA polymer electrolyte film is superior candidate for electrochemical applications than the other existing polymer electrolyte doped with mono- and divalent metal salts.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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