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Structural, optical and electrical properties of anhydrous $GdCl_3$ doped PEO polymer electrolyte films

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$GdCl_3$ doped PEO polymer electrolyte films were prepared using solution casting technique. XRD patterns, FTIR spectra and optical absorption studies confirm an amorphous nature and the formation of the polymer electrolyte films. The ionic conductivity increases with the $GdCl_3$ content and the maximum value at room temperature is about 1.83×10^{-2} S/cm for 20 mol% $GdCl_3$doped PEO film. This value is more than two orders of magnitude larger than the ionic conductivity of NASICON type Gd-doped solid electrolytes and other polymer electrolytes. The results suggest that the Gd^{3+} doped PEO polymer electrolyte films are good candidates for future electrochemical devices.

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1. Introduction

Polymer electrolytes have been extensively studied due to their potential applications in various electrochemical devices such as sensors, solid state batteries, fuel cells, electro chromic display devices, super capacitors, etc.At room temperature, polymer electrolytes show the lowest conductivity which limits their potential applications. The polymersdoped with suitable metal salts exhibit the improved electrical properties with the comparison of the properties of each polymer. The main benefits of the doping the metal salts in backbone of polymers arenot only enhance the electrical properties but also for separating the ion-pairs and increase the amorphous nature. Also the film formability with desirable mechanical, thermal and electrochemical stability is required for making the polymerelectrolytes as the attractive materials than the other representative solid electrolyte materials. This can be easily achieved by choosing the suitable polymer [1-4].

Among the polymers, poly ethylene oxide (PEO) has received a much attention due to its high chemical and thermal stability. PEO is a semi-crystalline polymer and can easily solvate a wide variety of salts even at very high salt concentrations. The solvation of salts occurs through the association of the metallic cations with oxygen atoms in the backbone of polymer. However, the multiphase nature of PEO is often regarded as a major problem in real working systems, since the ionic conduction has been shown to take place mainly in the amorphous phase. The suppression of crystallinity of polymer chains improves the polymer chain mobility, which, in turn, leads to better ionic conduction. The physical properties of polymer electrolytes can be modified by the addition of the migrating ion species depending on their reactivity with the host matrix [5-21].Until recently most of the migrating ion species had been only limited to mono- and divalent ions, and some of them have been already brought to the market in many industrial fields. In this regard, a target for the next generation is to develop a trivalent ion conducting electrolytes. Among the trivalent cations, gadolinium ion (Gd^{3+}) is a well known rare earth metal ion and extremely attractive on the grounds of high specific energy, stemming from the low atomic mass

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and high ionic radius as well as three-free electron reaction. Although a series of Gd^{3+} ion conducting solid electrolytes have been reported, a literature survey indicated that surprisingly no report on the complete charge transport studies of gadolinium ion doped polymer electrolyte films exists [8].In view of the above factors, for first time we report the $GdCl_3$ doped PEO polymer electrolyte films ($GdCl_3$ doped PEO film) prepared using solution casting technique. The influence of Gd^{3+} ion on structural, optical and electrical properties of PEO polymer electrolyte films over a wide range of frequency and temperature have been studied in detail.

2. Materials and methods

The amounts of the raw materials were taken as (100-x)PEO+(x)$GdCl_3$ for x=0, 10 and 20mol%. The PEO and $GdCl_3$ solutionswere prepared by dissolving a desired amount of PEO and $GdCl_3$in distilled water using magnetic stirrer. Then the two solutions were mixed and stirred vigorously using magnetic stirrer for 4 h at room temperature. The resulting solution was cast onto cleaned petri dishes and allowed to dry slowly at room temperature for 8 h until all traces of the solvent had completely evaporated. The dried polymer electrolyte films were peeled off from the petri dishes and stored inside a dry vacuum box. The thickness of the samples is estimated using screw gauge and was confirmed by air wedge method. The thickness is found to be 160 μm for all the films. X-ray diffraction (XRD) study was carried out using the Rigaku Miniflex-II desktop X-ray diffractometer at diffraction angle of 10-50° using CuKα radiation (λ=1.5406Å).The Fourier transform infrared (FTIR) spectra were recorded at room temperature using a Brucker Tensor 27 FTIR spectrophotometer with a resolution of 2 cm^{-1} in the wave number range of 400-4000 cm^{-1}. The optical absorption spectra were recorded using the PerkinElmer LAMBDA 35 UV-VIS-NIR spectrometer over the wavelength range of 200-800 nm at room temperature. The dielectric, impedance and electric modulus measurements were performed using 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 discussions

3.1. XRD studies

Figure 1 shows the XRD patterns of all the films. All the diffraction peaks observed in Fig. 1a could be assigned to the hexagonal structure of $GdCl_3$(JCPDS No.46-0395). Pure PEO film exhibits a characteristic diffraction peak at 19.4°due to the semi-crystalline nature of PEO [2, 3].

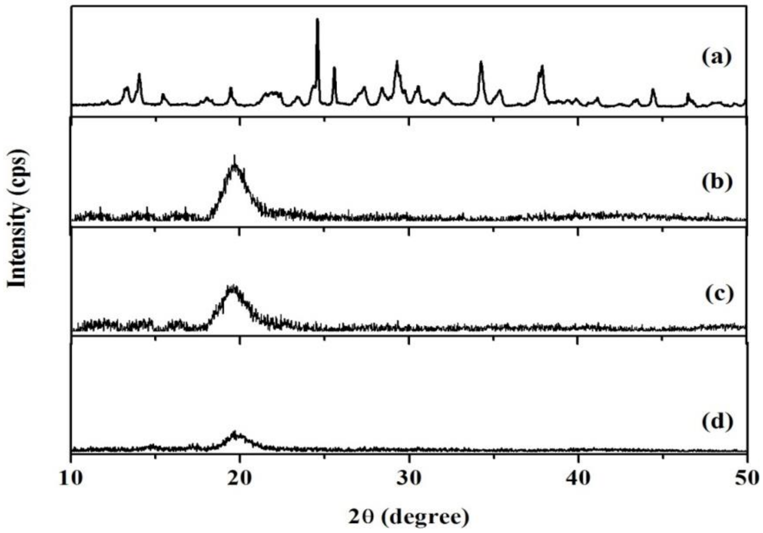


Fig. 1. XRD patterns of (a) anhydrous $GdCl_3$, (b) PEO, (c) 10 and (d) 20 mol% $GdCl_3$ doped PEO films.

The intensity of the peaks decreases gradually with increase of $GdCl_3$ concentration which indicates the decrease in the degree of crystallinity of complexes. This could be due to the disorder of the semi-crystalline structure of the film by the dopant. It is worthy to note that no sharp peaks were observed in the XRD pattern of 20 mol% $GdCl_3$ doped PEO film due to the presence of amorphous phase which results the diffusion of large amount of ions to improve the ionic conductivity [12]. The diffraction peaks of $GdCl_3$ salt observed in the Fig. 1(a) are not found in the XRD pattern of $GdCl_3$ doped polymer electrolyte films, indicating the complete dissolution of salt in the polymer matrix to enhance the conductivity.

3.2. FTIR analysis

FTIR spectra of the samples are shown in Fig.2. Undoped PEO showed a broad peak in the wavenumber range from 3547 to 3154 cm^{-1}which is attributed to the O-H symmetric. The other peaks at 2927, 1716, 1663, 1435, 1366, 1085, 943 and 846 cm^{-1}which could be assigned to C-H asymmetric, C=O stretching, acetyl C=C group, wagging of CH_2, C-H wagging, C-O stretching, C-C stretching and CH_2 stretching respectively [2,4,11,13].These bands shifted towards higher wavenumber with $GdCl_3$ doping confirm a successful complex formation between $GdCl_3$andPEO. This was expected to take place through interaction of Gd^{3+} ion with host PEO backbone. The 10 mol% $GdCl_3$ doped PEO film shows a small shift in wavenumber with that of pure PEO film which indicates weak interaction between polymer complex and salt concentration. However, the broadening of O-H stretching vibration with C-H asymmetric vibration and C=O stretching with acetyl C=C group vibration and disappearance of other bands can be observed in the Fig. 2c, which indicates the breaking of hydrogen bonding between the dopant and polymer complex by inducing charge transfer in complexation between the polymer and dopant [4, 11].

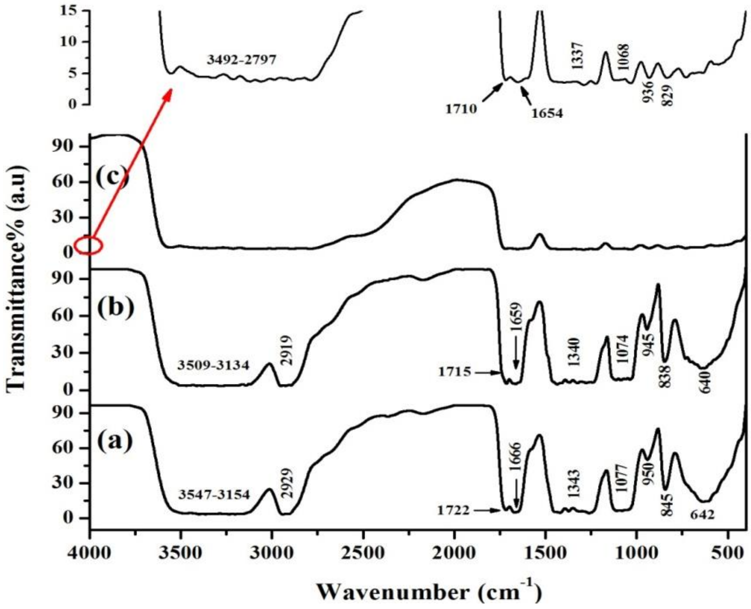


Fig. 2. FTIR spectra of (a) PEO film, (b) 10 and (c) 20 mol% Gd^{3+} ion doped PEO film.

3.3. Optical studies

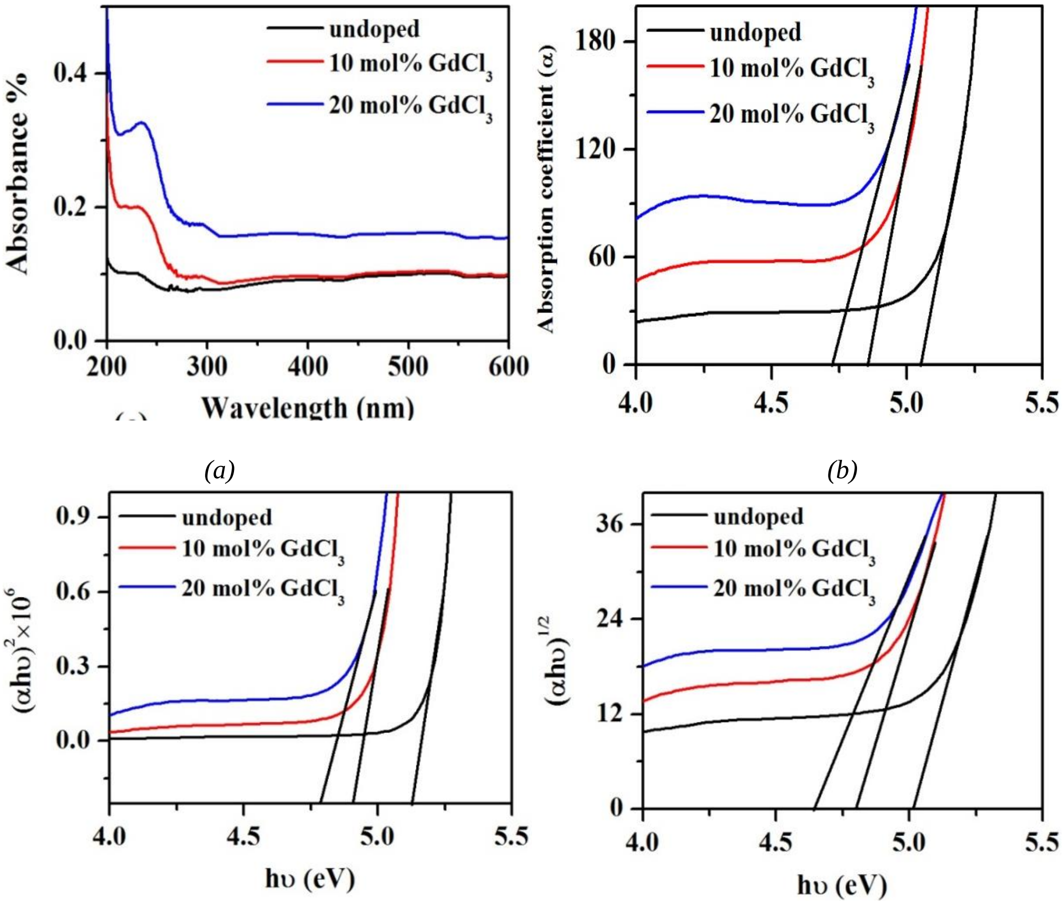
The optical absorption spectra are shown in Fig. 3. PEO film shows an absorption band at 231 nm which is attributed to π-π^* transition [16].The shift in absorption band towards the longer wavelength can be observed and the absorption band is found to be 233 and 236 nm for 10 and 20 mol% $GdCl_3$doped PEO films, respectively. The absorption coefficient (α)can be estimated using the following equation:

$$\alpha = 2.303 \times \frac{A}{d} \qquad (1)$$

Where A and d arethe absorbance and thickness of the sample. The optical band gap energy (E_g) can be calculated using the following equation:

$$(\alpha h\upsilon)^r = B(h\upsilon - E_g) \tag{2}$$

Where B is a constant, hυ is the photon energy and $r$may be considered as the value of 1, 2, 3, 1/2, 3/2 based on the electronic transitions in optical absorption [13, 14].The αcan be estimated by extrapolation of the linear portion of curve in Fig. 3b and is found to be 5.05, 4.85 and 4.72 eV for 0, 10 and 20 mol% $GdCl_3$ doped PEO films, respectively. Similarly, the direct and indirect optical energy band gaps were calculated from the Figs. 3(c and d). The direct energy band gap is 5.13, 4.91 and 4.78 eV whereas the indirect energy band gap is found to be 5.01, 4.80 and 4.64 eV for 0, 10 and 20 mol% $GdCl_3$ doped PEO films. The decrease in $\alpha$and E_g with $GdCl_3$dopant is attributed to the formation of localized states which are responsible for increasing the degree of disorder in polymer electrolyte films[13, 14, 16].



(a) (b)

(c) (d)

Fig. 3. (a) Optical absorption spectra, (b) α vs $h\upsilon$ plots, (c) $(\alpha h\upsilon)^2$ vs $h\upsilon$ plots and (d) $(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$ plots of different concentrations of $GdCl_3$ doped PEO films.

3.4. Dielectric studies

Figure 4presents the dielectric plots of(a) real (ε') and (b) imaginary (ε'') parts. The highest dielectric constant could be observed at lower frequencies due to the space charge polarization phenomena at the electrodes [2].

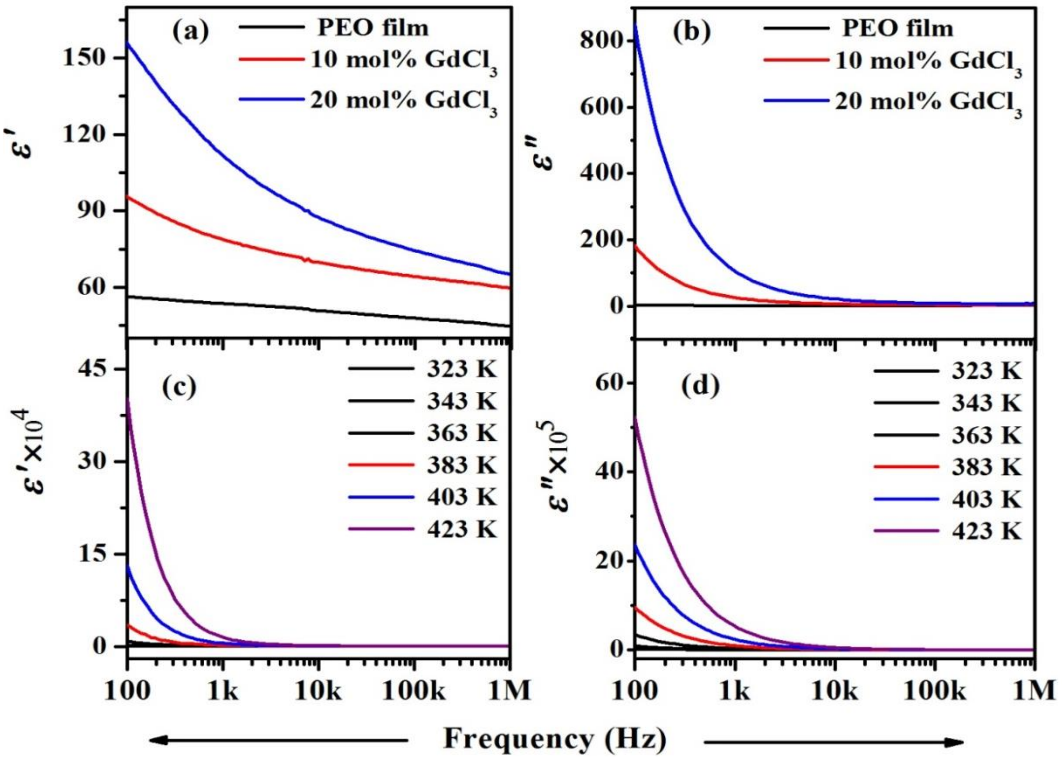


Fig. 4. (a) ε′ and (b) ε″ plots of GdCl$_3$ doped PEO films at room temperature. (c) ε′ and (d) ε″ plots of 20 mol% GdCl$_3$ doped PEO film at different temperatures.

At high frequencies, oscillating dipoles towards applied electric field are lagging behind the field. This can be associated with the inability of rotation of dipoles which decreases the dielectric constant values at higher frequencies. The enhanced low frequency dielectric constant with GdCl$_3$ doping clearly proves that the GdCl$_3$ dopant is a worthy candidate as the dopant for improving dielectric properties of polymer electrolytes. The highest dielectric constant is found to be 154 for 20 mol% Gd^{3+} doped PEO film. Figs. 4(c and d) show the dielectric plots of 20 mol% GdCl$_3$ doped PEO film at different temperatures. The dielectric constants increase with increasing temperature due to the facilitation of dipole orientation with increasing the temperature. It leads to an increment in polarization and causes the increase in low frequency dielectric constant [2, 4].

3.5. AC conductivity study

The room temperature ac conductivity spectraare shown in Fig. 5. As the concentration of GdCl$_3$ dopant increases in PEO film, the ac conductivity at high frequency side also increases. It is attributed to an increase in the mobility of Gd^{3+} ions in PEO polymer and the restriction of anions mobility and causes the enhanced conductivity of PEOwith GdCl$_3$ doping. The ac conductivity value is 0.05×10^{-3}, 0.09×10^{-3} and 0.13×10^{-3}S/cm for 0, 10 and 20 mol% GdCl$_3$ doped PEO film, respectively. As the frequency and GdCl$_3$concentration increase, the conductivity of PEO also increases. From the Fig. 5, a plateau at low frequency can be observed due to the dc conductivity (σ_0) of bulk material whereas dispersion at high frequency due to the ac conductivity. Hence, the Jonchers's power lawis valid and given as:

$$\sigma_{ac}(\omega) = \sigma_0 + A\omega^n \tag{3}$$

Where A is the pre-exponential factor and n is the power law exponent [15].For an ideal electrolyte, ns hould be between 0 and 1, indicating the ideal long-range pathways and tortuous pathway. The n values are in the range of 0.76-0.97. The enhancement in n with GdCl$_3$dopant confirms that the ions are highly drifted towards the electrodes for increasing ionic conduction [11].

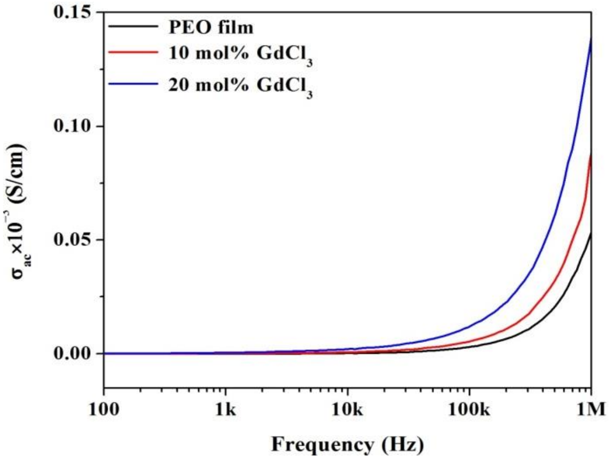


Fig. 5. AC conductivity plot of $GdCl_3$ doped PEO films at room temperature.

Fig. 6shows the ac conductivity of 20 mol% $GdCl_3$doped PEO film at different temperatures. The increase in conductivity with temperature is attributed to the contribution of large number of mobile charge carriers to transport the ions [15].

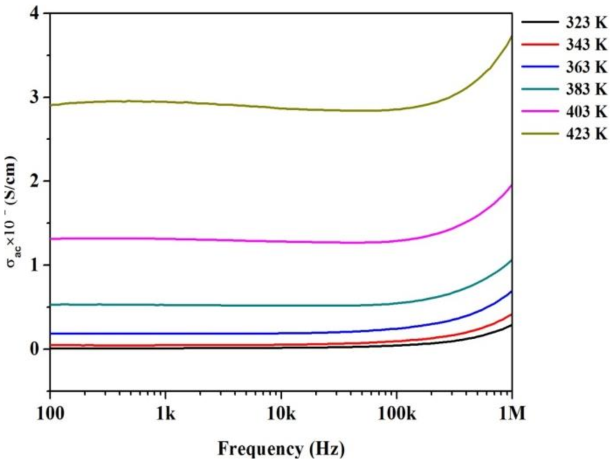


Fig. 6. AC conductivity plot of 20 mol% $GdCl_3$ doped PEO film at different temperatures.

3.6. Complex impedance study

The room temperature complex impedance plots are presented in Fig. 7. The plots show a semicircular arc due to the attribution of the bulk properties of grain (dc resistivity) and obey the relaxation of Cole-Cole type. The ionic conductivity (σ_{dc}) was estimated using the standard equation, $\sigma_{dc} = d/R_bA$, where d is the thickness of the sample, A is area of the sample and R_b is the bulk resistance derived from the intercept of the impedance plot on real axis [5, 6].

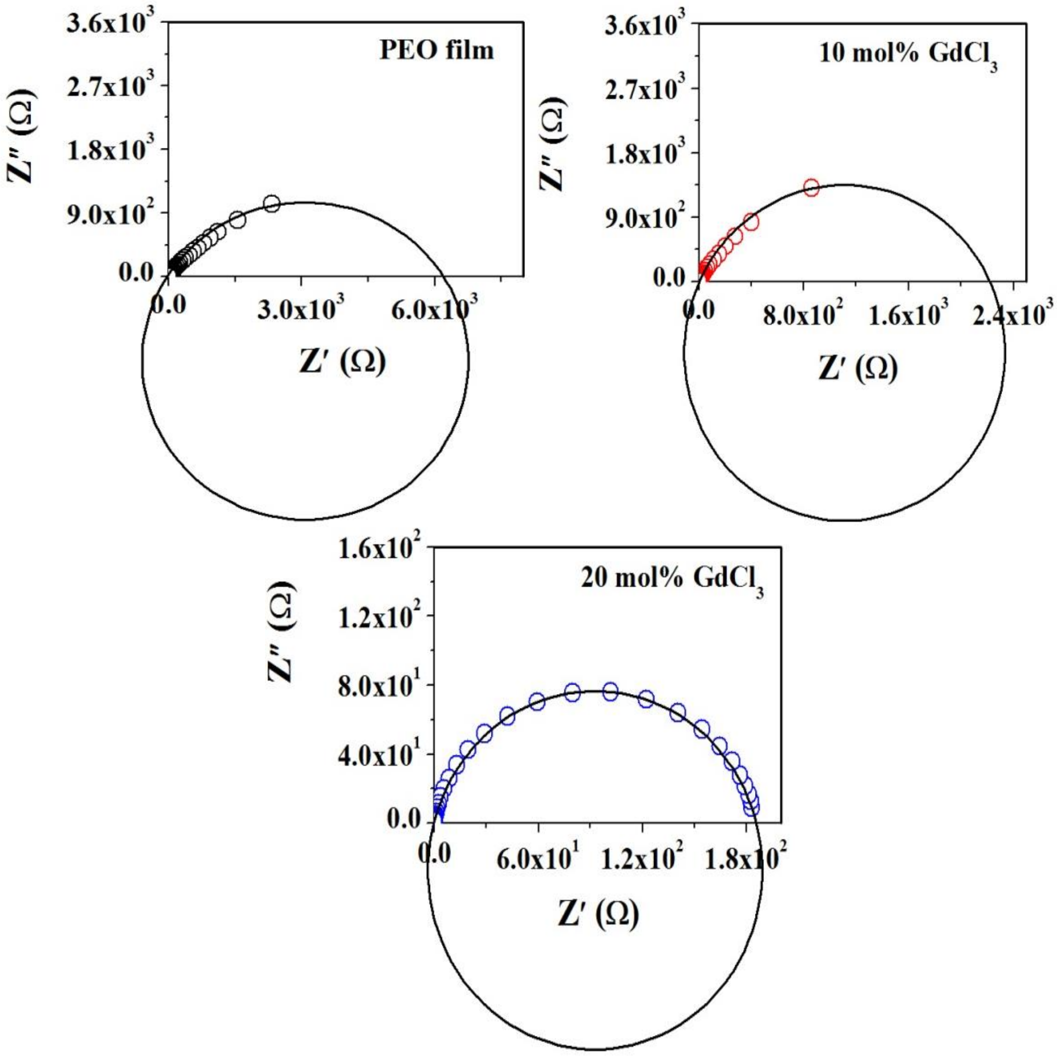


Fig. 7. Room temperature complex impedance plots of PEO and $GdCl_3$ doped PEO films

The estimated ionic conductivity values are found to be 1.25×10^{-2}, 1.55×10^{-2} and 1.83×10^{-2} S/cm for 0, 10 and 20 mol% $GdCl_3$ doped PEO films. The ionic conductivity increases with $GdCl_3$concentration, attributing to the presence of amorphous phase in polymer electrolyte film by the enhancement of mobile charge carriers. The ionic conductivity value of 20 mol% $GdCl_3$ doped PEO film is two orders of magnitude larger than the value of Gd doped $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ NASICON type solid electrolyte reported by Mingxia Fan el [8] and many orders of magnitude higher than those reported on the other polymer blend electrolytes[5-23].It confirms that trivalent Gd^{3+}ion is the promising candidate as the dopant to improve the ionic conductivity of PEO polymer.

Fig. 8 shows the complex impedance plots of 20 mol% $GdCl_3$ doped PEO film at different temperatures. The decrease in bulk resistance leads to the enhancement in ionic conductivity with increasing temperature. When the temperature increases, the vibration energy also increases in polymer chain segment. After reaching the sufficient energy, the hydrostatic pressure created by the neighbouring atoms is reduced and vibrational motion takes place. Therefore, ions can be easily moved within the free volume around the polymer chain and the enhancement in the conductivity is drastically improved due to the segmental motion of polymer chain [4].Moreover, the complex impedance plots demonstrate the pronounced temperature dependence of the device impedance in low frequency range. The electrical conduction of the films can be represented using an equivalent circuit, as shown in the inset of Fig. 8. The equivalent circuit for the present study is showed as the parallel combination of bulk resistance (R_b) and grain capacitance (C_b)with a series resistor (R_s) [16, 18].At high temperature (>403 K), impedance plot exhibits two semicircular arcs. The high frequency arc corresponds to the bulk property whereas the low frequency arc indicates the grain boundary effect. Hence, the equivalent circuit is given by the series of parallel combination of R_bC_b and $R_{gb}C_{gb}$ where R_{gb} and C_{gb} are the grain boundary resistance and capacitance.

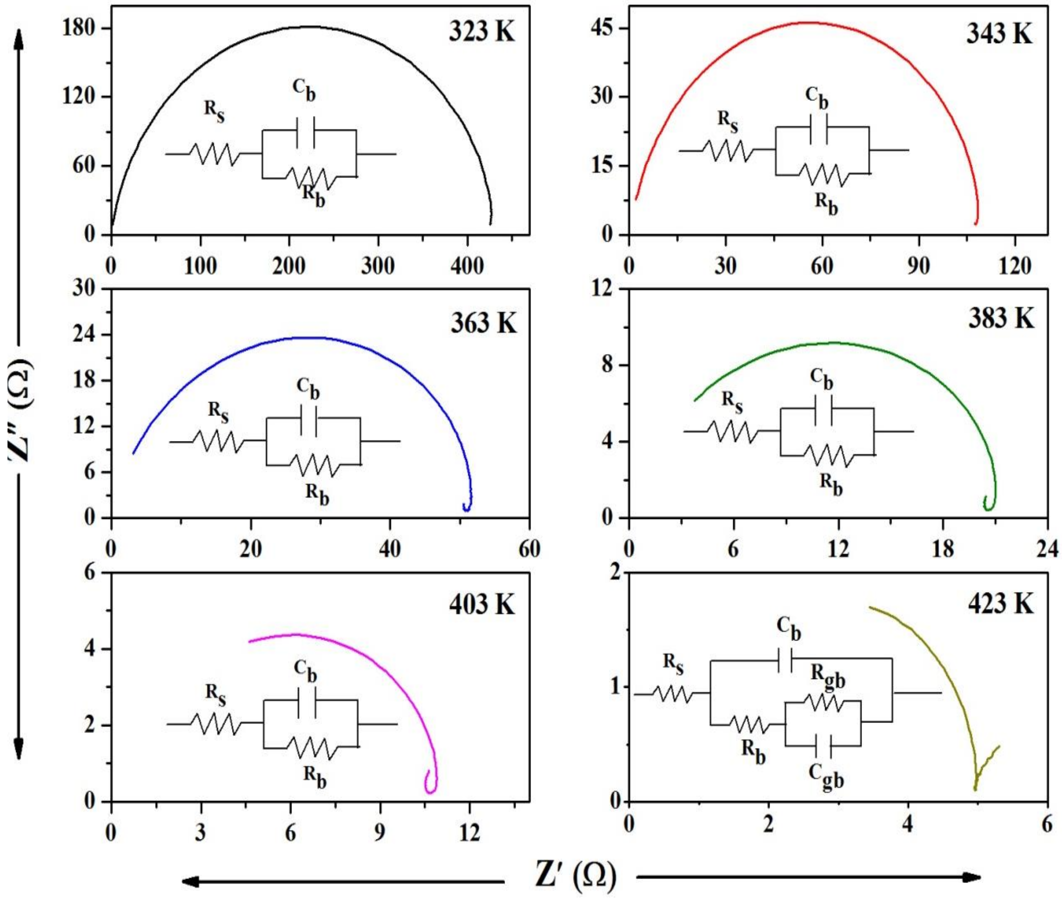


Fig. 8 Complex impedance plots of 20 mol% $GdCl_3$ doped PEO film at different temperatures.

The plot of log σ_{dc} vs 1000/T of 20 mol% $GdCl_3$ doped PEO film is presented in Fig. 9. The plot exhibits a straight line, suggesting the Arrhenius-type thermally activated process represented by the following equation

$$\sigma_{dc} = \sigma_0 exp\left(\frac{-E_a}{k_B T}\right) \tag{4}$$

whereσ_0 is the pre-exponential factor, k_B is the Boltzmann constant, T is the absolute temperature and E_a is activation energy estimated using the slope value by fitting the straight line with the experimental data using the above equation. The estimated E_a is about 0.17 eV and is very small due to the amorphous nature of PEO polymer, facilitating a large free volume in electrolyte for allowing Gd^{3+} ions to hop from one site to another, thereby conductivity increases [15,17,23].

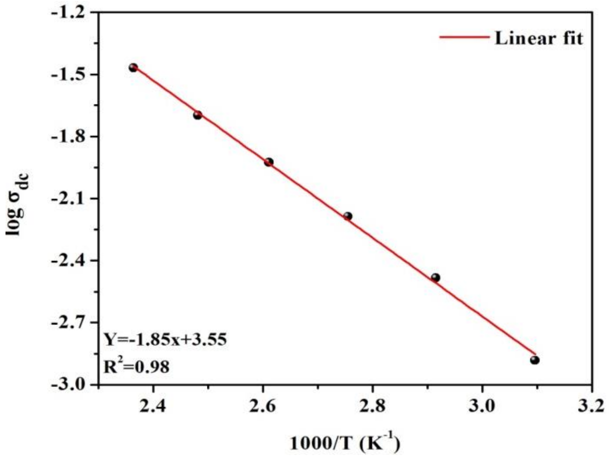


Fig. 9. Plot of log σ_{dc} *vs 1000/T for 20 mol%* $GdCl_3$ *doped PEO film.*

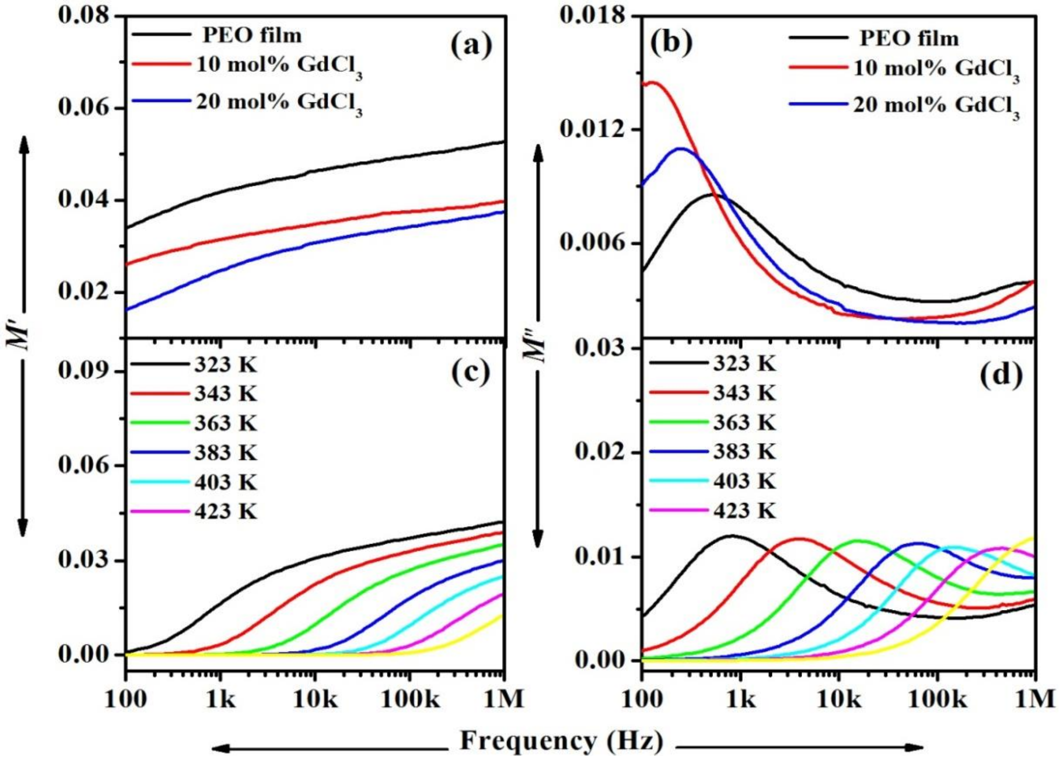


Fig. 10 (a) M′ and (b) M″ of $GdCl_3$ *doped PEO films. (c) M′ and (d) M″ plots of 20 mol%* $GdCl_3$ *doped PEO film at different temperatures.*

3.7. Modulus spectra anaysis

The electric modulus plots are displayed in Fig. 10. The values of M′ and M″ at low frequency side decreased with increasing salt concentration, confirming the removal of electrode polarization and the low conductivity relaxation time. Temperature dependent electrical modulus spectra are shown in Fig. 9(c and d). The value of M′ and M″ were found to be small and finally it remains constant. The decrease in electrical modulus with increasing temperature results the increase in the mobility of charge carriers in PEO film with Gd^{3+} doping [2-5]. As seen in Fig. 10d, M″shows an asymmetric peak centered at the dispersion region of M′ which indicates the conductivity relaxation peak for the distribution of relaxation times of the free charges and the broadening of the peaks suggests a non-Debye type of relaxation in the film. The shift in the peak position towards higher frequency side with increasing temperature can be associated to thermally activated relaxation process, and charge carrier hopping takes place. The frequency region on the pre-peak decides the range whereas the mobility of charge carriers are on long distances while region to the post-peak is where the confinement of carriers in potential wells, being mobile on short distances which are consistent with conductivity studies as mentioned above [20-23]. The frequency maximum (f_{max}), which corresponds to the M''_{max}, gives the relaxation time (τ_c) from the condition, $\omega_{max}\tau_c=1$. The migration energy (E_m) can be calculated using the Arrhenius equation:

$$f_{max} = f_0 exp\left(\frac{-E_m}{k_B T}\right) \tag{5}$$

wheref_0 is the pre-exponential factor[22, 23].

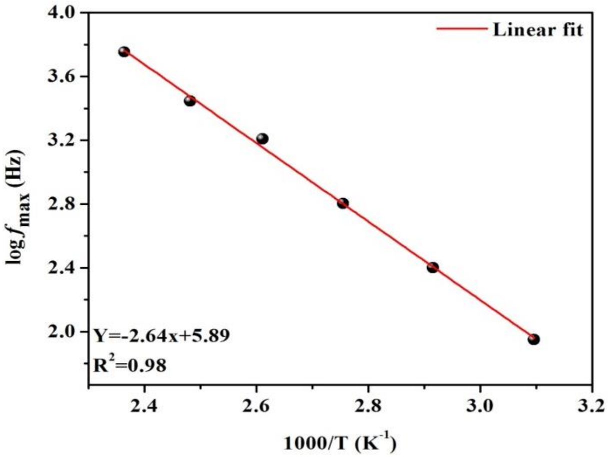


Fig. 11. Plot of log f_{max} vs 1000/T for 20 mol% $GdCl_3$ doped PEO film.

As shown in the Fig. 11, the $E_m$was estimated using least square fitting method to the experimental data and found to be 0.17 eV. It implies that the chargecarriers responsible for both conductivity and relaxationare the same, and that the enthalpy of carrier formation is negligible in this system.

4. Conclusions

Gd^{3+}doped PEO polymer electrolyte films were prepared by solution casting technique. XRD patterns and FTIR spectra confirmed the formation of $GdCl_3$ doped PEO film with amorphous phase. Optical absorption spectra revealed the presence of some defects in the polymer electrolytes. AC conductivity plot obeyed the Jonscher power law. The complex impedance plots exhibit a semicircular arc. The ionic conductivity was calculated and is found to be 1.83×10^{-2} S/cm for 20 mol% $GdCl_3$doped PEO film. The electrical conduction of the sample was depicted using an equivalent circuit. The electrical modulus plots confirmed the removal of electrode polarization. The present results suggest that the $GdCl_3$ion doped PEO polymer electrolyte films are the superior candidates for fabricating future electrochemical devices.

References

[1] J. Płocharski, W. Wieczorek, J. Przyłuski, K. Such, Appl. Phys. A 49, 55 (1989); https://doi.org/10.1007/BF00615464

[2] M. Abdelaziz, Physica B 406, 1300 (2011); https://doi.org/10.1016/j.physb.2011.01.021

[3] G. K. Prajapati, P. N. Gupta, Physica B 406, 3108 (2011); https://doi.org/10.1016/j.physb.2011.05.019

[4] K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma, V. V. R. NarasimhaRao, Physica B 406, 1706 (2011); https://doi.org/10.1016/j.physb.2011.02.010

[5] K. Naveen Kumar, K. Saijyothi, Misook Kang, Y. C. Ratnakaram, K. Hari Krishna, DaheeJin, Yong Min Lee, Appl. Phys. A 122, 698 (2016); https://doi.org/10.1007/s00339-016-0212-7

[6] S. Jayanthi, A. Arulsankar, B. Sundaresan, Appl. Phys. A 122, 109 (2016); https://doi.org/10.1007/s00339-016-9623-8

[7] Reda Khalil, Appl. Phys. A 123, 422 (2017); https://doi.org/10.1007/s00339-017-1026-y

[8] Mingxia Fan, Xiangyu Deng, Anqiao Zheng, Songdong Yuan, Funct. Mater. Lett. 14, 2140002 (2021).

[9] H. T. Ahmed, V. J. Jalal, D. A. Tahir, A. H. Mohamad, O. G. Abdullah, Results Phys. 15, 102735 (2019); https://doi.org/10.1016/j.rinp.2019.102735

[10]Lingzhu Zhao, Jingchuan Fu, Zhi Du, Xiaobo Jia, Yanyu Qu, Feng Yu, Jie Du, Yong Chen, J. Membrane Sci. 593, 117428 (2020); https://doi.org/10.1016/j.memsci.2019.117428

[11]Devesh Chandra Bharati, Horesh Kumar, Mater. Res. Express 6, 125360 (2019); https://doi.org/10.1088/2053-1591/ab66a3

[12] R. M. Hodge, C. H. Edward, G. P. Simon, Polymer 37, 1371 (1996); https://doi.org/10.1016/0032-3861(96)81134-7

[13] P. W. Davis, T. S. Shilliday, Phys. Rev. 118, 1020 (1960); https://doi.org/10.1103/PhysRev.118.1020

[14] G. K. M. Thutupalli, S. G. Tomlin, J. Phys. D: Appl. Phys. 9, 1639 (1976); https://doi.org/10.1088/0022-3727/9/11/010

[15] J. K. Jonscher, Dielectric relaxation in solids, Chelsea Dielectric Press, London (1983).

[16] Bingbing Wang, Hongming Lou, Hongli Xu, Junpeng Zhao, Qiujun Wang, Qiao Shi, Yonghong Deng, RSC Adv. 8, 6373 (2018); https://doi.org/10.1039/C7RA13664A

[17] Anjireddypolu, Ranveerkumar, Bull. Mater. Sci. 37, 309 (2014); https://doi.org/10.1007/s12034-014-0654-5

[18] KallaRamamohan, V. B. S. Achari, A. K. Sharma, LuXiuyang Ionics 21, 1333 (2015); https://doi.org/10.1007/s11581-014-1302-1

[19]Kuldeep Mishra Saurabh Singh Pundir, D. K. Rai, Ionics 23, 105 (2017); https://doi.org/10.1007/s11581-016-1790-2

[20] R. Rathika, O. Padmaraj, S. Austin Suthanthiraraj, Ionics 24, 243 (2018); https://doi.org/10.1007/s11581-017-2175-x

[21]Qiang Ma, Amartya Chakrabarti, Xinyi Mei, Zheng Yue, Hamza Dunya, Robert Filler, B. K. Mandal, Ionics 25, 1633 (2019); https://doi.org/10.1007/s11581-018-2752-7

[22] Pankaj Singh, Devesh Chandra Bharati, P. N. Gupta, A. L. Saroj, J. Non. Cryst. Solids 494, 21 (2018); https://doi.org/10.1016/j.jnoncrysol.2018.04.052

[23] R. M. Putri, C. D. D. Sundari, OctiaFloweri, T. R. Mayangsari, A. L. Ivansyah, S. P. Santosa, I. M. Arcana, Ferry Iskandar, J. Non. Cryst. Solids 556, 120549 (2020); https://doi.org/10.1016/j.jnoncrysol.2020.120549