

# Synthesis and analysis of Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>: PEO + PVP blended polymer composite films for multifunctional polymer applications

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**Abstract.** Blended polymer films of polyethylene oxide + polyvinyl pyrrolidone (PEO + PVP) containing transition metal (TM) ions like Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> have been synthesized by a solution casting method. For these films, structural, thermal, magnetic and optical properties have been studied. X-ray diffraction results reveal the semi-crystalline nature of the polymer films. Thermal stability of the host (undoped) polymer film has been investigated from its thermogravimetric–differential thermal analysis profiles. Raman spectral profiles indicate a complex formation trend owing to the addition of TM ions into the host matrix. Co<sup>2+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup> ions doped polymer films have revealed ferromagnetism based on their vibrating sample magnetometer profiles. However, the host polymer film has exhibited a paramagnetic nature. Further, ionic conductivities have been calculated using an impedance analyser at different temperatures for all the samples. Among these films, a maximum ionic conductivity ( $\sigma = 7.5 \times 10^{-6} \text{ S cm}^{-1}$ ) has been noticed from PEO + PVP : Ni<sup>2+</sup> polymer film at 373 K. Emission analysis of Co<sup>2+</sup>: PEO + PVP polymer film has exhibited a strong red emission under an UV source and from both PEO + PVP : Fe<sup>3+</sup>; PEO + PVP: Ni<sup>2+</sup>, green emissions have commonly been noticed under an UV source. Thus, based on these results, it could be suggested that these TM ions doped PEO + PVP polymer films are found to be potential multifunctional materials for magneto-electric, magneto-optic fields with encouraging electrical, dielectric and optical properties as well as displaying with ferromagnetic nature from the doped films.

**Keywords.** Polymer films; TM ions; ferromagnetism; electrical properties; PL-analysis.

## 1. Introduction

The metal-organic coordination polymers have drawn a great deal of attention in the progress of fields like supramolecular chemistry and crystal engineering because their possessing potentiality emerges as functional materials. Among the different organic ligands, bridging N-donor ligands is commonly used due to their strong extension ability both in covalent bonding and supramolecular interactions (H-bonding and aromatic stacking). As a result, a great number of metal/N-donor compounds from one dimensional (1D) to three dimensional (3D) have been reported.<sup>1</sup> Magnetic properties of composite polymer materials could be suitably tailored using an effective medium. Composites with magnetic fillers dispersed in polymer matrices could transform as potential materials. Further, magnetic ions embedded in polymer matrices have excellent potential for electromagnetic device applications like electromagnetic interference suppression. The high-spin organic polyradical molecules with chemical stability will open a new field of magnetic organic materials for sensor applications.<sup>2</sup> Magnetopolymer composites could significantly possess several applications.<sup>3</sup> A polymer exhibiting one or more properties by different

operations has been considerably stated as multifunctional polymer. By changing the functional group of polymer or by the addition of nanomaterials, the polymer composite properties could be remarkably changed. In earlier studies, multifunctional polymer nanocomposites have been studied by undertaking some nanoparticles for obtaining the several properties in a single polymer composite.<sup>4</sup> But as of now, there are no reports based on transition metal (TM) ions doped polymer composites which exhibit multifunctional properties such as electrical, magnetic and optical properties. This study was mainly aimed to enhance the polymer properties of multifunctional polymer composite films for several applications by using TM ions. Polyethylene oxide (PEO) is an interesting base material because of its high thermal stability and with regard to PEO, it is a semi-crystalline polymer, which demonstrates both amorphous and crystalline phases.<sup>5</sup> Polyvinylpyrrolidone (PVP) has been selected as the second polymer for preparing polymer blend with PEO. Firstly, PVP is an amorphous polymer, which can permit faster ionic mobility compared to other semi-crystalline natured polymers. Due to the presence of carbonyl group (C=O) in the side chains of PVP, it forms a variety of complexes with TM ions. Another advantage of using PVP is that it can be thermally cross-linked, with a good thermal stability.<sup>6,7</sup> Therefore, the TM ions doped

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polymeric materials have been characterized by vibrating sample magnetometre (VSM) system in understanding their magnetic properties. Further, these materials exhibit a paramagnetic behaviour from the host film and ferromagnetism from the doped films. In addition, ionic conductivity and dielectric properties have also been evaluated, along with their photoluminescence properties. When a close observation of these materials was made, the potential magnetic, electrical and photoluminescence properties in a single polymer material at ambient temperature were identified. Based on these unique results, it was affirmately stated that these polymer films could suggest for multifunctional applications like electrochemical devices, spintronic and luminescent display device applications.

## 2. Experimental

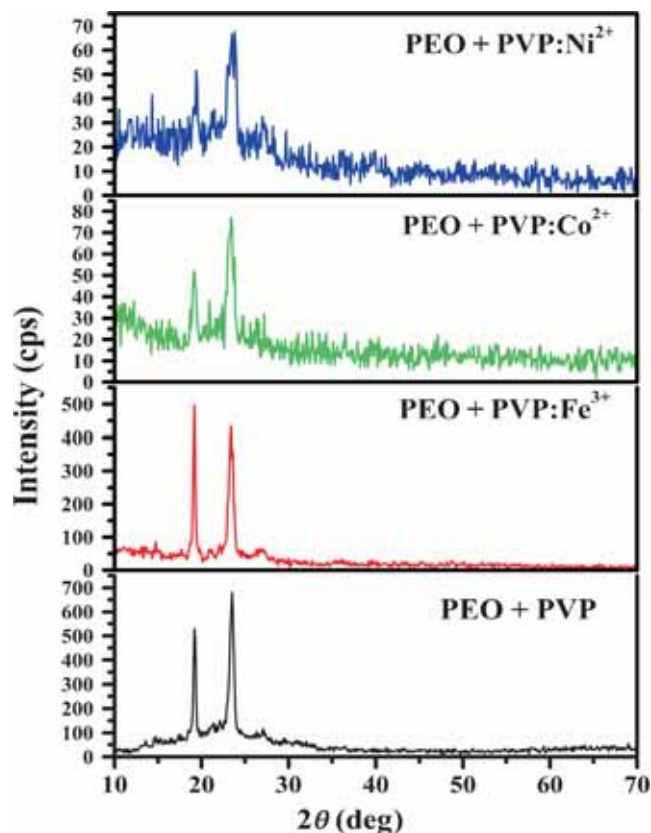
Blended polymer films were prepared by using a traditional solution casting method. Initially PEO (MW =  $6 \times 10^5$ ) and PVP (MW =  $13 \times 10^5$ ) were obtained from Sigma-Aldrich. Films of (thickness  $\sim 100 \mu\text{m}$ ) PEO + PVP blended polymers were doped with TM ions such as  $\text{CoCl}_2$ ,  $\text{FeCl}_3$  and  $\text{NiCl}_2$ . The precursor materials that are PEO, PVP and TM salts were taken in weight percent ratio (0.45 : 0.45 : 0.1 wt%), the triple distilled water was taken as solvent. PEO, PVP and dopant salts were dissolved in triple distilled water and stirred at room temperature ( $30^\circ\text{C}$ ) for 10–12 h to obtain a homogeneous mixture. The solution was cast onto polypropylene dishes and allowed to evaporate slowly at room temperature. The dried composite polymer films were collected and analysed.

The X-ray diffraction (XRD) spectra of TM: PEO + PVP polymer blended films were measured on SEIFERT 303 TT X-ray diffractometer with  $\text{CuK}\alpha$  (line of  $1.5405 \text{ \AA}$ ), and it was operated at 40 kV voltage and 50 mA anode current. The thermo-gravimetric–differential thermal analysis (TG–DTA) measurements for the TM : PEO + PVP polymer blended films were carried out by using thermo-gravimetric analysis and differential scanning calorimetry, Model: -SDTQ600TA Instrument (specimens were scanned in the nitrogen atmosphere from  $30^\circ$  to  $60^\circ$  at heating rate of  $10^\circ\text{C min}^{-1}$ ) from room temperature to  $800^\circ\text{C}$ . Energy-dispersive X-ray spectrometry (EDAX) analysis attached to the scanning electron microscope (SEM) was used to investigate and carry out the elemental analysis of the sample studied. Raman spectra of TM: PEO + PVP were carried out at room temperature in the range of  $100\text{--}2000 \text{ cm}^{-1}$  using LabRam HR 800 confocal Raman spectrometer, which is having Nd: YAG laser source ( $532 \text{ nm}$ ). The VSM measurement was made on Lakeshore new 7400 series at room temperature. The electron paramagnetic resonance spectra measurement was carried out by using Bruker EMX EPR spectrometer. The impedance measurements were performed using a computer-controlled phase-sensitive multimeter (PSM 1700) from 1 Hz to 1 MHz at different varied temperatures.

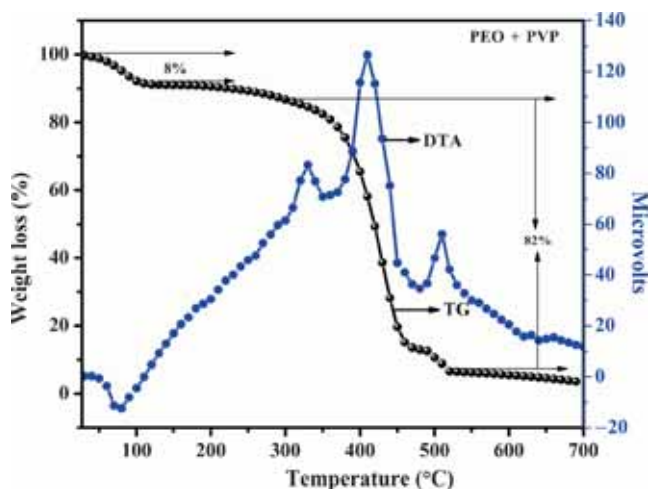
## 3. Results and discussion

### 3.1 XRD analysis

XRD analysis has been performed to identify the crystalline peaks of PEO + PVP host polymer film and doped  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ : PEO + PVP films. The obtained patterns are shown in figure 1. The observed three crystalline peaks of PEO, a prominent peak at  $19.2^\circ$  (1 2 0), second prominent peak at  $23.6^\circ$  (1 1 2) and a third less intense peak at  $27.1^\circ$  have been noticed. In the case of PVP, a broad peak has been observed at  $13^\circ$ , showing an amorphous nature of PVP. The characteristic peaks of PEO + PVP film shows a variation of intensity, suggesting that the ordering of the PEO polymer crystallinity has been changed because of the existence of coordination interactions between the TM ions and etheric oxygen. These observations confirm that the present polymer films possess both crystalline and amorphous nature.<sup>8,9</sup> By adding the TM ions to PEO + PVP polymer film, the decreasing trends in relative intensity, signal-to-noise ratio and also increasing behaviour of full-width at half-maximum (FWHM) when compared with pure PEO + PVP polymer film could be observed. In the case of  $\text{Ni}^{2+}$ -doped polymer film, the signal-to-noise ratio and relative intensity has significantly decreased and also FWHM is appreciably enhanced when compared with all these polymer samples. From these quite encouraging



**Figure 1.** The XRD profiles of (a) PEO + PVP, (b)  $\text{Fe}^{3+}(0.1)$ : PEO + PVP, (c)  $\text{Co}^{2+}(0.1)$ : PEO + PVP and (d)  $\text{Ni}^{2+}(0.1)$ : PEO + PVP polymer films.



**Figure 2.** TG/DTA plots for pure PEO + PVP blended polymer film.

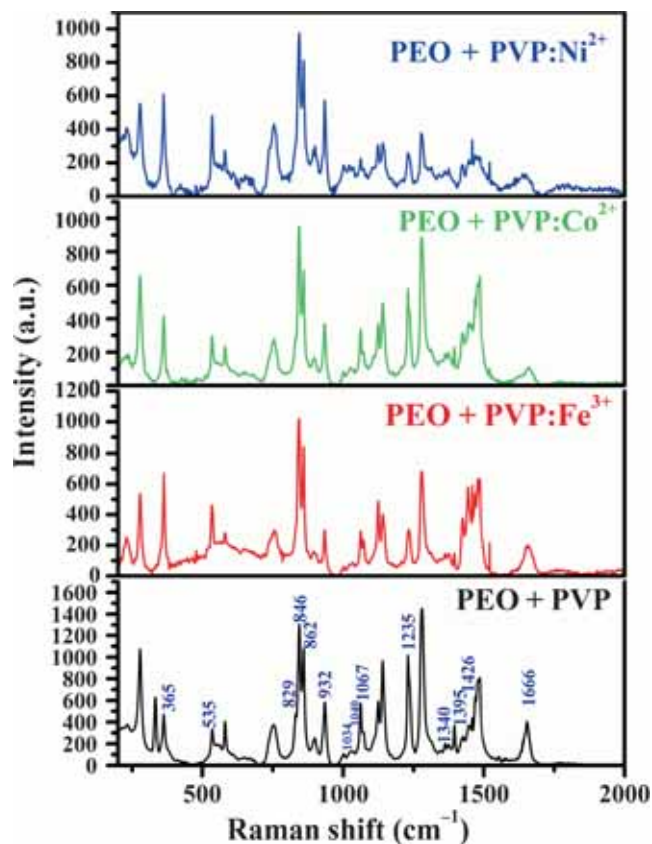
results, it could be stated that the degree of crystallinity has significantly decreased in  $\text{Ni}^{2+}$ -doped polymer sample so that this polymer film could be reached to amorphous domain. However, the addition of TM ions like  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  in the host films shows semi-crystalline nature.

### 3.2 Thermal analysis

Figure 2 shows TG/DTA profiles of host film with an initial decomposition taking place at  $46^\circ\text{C}$  and with a weight loss of 8% due to the presence of moisture. Further decomposition is observed at  $330^\circ\text{C}$ , which indicates that the film is stable up to  $330^\circ\text{C}$  concerning the host PEO + PVP film. The DTA profile of host film shows an endothermic peak at  $84^\circ\text{C}$  which corresponds to glass transition temperature. Also exothermic peaks are located at 330, 409 and  $510^\circ\text{C}$  for the host PEO + PVP polymer film.<sup>10,11</sup> In fact, the peak at  $330^\circ\text{C}$  indicates the decomposition of PEO + PVP polymer film as evidenced by rapid weight loss that is observed in the TG curves. No further significant changes have occurred in the thermal properties of TM ions doped polymer films. Therefore, thermal properties have been carried out only for the host polymer film.

### 3.3 Raman spectra analysis

Figure 3 shows the Raman spectra of PEO + PVP host film and also  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ : PEO + PVP polymer films. The bands at 1235, 1426 and  $1666\text{ cm}^{-1}$  are attributed to C–N stretching, C–H bending and C=O vibrations of PVP, respectively.<sup>12</sup> The bands pertaining to PEO are located at 1067, 1040, 932, 862, 829, 846, 535, 1395 and  $365\text{ cm}^{-1}$ .<sup>13</sup> Three bands at 862, 829 and  $846\text{ cm}^{-1}$  are noticed as active modes of  $\text{CH}_2$  rocking and CO stretching modes. The band at  $932\text{ cm}^{-1}$  is assigned to CO stretching combined with  $\text{CH}_2$  rocking vibrations of PEO.<sup>14</sup> Further, the bands at 1340 and  $1367\text{ cm}^{-1}$  are in good agreement with the earlier reports.

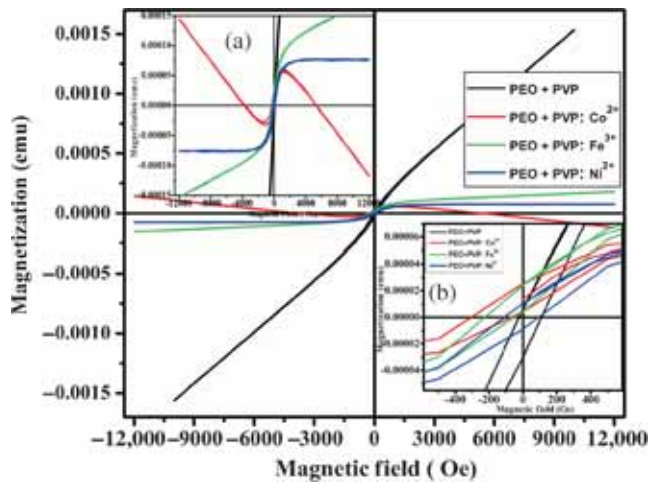


**Figure 3.** (a) Raman spectra of PEO + PVP, (b)  $\text{Fe}^{3+}(0.1)$ : PEO + PVP, (c)  $\text{Co}^{2+}(0.1)$ : PEO + PVP and (d)  $\text{Ni}^{2+}(0.1)$ : PEO + PVP polymer films.

In addition, new bands that are observed at 1340, 1445 and  $1464\text{ cm}^{-1}$  could also be attributed to PEO.

Upon doping with TM ions into the PEO + PVP, the intensity band at  $1063\text{ cm}^{-1}$  due to C–O stretching and/or rocking modes of  $\text{CH}_2$  vibrations has significantly been reduced because of the complex formation.<sup>15</sup> The significant changes in the C–C vibrational band can be associated with the formation of ionic bond with less polarization. The intensity of the band at  $1665\text{ cm}^{-1}$  has been attributed to PVP that also decreases in its intensity with the addition of dopant ions into host polymer film. It has been reported that this type of anion present in the polymer matrix improves amorphous nature of the host polymer film. Further, this situation is confirmed by broadening of Raman modes at 1445 and  $1365\text{ cm}^{-1}$  which arises due to the mixture of C–H bending and O–H bending vibrations. This has been in good agreement with the XRD results also. The spectra of the blended polymer film, the most intense feature band at around  $936\text{ cm}^{-1}$  is associated with the symmetric stretching mode of the anion. This mode is very important and suitable for investigating ionic association. The intensity of the Raman band at  $932\text{ cm}^{-1}$  decreases with the addition of the salt. In case of PEO + PVP : TM, only a single band at  $1034\text{ cm}^{-1}$  is observed which is associated with the presence of the free chloride anion. The broadening in Raman spectra indicates

an amorphous or semi-crystalline nature of the blended polymer.<sup>16</sup> By the addition of TM ions to the PEO + PVP polymer film, the broadening of the Raman modes increases and also peak intensity becomes diminished simultaneously.

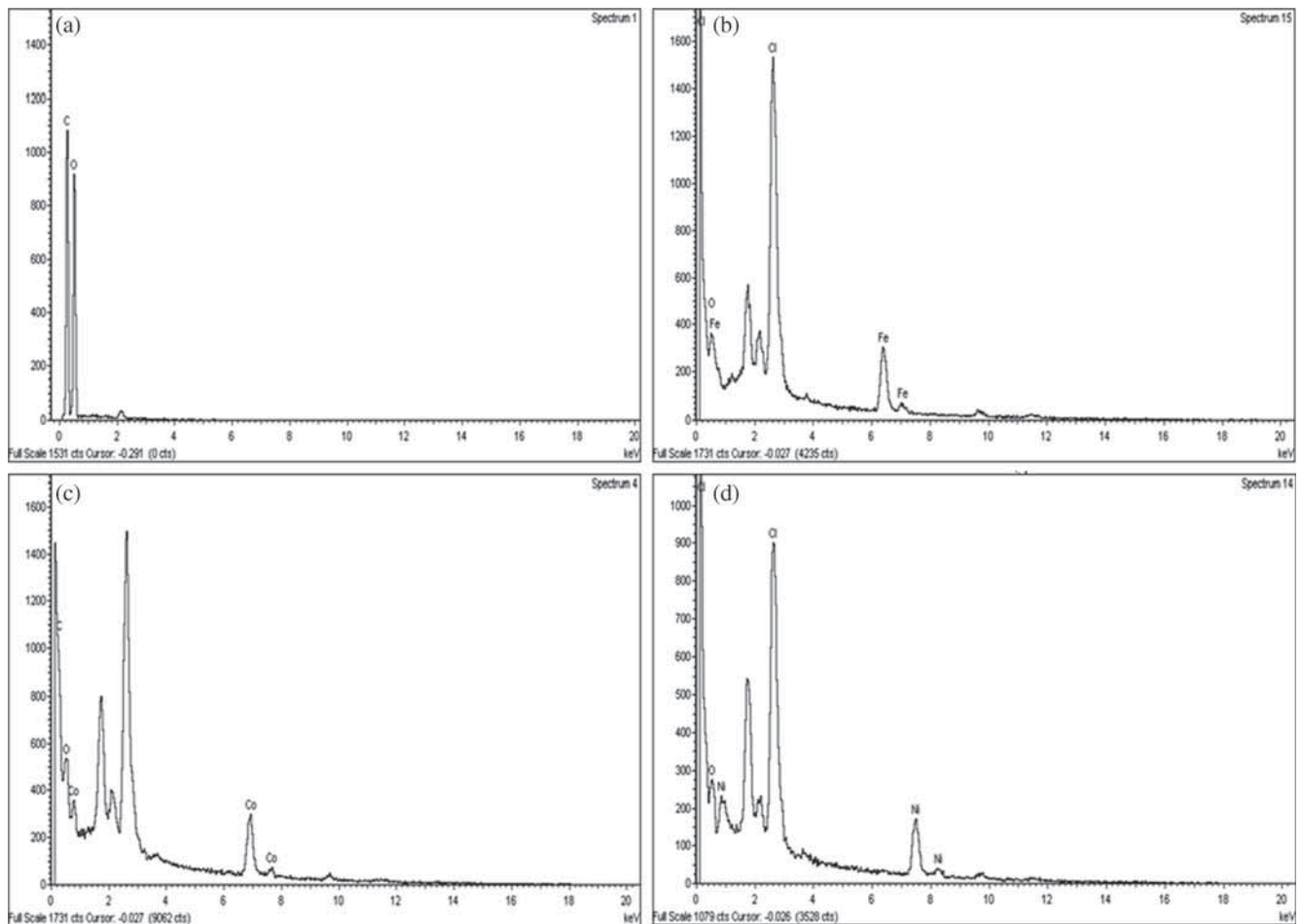


**Figure 4.** VSM data of PEO + PVP and  $\text{Co}^{2+}$ -,  $\text{Fe}^{3+}$ - and  $\text{Ni}^{2+}$ -doped polymer films.

More decreased nature and an asymmetric nature of the Raman peaks in the  $\text{Ni}^{2+}$ -doped polymer film when compared with other prepared polymer films were observed. This quite informative result could indicate that the degree of crystallinity decreases increasing the amorphous nature of the polymer. These results could also be in good agreement with the XRD results of previous studies. From the Raman spectra, the degree of crystallinity decreased in the  $\text{Ni}^{2+}$ : PEO + PVP polymer film, when compared to other ions doped polymer films. Therefore, this polymer film exhibits a high ionic conductivity that has been reported in the next section.

#### 3.4 VSM analysis

Figure 4 shows the hysteresis curves of the magnetization ( $M$ ) as a function of magnetic field ( $H$ ) at the room temperature for both the host and doped PEO + PVP polymer films. The host film has shown paramagnetic nature, which can be attributed to the existence of free mobile spins in the blended polymer films. The saturation magnetization and remanent magnetic fields are at  $4.416 \times 10^{-4}$  and  $1.524 \times 10^{-5}$  emu.<sup>17</sup> For this host PEO + PVP polymer film,  $M-H$  curve profile has been plotted which confirms the paramagnetic nature.



**Figure 5.** EDAX profiles of (a) PEO + PVP, (b)  $\text{Fe}^{3+}$ (0.1): PEO + PVP, (c)  $\text{Co}^{2+}$ (0.1): PEO + PVP and (d)  $\text{Ni}^{2+}$ (0.1): PEO + PVP polymer films.

The magnetic measurement of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ : PEO + PVP polymer films has been reported in figure 4. 'S' shaped behaviour with the saturation of the hysteresis graph can be seen, indicating a ferromagnetic nature.<sup>18</sup> At lower fields, all the doped polymer samples exhibited a clear ferromagnetic hysteresis loop as shown in the inset of figure 4. Several models have been presented to explain the ferromagnetic origin in those ferromagnetic TM ions doped composites. In recent times, Coey *et al*<sup>19</sup> reported a spin split impurity-band model to explain the variation of the magnetic moment across TM ions doped composite series. From this model, the composites exhibit the ferromagnetic behaviour only when they are doped by some 3d atoms, such as Co, and which induced a strong hybridization of 3d impurity band near the Fermi level. These results suggest that the ferromagnetism originates from the doping effect of  $\text{Co}^{2+}$  ion. When TM ion was doped in the pure blended film it increases the electrons which induce more effective ferromagnetic couplings between doped  $\text{Co}^{2+}$  ions. Further TM ( $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ ) doped PEO + PVP blended polymer films exhibited the remnant magnetization; it could be due to the strong ferromagnetic interaction between the TM–TM ions. The ferromagnetic exchange interaction occurred between the same TM ions mediated by their neighbouring  $\text{O}^{2-}$  ions, i.e., a strong hybridization between the d shells of TM ions and p shells of their neighbouring  $\text{O}^{2-}$  ions. The competition between these two exchange interactions will finally determine the magnetic properties of the samples. According to the above discussion it could be explained that the magnetic properties of the samples with TM ions that exhibited a strong ferromagnetism overlapped on the paramagnetic signal of the pure polymer. Following the literature,<sup>20</sup> measured hysteresis loop contributed by ferromagnetism and paramagnetic nature could be separated using the equation

$$M(H) = \frac{2M_s}{\pi} \tan^{-1} \left[ \frac{H \pm H_c}{H_c} \tan \left( \frac{\pi S}{2} \right) \right] + \chi H, \quad (1)$$

where  $M_s$  and  $H_c$  are the saturation magnetization and coercivity of the ferromagnetic component, respectively.  $S$  is defined as the ratio of remnant magnetization ( $M_r$ ) to saturation magnetization ( $M_s$ ) of the ferromagnetic component;  $\chi$  the magnetic susceptibility of the paramagnetic component.

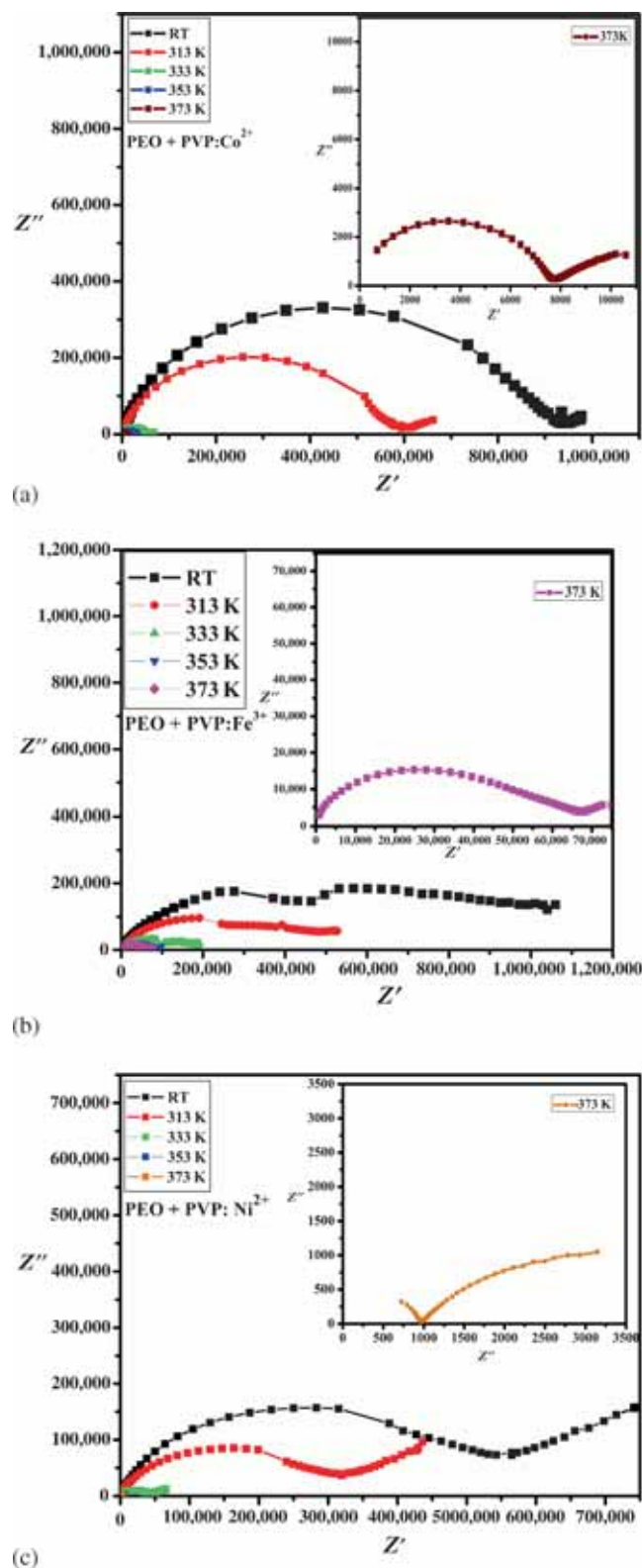
### 3.5 EDAX profile analysis

EDAX profiles of the TM ions doped PEO + PVP films are shown in figure 5, revealing the presence of C, O, Co, Ni and also Fe ions in the prepared films.

### 3.6 Impedance analysis

The samples were vacuum dried at 300 K for 1 h and the impedance measurements were carried out by sandwiching the polymer film between two aluminium electrodes. The impedance, dielectric loss and dielectric constant parameters have been reported in the earlier work.<sup>21</sup> Figure 6a–c shows the complex impedance plane plots ( $Z'$  vs.  $Z''$ ) of

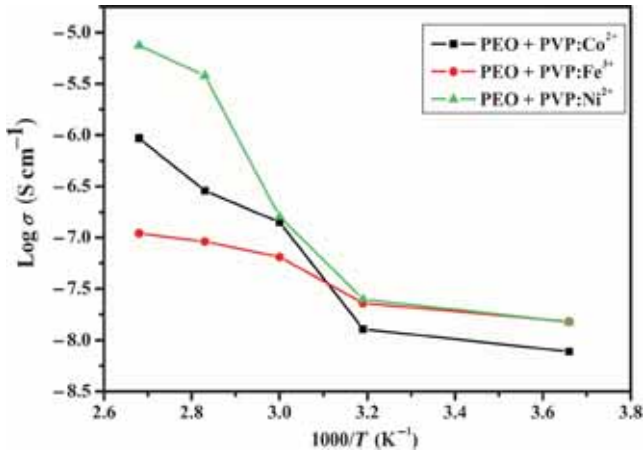
PEO + PVP :  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  films, respectively. Among them,  $\text{Ni}^{2+}$  ion doped film exhibited a prominent



**Figure 6.** Cole–Cole plots of (a)  $\text{Co}^{2+}$ (0.1): PEO + PVP, (b)  $\text{Fe}^{3+}$ (0.1): PEO + PVP and  $\text{Ni}^{2+}$ (0.1): PEO + PVP blended polymer films.

**Table 1.** Ionic conductivity values of prepared polymer electrolyte films at different temperatures.

| Polymer electrolyte film    | Ionic conductivity (S cm <sup>-1</sup> ) |                        |                        |                        |                        |
|-----------------------------|--|------------------------|------------------------|------------------------|------------------------|
|                             | RT                                       | 313 K                  | 333 K                  | 353 K                  | 373 K                  |
| PEO + PVP: Co <sup>2+</sup> | 7.8 × 10 <sup>-9</sup>                   | 1.3 × 10 <sup>-8</sup> | 1.4 × 10 <sup>-7</sup> | 2.9 × 10 <sup>-7</sup> | 9.4 × 10 <sup>-7</sup> |
| PEO + PVP: Fe <sup>3+</sup> | 1.5 × 10 <sup>-8</sup>                   | 2.3 × 10 <sup>-8</sup> | 6.4 × 10 <sup>-8</sup> | 9.2 × 10 <sup>-8</sup> | 1.1 × 10 <sup>-7</sup> |
| PEO + PVP: Ni <sup>2+</sup> | 1.5 × 10 <sup>-8</sup>                   | 2.5 × 10 <sup>-8</sup> | 1.6 × 10 <sup>-7</sup> | 3.8 × 10 <sup>-6</sup> | 7.5 × 10 <sup>-6</sup> |

**Figure 7.** Arrhenius plots for Co<sup>2+</sup>(0.1): PEO + PVP, Fe<sup>3+</sup>(0.1): PEO + PVP and Ni<sup>2+</sup>(0.1): PEO + PVP blended polymer films.

ionic conductivity at 373 K temperature. From the figure two well-defined regions such as a high frequency semicircle related to the parallel combination of a resistor and capacitor and a low frequency spike representing formation of double layer capacitance at the electrode–electrolyte interface due to migration of ions at low frequency were observed. The low frequency response appearing as an inclined spike at an angle less than 90° to the real axis indicates the inhomogeneous nature of the electrode–electrolyte interface. By the intersection of semicircle with the real axis the bulk resistance of the polymer electrolytes can be found. The ionic conductivity of the solid polymer electrolyte has been calculated from

$$\sigma = \frac{l}{R_b \cdot A}, \quad (2)$$

where ‘*l*’ is the thickness of the polymer electrolyte (cm), *A* the area of the blocking electrode (cm<sup>2</sup>) and *R<sub>b</sub>* the bulk resistance of the solid polymer electrolyte film.<sup>22</sup> In the case of Co<sup>2+</sup>: PEO + PVP polymer electrolyte exhibits a high ionic conductivity in the order of 9.42 × 10<sup>-7</sup> S cm<sup>-1</sup>. Further, Fe<sup>3+</sup>: PEO + PVP polymer film exhibits a high ionic conductivity in the order of 1.11 × 10<sup>-7</sup> S cm<sup>-1</sup> and also Ni<sup>2+</sup>: PEO + PVP polymer film exhibits high ionic conductivity in the order of 7.5 × 10<sup>-6</sup> S cm<sup>-1</sup> at 373 K. Due to increasing amorphous nature, the Ni<sup>2+</sup>-doped PEO + PVP polymer film exhibited a high ionic conductivity when compared with other ions doped polymer films. The degree of crystallinity nature decreased in the Ni<sup>2+</sup> polymer film as evidenced by

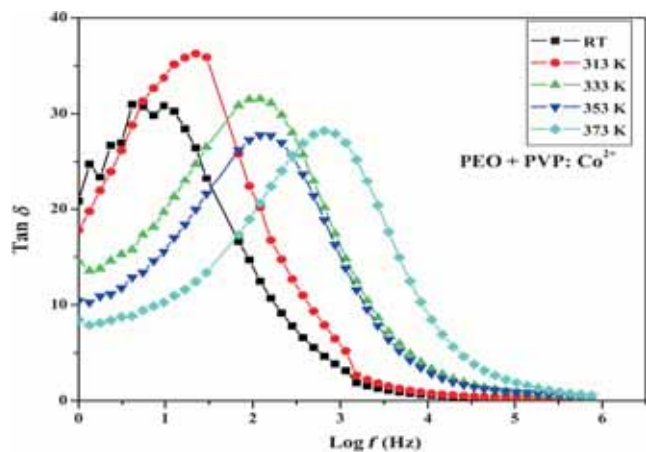
the Raman spectra. The ionic conductivity values of the prepared TM ions doped PEO + PVP blended polymer films are shown in table 1.

### 3.6a Temperature-dependent ionic conductivity analysis:

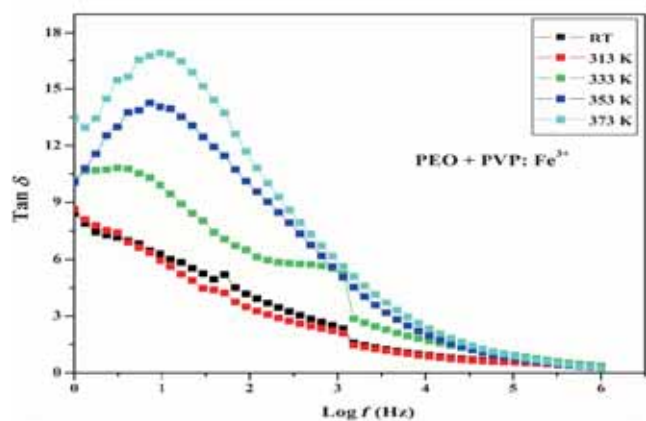
The temperature-dependent ionic conductivity plots are shown in figure 7. The Arrhenius plots suggest that the ion transport in the polymer electrolytes depends on the polymer segmental motion. Figure 7 explains that the ionic conduction in the polymer electrolyte system obeys the Vogel–Tammann–Fulcher (VTF) relation, which describes the transport properties in a viscous matrix. The increase of conductivity with temperature is interpreted as being due to a hopping mechanism between co-ordination sites, local structural relaxations and segmental motion of polymers. The enhancement of conductivity with temperature can be linked to the decrease in viscosity and hence, increased chain flexibility. In polymer electrolyte, the change of conductivity with temperature can be explained by increase in the free volume of the system that facilitates the migration of ions. For devices operating over a wide temperature range, it is desirable to have a uniform conductivity.<sup>23</sup>

### 3.7 Dielectric analysis

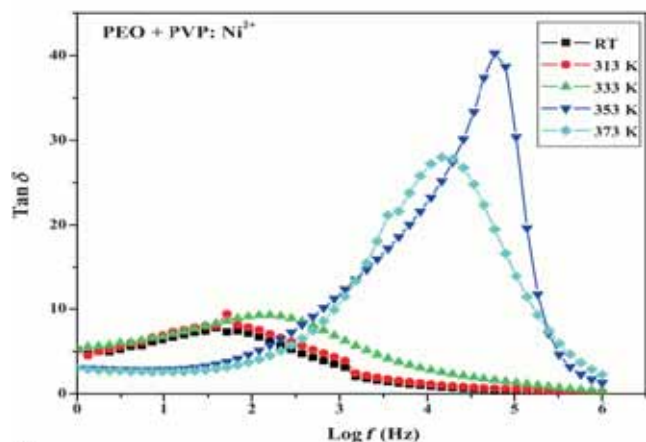
The dielectric relaxation parameter of the polymer can be obtained from the study of tan δ as a function of frequency. The dielectric loss tangent, tan δ can be defined by the equation tan δ = ε''/ε'. The variation of tan δ with frequency for all the prepared Co<sup>2+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup> ions doped PEO + PVP-blended polymer complexes at different temperatures is presented in figure 8. The high values of tan δ with the decrease in frequency at different temperatures may be attributed to the face charge build up at the interface between the sample and the electrode (space-charge polarization). The appearance of peaks for each ion in the loss spectrum (tangent loss) suggesting the presence of relaxing dipoles in the polymer film. The electrode polarization (EP) relaxation frequency, *f<sub>EP</sub>*, is used to evaluate the EP relaxation time is *f<sub>EP</sub>* = (2π*f<sub>EP</sub>*)<sup>-1</sup>. In figure 9 the variation of ε' (the real part of the complex dielectric permittivity: ε\* = ε' - jε'') as a function of frequencies at different temperatures for the polymer samples which are incorporated with Co<sup>2+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup> ions is shown. As expected, the variation in tendency of dielectric constant with frequency is the reverse of the electrical conductivity. ε' attains high value at low frequency and decreases



(a)



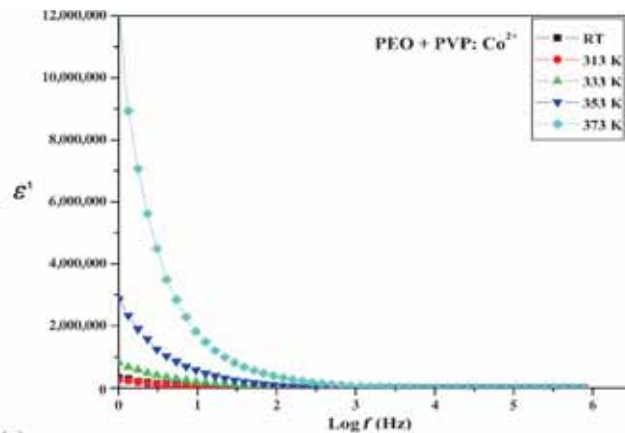
(b)



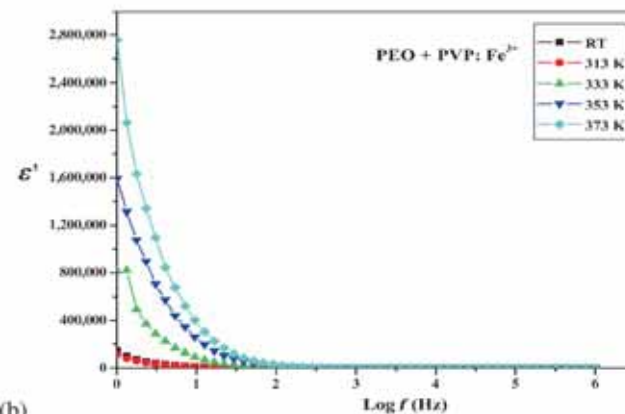
(c)

**Figure 8.** Dielectric loss profiles of (a)  $\text{Co}^{2+}(0.1)$ : PEO + PVP, (b)  $\text{Fe}^{3+}(0.1)$ : PEO + PVP and (c)  $\text{Ni}^{2+}(0.1)$ : PEO + PVP blended polymer films.

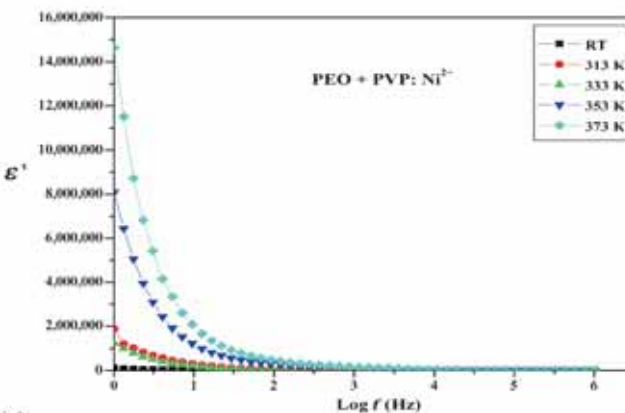
exponentially with the increase in frequency. The decrease of dielectric constant is mainly attributed to the mismatch of interfacial polarization of composites to external electric fields at elevated frequencies. The permittivity also enhances near the percolation threshold. It is usually behind that the percolation threshold is an important point at which electrical



(a)



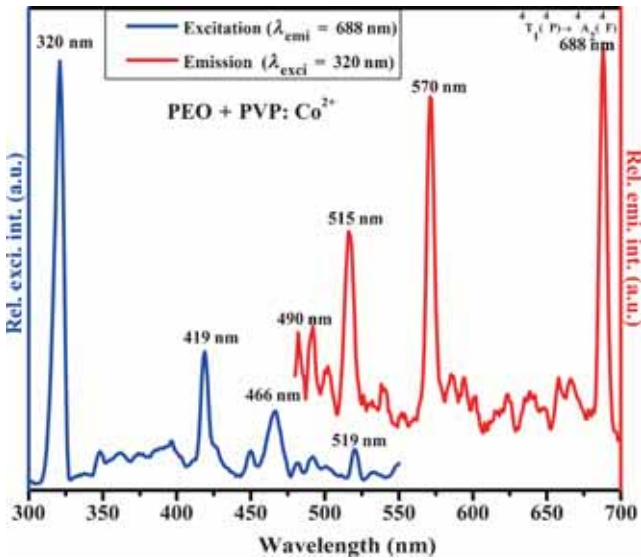
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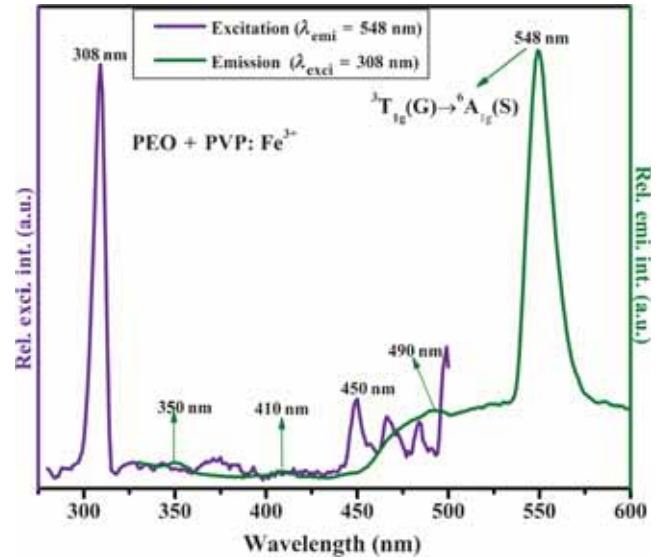
(c)

**Figure 9.** Dielectric constants ( $\epsilon'$ ) behaviour of (a)  $\text{Co}^{2+}(0.1)$ : PEO + PVP, (b)  $\text{Fe}^{3+}(0.1)$ : PEO + PVP and (c)  $\text{Ni}^{2+}(0.1)$ : PEO + PVP blended polymer films.

property varies a lot. Therefore, to study the behaviour of the polymer composites in the vicinity of percolation threshold is an effective way to know the electrical transport behaviour of composites. The dielectric response is explained by complex permittivity  $\epsilon^* = \epsilon' - j\epsilon''$ , where  $\epsilon'$  and  $\epsilon''$  are the dielectric components for energy storage and energy loss of applied electric field, respectively. Dielectric properties of ionic conducting polymers are due to the contribution of electronic, ionic, dipole orientations and space-charge



**Figure 10.** Emission and excitation spectra of  $\text{Co}^{2+}$ : PEO + PVP polymer film.



**Figure 11.** Emission and excitation spectra of  $\text{Fe}^{3+}$ : PEO + PVP polymer film.

polarizations. The complex permittivity of the polymer is obtained from the impedance data from the equation:

$$\varepsilon^* = \frac{1}{(j\omega C_0 Z^*)} = \varepsilon' - j\varepsilon'', \quad (3)$$

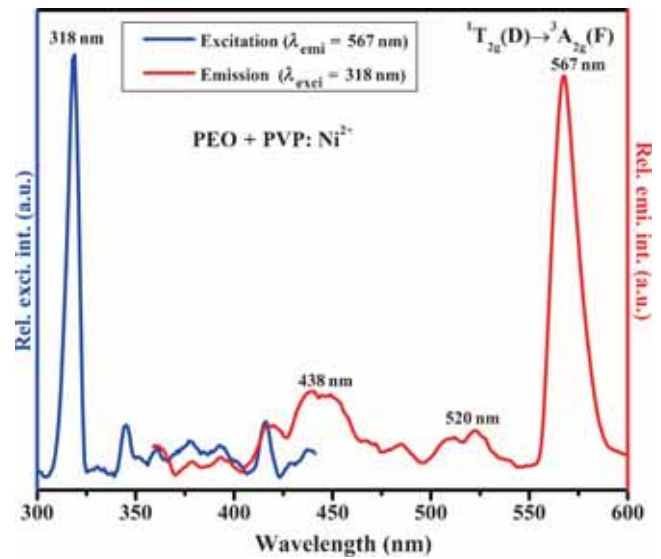
where  $Z^*$  is the complex impedance,  $C_0$  the capacitance of free medium. The real part of the permittivity (dielectric constant  $\varepsilon'$ ) represents the polarizability, while the imaginary part (dielectric loss)  $\varepsilon''$  represents the energy loss due to polarization and ionic conduction. The dielectric constant  $\varepsilon'$  is calculated from

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}, \quad (4)$$

where  $C$  is the capacitance of the sample,  $\varepsilon_0$  the permittivity of the free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ) and  $A$  the cross-sectional area of electrode.<sup>24,25</sup>

### 3.8 Photoluminescence analysis

Figures 10–12 show the emission spectra along with excitation spectral profiles in each case of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ : PEO + PVP polymer films. The excitation spectra of  $\text{Co}^{2+}$ : PEO + PVP blended polymer film show three excitation bands at 320, 490 and 519 nm by monitoring its emission at 688 nm. Among the excitation peaks, 320 nm peak is intense, and hence it is chosen in measuring the emission spectral profiles that has shown four emission peaks at 490, 515, 570 and 688 nm. Of those, 688 nm emission is a prominent one and it is assigned to  ${}^4T_1(4P) \rightarrow {}^4A_2(4F)$ <sup>26</sup> as shown in figure 10. The emission spectra of  $\text{Fe}^{3+}$ : PEO + PVP polymer film reveal a strong green emission at 548 nm ( ${}^3T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ ) and also show an additionally a weak emission at 490 nm with an excitation at 308 nm.<sup>27</sup>



**Figure 12.** Emission and excitation spectra of  $\text{Ni}^{2+}$ : PEO + PVP polymer film.

Excitation spectrum has shown bands at 308 and 450 nm upon using an emission at 548 nm as shown in figure 11. In case of  $\text{Ni}^{2+}$ : PEO + PVP polymer film, only a single excitation band is observed with emission at 567 nm, we have also observed two more emissions at 438, 520 nm. Among all these emission bands the 567 nm emission ( ${}^1T_{2g}(D) \rightarrow {}^3A_{2g}(F)$ ) is more intense, under the excitation at 318 nm<sup>28</sup> as shown in figure 12. Therefore, from the above photoluminescence spectral analyses the red ( $\text{Co}^{2+}$ ) and green ( $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ ) emissions have been identified from the surface of the  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$ : PEO + PVP polymer films under UV excitation source.



#### 4. Conclusion

In summary, it could be concluded that we have successfully synthesized a transparent PEO + PVP polymer films with and without  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  dopant ions. Further, semi-crystalline nature has been confirmed from their XRD and Raman spectral profiles. Host PEO + PVP polymer film exhibited a paramagnetic nature, polymer films of PEO + PVP :  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  ions have commonly shown ferromagnetic nature from their VSM profiles. Ionic conductivities of these doped polymer films have been carried out using an impedance analyzer from 1 Hz to 1 MHz at different temperatures and those results have been analysed. Among the three doped polymer films,  $\text{Ni}^{2+}$ : PEO + PVP polymer film has revealed a maximum conductivity of  $7.5 \times 10^{-6} \text{ S cm}^{-1}$  at 373 K. Temperature-dependent ionic conductivity behaviour has been explained. Dielectric constants and dielectric losses have been investigated. From photoluminescence analysis, it is noticed that  $\text{Co}^{2+}$ : PEO + PVP film has shown a *red* emission at 688 nm ( ${}^4\text{T}_1({}^4\text{P}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ ) with an excitation at 320 nm. In the case of  $\text{Fe}^{3+}$ : PEO + PVP film, a *green* emission at 548 nm ( ${}^3\text{T}_{1\text{g}}(\text{G}) \rightarrow {}^6\text{A}_{1\text{g}}(\text{S})$ ) with an excitation at 308 nm and also in the case of  $\text{Ni}^{2+}$ : PEO + PVP film too, a *green* emission has been noticed at 567 nm ( ${}^1\text{T}_{2\text{g}}(\text{D}) \rightarrow {}^3\text{A}_{2\text{g}}(\text{F})$ ) with an excitation at 318 nm. Thus it has been found that these polymer films possess required electrical and magnetic properties for their use in developing functional devices. Therefore, based on these results, it could be suggested that these TM ions doped PEO + PVP polymer films are found to be potential novel multifunctional materials for various magneto-electric, magneto-optic and display device applications.

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