Research Article

Structural, Dielectric, Optical and Magnetic Properties of Ti^{3+} , Cr^{3+} , and Fe^{3+} : PVDF Polymer Films

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Highly transparent and very clear nature of PVDF: Ti^{3+} , PVDF: Cr^{3+} , and PVDF: Fe^{3+} polymer films of good quality have been synthesized by employing solution casting method. XRD profiles have confirmed semicrystalline structures in α -, β -, and γ -PVDF phases. IR spectra have confirmed these findings and revealed some structural defects such as monofluorinated alkenes. Emission spectra reveal that PVDF: Ti^{3+} has a *blue* emission, PVDF: Cr^{3+} has *blue* emission, and PVDF: Fe^{3+} *red* emission was observed. The conductivity and dielectric measurements have also been carried out as function of frequency and temperature changes. Due to the presence of the transition metal ions in these films, significant improvement in the ionic conductivity has been noticed. The dielectric behaviors of these films have been analyzed using dielectric permittivity (ϵ'), dissipation factor ($\tan \delta$), and impedance spectra (Z' and Z''). VSM measurements have confirmed that the PVDF: Ti^{3+} exhibits antiferromagnetic nature, PVDF: Cr^{3+} film ferromagnetic nature, and PVDF: Fe^{3+} film strong paramagnetic nature. Thus, the present study has successfully explored the fact that these optical materials are also potential enough in both conductivity and magnetic properties for their use in applications suitably.

1. Introduction

Polymer based magnetoelectric materials are promising materials such as conductive adhesives, supported catalysts, sensors, luminescent films, electrooptical devices, integrated optics, memory devices, and optical data processing technologies, and it is possible to achieve impressive enhancements of material properties as compared with the pure polymers, as being metal free and environmentally acceptable, due to the polymers unique characteristics such as flexibility, light weight, versatility, and low cost, and in some cases, biocompatibility can be taken to advantage [1–8].

As a semicrystalline polymer, poly(vinylidene fluoride) (PVDF) is fit for membrane material due to its excellent chemical resistance, physical and thermal stability, high strength, high dielectric constant, and flexibility. Another feature that distinguishes PVDF from other polymers is its polymorphism; that is, it may present at least four crystalline phases of α , β , δ , and γ . Moreover, an increasing interest has been devoted to PVDF in the development of electric or magnetic field sensors. For this application PVDF was added with

transition metal (Ti^{3+} , Cr^{3+} and Fe^{3+}) ions to evaluate their electrical and magnetic properties.

2. Experimental Study

2.1. Sample Preparation and Characterization. The materials used in the present work are all high purity grade. PVDF, DMA, TiCl_3 , CrCl_3 , and FeCl_3 are used for this study. Both the host polymer and dopant chemicals have been dissolved separately in 99.9% pure dimethylacetamide (DMA) in the proportion of 9:1 (Wt%) and such mixed solutions were stirred thoroughly using a magnetic stirrer at temperature 323 K for 24 hrs and each of these polymer solutions was cast onto Petri dishes and was kept in a vacuum oven at 333 K for two days in removing solvent traces while evaporation process takes place. The thickness of the films was in the range of $\approx 100 \mu\text{m}$.

The structures of the prepared polymers were characterized on XRD 3003 TT Seifert diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 KV and 20 mA and the 2θ

TABLE 1: X-ray diffraction peaks semi-crystalline PVDF phases.

Values of 2θ and respective d spacing observed in the X-Ray Diffraction			
2θ (in degrees)	d (Å)	Assignment	Plane
20.25	4.30	β	110
39.64	2.28	α	002
42.06	2.13	α	042
46.21	2.06	γ	114

FIGURE 1: ((a)–(c)) XRD profile of PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films. FIGURE 2: ((a)–(c)) FTIR spectra of PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films.

range was varied between 10° and 70° . Perkin-Elmer FT-IR spectrophotometer was used for recording FTIR spectrum of the PVDF film in the region of $4000\text{--}400\text{ cm}^{-1}$. Both excitation and emission spectra of these polymer films were recorded on a SPEX FLUOROLOG (model-II) attached with a Xe-arc lamp (150 W). The dielectric constant, dielectric loss, and conductivity measurements were carried out on a Phase Sensitive Multimeter (PSM) Model-1700. The magnetic moment profile as function of applied magnetic field was measured on a Vibrating Sample Magnetometer (VSM) (Model-4500 magnet walker (model HF-20H)).

3. Results and Discussion

3.1. XRD Analysis. XRD diffraction reveals that the PVDF polymer films under investigation are characterized by semi-crystalline structure and it has three crystal structures including α -, β - and γ -phases [9, 10]. From Figures 1(a)–1(c), the spectra of the (a) PVDF: Ti^{3+} , (b) PVDF: Cr^{3+} , and (c) PVDF: Fe^{3+} polymer films present peaks at $2\theta \approx 20.25^\circ$, 39.64° , 42.06° and 46.21° and labeled to the diffractions in planes of (110), (002), (042) and (114), respectively; those could be due to the characteristic peaks of α , β , and γ crystalline phases, and are confirmed by FTIR analysis as well. The results is shown in Table 1 and in good agreement with the reports made available in the literature [11, 12].

3.2. FTIR Analysis. Figures 2(a)–2(c) show the plots of IR transmission spectra of the PVDF: Ti^{3+} , PVDF: Cr^{3+} , and PVDF: Fe^{3+} polymer films in the spectral range of $4000\text{--}400\text{ cm}^{-1}$ and all the spectra are found to be more similar

in nature. The main PVDF characterizing frequencies are observed, where β phase occurs mostly at 440 cm^{-1} , 510 cm^{-1} and 840 cm^{-1} and, for α phase at 430 cm^{-1} , 610 cm^{-1} , 765 cm^{-1} , and 1420 cm^{-1} . However, the peaks at 880 cm^{-1} and 950 cm^{-1} were identified as belonging to the γ -phase. Couple bands that are identified at 1665 cm^{-1} and 1629 cm^{-1} have been assigned to the C=C stretching as was reported earlier [13, 14] and this indicates the presence of polarons in the polymeric matrix. The band at 748 cm^{-1} which refers to the head to head (h-h) and tail to tail (t-t) defects [15]. The change of the intensities of these IR bands indicates a change of the chelation mode of Ti^{3+} , Cr^{3+} , and Fe^{3+} in PVDF matrix. It is interesting to notice that the C=C mode and the h-h defects are suitable sites for polarons and bipolarons formation in the PVDF matrix.

3.3. Photoluminescence Analysis. Figures 3(a)–3(f) show both excitation and emission spectra of PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films. For PVDF: Ti^{3+} , the emission spectrum has been obtained with $\lambda_{\text{exci}} = 387\text{ nm}$, the emission spectrum displays emissions at 413 nm (could not be assigned) 435 nm ($^3\text{T}_1(\text{F}) \rightarrow ^3\text{A}_2(\text{F})$), and 457 nm (also could not be assigned to a transition). For PVDF: Cr^{3+} , the emission spectrum has been measured with $\lambda_{\text{exci}} = 385\text{ nm}$, strong emission bands are observed at 421 nm ($^2\text{E}_g \rightarrow ^4\text{T}_{2g}$) and 435 nm ($^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$). For PVDF: Fe^{3+} emission spectrum has been recorded with $\lambda_{\text{exci}} = 329\text{ nm}$, strong emission bands are observed at 588 nm and 625 nm ($^4\text{A}_2 \rightarrow ^4\text{T}_1$ (^4P)). All assignments that are made on the measured emission bands are in agreement with the literature reported results [16].

FIGURE 3: ((a)-(b)) Excitation and emission of PVDF: Ti^{3+} polymer films. ((c)-(d)) Excitation and emission of PVDF: Cr^{3+} polymer films. ((e)-(f)) Excitation and emission of PVDF: Fe^{3+} polymer films.

3.4. Impedance Analysis. Impedance analysis reflects the collective response of microscopic polarization process under an external electric field. Under an alternating field, frequency dispersion or dielectric relaxation is observed due to different polarization mechanisms within a dielectric. Typical spectroscopic plots of dielectric constant (ϵ^1) versus frequency (f)

for the three polymer (PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+}) films are shown in Figures 4(a)–4(c). It is observed that the ϵ^1 decreases rapidly with increasing frequency. The rapid fall of dielectric constant (ϵ^1) in their frequency range shows that space charge polarization contributes significantly to the total polarization observed in these films. Space

FIGURE 4: ((a)–(c)) Dielectric constant as function of frequency for PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films.

charge polarization (interfacial polarization) arises whenever phases of different conductivities are present in the same material. When an electric field is applied, the charges move through a conducting phase but are interrupted as they come across a high resistivity phase. This leads to a buildup of charge at the interface, which is manifested as enhanced polarization. These buildup charges cannot follow the applied field rapidly at high frequencies and hence, the resultant loss. The dielectric loss ($\tan\delta$) versus frequency (f) for the three polymer (PVDF: Ti^{3+} , PVDF: Cr^{3+} , and PVDF: Fe^{3+}) films are shown on Figures 5(a)–5(c). A single relaxation peak was

observed. The loss peak maximum shifts to a lower frequency with decreasing temperature, and the peak intensity decreases and the distribution broadens. This may be due to the result of a dominant effect of the polarization by migrating charges at low frequency. The dispersion observed at low frequencies could be attributed to the interfacial polarization mechanism and the dispersion observed at high frequencies could be attributed to the dipolar relaxation [15, 17].

Complex plane plots (Z^1 versus Z^{11}) for a typical polymer films are shown in Figures 6(a)–6(c). The behaviour of films and at different temperatures is similar. The Cole-Cole

FIGURE 5: ((a)–(c)) Dielectric loss as function of frequency for PVDF: Ti³⁺, PVDF: Cr³⁺ and PVDF: Fe³⁺ polymer films.

plots showed two well-defined regions. semi circle pattern indicating the involvement of a single conduction mechanism in the composite system. The single mechanism is attributed to grain size or due to the mobility of free charges (polaron or free ions) induced by the increment of temperature. The bulk dc resistance (R_b) of the electrolyte was determined as

the point where the high frequency semicircle in the plots cuts the Z^1 axis. The ionic conductivity (σ) is calculated

$$\sigma_{dc} = \frac{d}{(R_b \cdot A)}, \quad (1)$$

FIGURE 6: ((a)–(c)) Cole-Cole plots for PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films.

where d = thickness of the film and A = area of the electrodes. It has been observed in polymer films that σ_{dc} values first increased with increased temperature; this can be explained with the help of free volume theory. As the temperature increases, the polymer can expand easily and produce free volume. Thus ions, solvated molecules, or polymer segments can move to the free volume and hence the increase in conductivity. At higher temperatures σ_{dc} values

decrease due to that metal halide cations act as transient crosslinker, resulting in progressive immobilization of the polymer chain segments thereby decreasing the conductivity. Figures 7(a)–7(c) shows the temperature dependence of ionic conductivity for the PVDF: Ti^{3+} , PVDF: Cr^{3+} , and PVDF: Fe^{3+} polymer films. The conductivity values of these polymer films are shown in Table 2. These results suggest that Arrhenius phenomenological relationship can be used to

FIGURE 7: ((a)–(c)) Conductivity with temperature change for PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films.

TABLE 2: The σ_{dc} conductivity values of PVDF: Ti^{3+} / Cr^{3+} / Fe^{3+} polymer films.

Temperature (K)	PVDF: Ti^{3+} ($\times 10^{-4}$ S/cm)	PVDF: Cr^{3+} ($\times 10^{-4}$ S/cm)	PVDF: Fe^{3+} ($\times 10^{-4}$ S/cm)
303	1.667	0.1183	0.1625
313	1.782	0.1235	0.1735
323	1.891	0.1335	0.2114
333	1.983	0.1747	0.2684
343	2.054	0.1938	0.3273
353	2.243	0.2170	0.3827
363	2.592	—	0.4672
373	3.673	—	0.6063

FIGURE 8: ((a)–(c)) Arrhenius plots for PVDF: Ti³⁺, PVDF: Cr³⁺ and PVDF: Fe³⁺ polymer films.

describe the conductivity behaviour for the aforementioned polymer films. Indicating Arrhenius type thermally activated process given by the relation $\sigma = \sigma_0 \exp(-Ea/KT)$, where σ_0 is the preexponential factor, Ea the activation energy, and K is the Boltzmann constant.

The activation energies are calculated from the slopes of $\log \sigma_{dc}$ versus $1000/T$ plots as shown in Figures 8(a)–8(c) and it has been found that the activation energy decreases from region I to region II. The activation energy of PVDF: Ti³⁺ is 0.452 eV, PVDF: Cr³⁺ is 0.460 eV, and for PVDF: Fe³⁺ 1.16 eV. It is noteworthy that the films with low activation energies are desirable for practical applications [18].

3.5. Magnetic Properties. Figures 9(a)–9(c) show the room temperature magnetization (M-H) hysteresis loops of PVDF:

Ti³⁺, PVDF: Cr³⁺, and PVDF: Fe³⁺ polymer films with a maximum field of 20 kOe. Figure 9(a) shows the results of PVDF: Ti³⁺ polymer film and depicts the reverse-S-type curve, indicating the intrinsic diamagnetism. From the loop the coercive field (H_c), saturation magnetization (M_s), and remanent magnetization (M_r) were estimated to be 839.57 Oer, 1.01×10^{-3} emu/gm and 75.96×10^{-6} emu, respectively. Figure 9(b) shows the results of PVDF: Cr³⁺ polymer film, indicating the existence of RT ferromagnetism nature. From the loop coercive field, saturation magnetization (M_s) and remnant magnetization (M_r) were estimated to be 38.19 Oer, 1.211×10^{-3} emu/gm and 61.156×10^{-6} emu respectively, we conform that the observed ferromagnetism is intrinsic. Therefore it is reasonable to suggest that the observed ferromagnetism is due to oxygen vacancies and/or defects in the polymer

FIGURE 9: ((a)–(c)) Hysteresis loops for PVDF: Ti^{3+} , PVDF: Cr^{3+} and PVDF: Fe^{3+} polymer films.

film. Figure 9(c) shows the results of PVDF: Fe^{3+} polymer film, indicating weak ferromagnetic nature. From the loop coercive field, saturation magnetization (M_s) and remnant magnetization (M_r) were estimated to be 118.84 Oer, 5.875×10^{-3} emu/gm and 114.04×10^{-6} emu respectively, which reveals the existence of defects and impurities; we believe that the observed weak ferromagnetism is caused both by the defects (such as oxygen vacancies) and with Fe ions incorporation [19, 20]. From the graphs PVDF: Ti^{3+} shows antiferromagnetism, PVDF: Cr^{3+} shows ferromagnetism, and PVDF: Fe^{3+} shows weak ferromagnetic nature.

4. Conclusion

In summary, it is concluded that we have successfully synthesized both undoped (reference) and doped PVDF films containing transition metal ions such as Ti^{3+} , Cr^{3+} , and Fe^{3+} , respectively, and analyzed their structural, electrical and magnetic properties from the measurements of their XRD, FTIR spectra, photoluminescent spectra, dielectric constant, dielectric loss, and magnetic properties. XRD results have revealed that these polymer films possess monoclinic, α -, β -, and γ -phases. Conductivity σ_{dc} in the place of electrical

conductivity. From magnetic profile measurements, PVDF: Ti^{3+} film has shown antiferromagnetic nature, PVDF: Cr^{3+} film has revealed ferromagnetic nature, and PVDF: Fe^{3+} has displayed strong paramagnetic nature.

Disclosure

The authors confirm that the paper has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. The authors further confirm that the order of authors listed in the paper has been approved by all of them. The authors confirm that they have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing they confirm that they have followed the regulations of their institutions concerning intellectual property.

Conflict of Interests

The authors wish to confirm that there is no known conflict of interests associated with this paper and there has been no

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