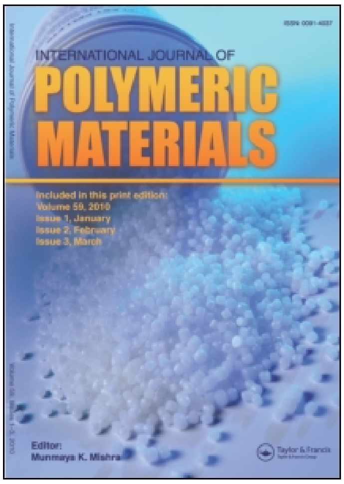
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Crystal Structure and Physical Properties of PVDF Films Filled with $CuCl_2$-$MnCl_2$ Mixed Fillers

A. El-Khodary[a]; M. Abdelaziz[a]; Gamal M. Hassan[b]
[a] Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt [b] Department of Ionizing Radiation Metrology, National Institute for Standards (NIS), El-Giza, Egypt

To cite this Article El-Khodary, A. , Abdelaziz, M. and Hassan, Gamal M.(2005) 'Crystal Structure and Physical Properties of PVDF Films Filled with $CuCl_2$-$MnCl_2$ Mixed Fillers', International Journal of Polymeric Materials, 54: 7, 633 — 650

To link to this Article: DOI: 10.1080/00914030490499125

URL: http://dx.doi.org/10.1080/00914030490499125

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Journal of Polymeric Materials, 54:633–650, 2005

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490499125

Taylor & Francis
Taylor & Francis Group

Crystal Structure and Physical Properties of PVDF Films Filled with $CuCl_2$–$MnCl_2$ Mixed Fillers

A. El-Khodary
M. Abdelaziz
Physics Department, Faculty of Science, Mansoura University,
Mansoura, Egypt

Gamal M. Hassan
National Institute for Standards (NIS), Department of Ionizing
Radiation Metrology, El-Giza, Egypt

Poly(vinylidene fluoride) (PVDF) films filled with mixed fillers of $CuCl_2$–$MnCl_2$ were prepared. The differential thermal analysis (DTA) indicates the existence of two main endothermic peaks and the crystallization exothermic temperature. X-ray diffraction (XRD) evidenced the presence of a semicrystalline structure containing α, β, and γ crystalline phases. The optical absorption spectra depicted two shoulder-like bands as well as a strong valley. The IR spectra confirmed the XRD implications about the presence of α, β, and γ phases. The dc electrical resistivity results are discussed on the basis of Kuivalainen modified interpolaron hopping model. The temperature and filling level dependence of the hopping distance R_0 were studied. The dc magnetic susceptibility data follow the Curie-Weiss law. The electron spin resonance (ESR) investigation suggested the existence of aggregated Mn^{2+} for higher values of x where the spectra were characterized by Lorentzian signal. On the other hand, at lower values of x, the spectra were characterized by two unresolved sharp peaks.

Keywords: PVDF, $CuCl_2$–$MnCl_2$ mixed fillers, optical, electric, and magnetic properties

INTRODUCTION

Poly(vinylidene fluoride), PVDF, is one of the functional polymers extensively arousing the scientific and technological interest of many

Received 29 March; in final form 3 May 2004.

Address correspondence to M. Abdelaziz, Physics Department, Faculty of Science, Mansoura University 35516, P.O. Box 19, Mansoura, Egypt. E-mail: mabdelaziz62@yahoo.com

investigators. Due to its high piezoelectric [1] and pyroelectric [2] activity, PVDF has been considered as a good condidate for the following sensing applications: pressure [3], temperature [4], gas [5], and electromagnetic wave sensors. It is used in nonlinear optics [6] and microwave transducers [7]. PVDF is water-resistive material; therefore, it is suitable for outdoor and indoor paint [8]. Moreover, it has important medical applications [9] because it is nonrejectable in human tissues.

Polymeric systems containing metal particles are attractive systems because they are expected to exhibit properties that are of scientific as well as practical interests. The doping of polymer with metal salts causes changes in the structural and therefore in the chemical and physical properties [10]. The change in physical properties of polymers due to doping depends on the chemical nature of the doping substances and the ways in which they interact with the host matrix [11]. One may select the suitable type and doped level of transition-metals halides to prepare a doped polymer with a disired physical property [12].

The foregoing features generated vast research aiming to get more efficient PVDF technical elements. In previous works the present research group investigated the physical properties of PVDF films filled with $CuCl_2$ [13] and $MnCl_2$ [14]. These investigations revealed that the used fillers modified the structural, electrical, and/or magnetic properties of PVDF. However, a nonlinear (even non-monotonic) filling level (FL) dependence of the contents of the active structural forms was found. This exerted strong influences on the electrical and magnetic properties of the filled PVDF films. Searching for a linear (or monotonic) FL dependence of the electric and magnetic properties over a fair FL range, it was thought to use the intrasubstituted mixed fillers $(x)CuCl_2(15-x)MnCl_2$ where x is the percent mass fraction.

The present work continues the authors efforts to study the FL effect of these mixed metal halides on the structural modification, electric, and magnetic properties of PVDF.

EXPERIMENTAL

Materials Used and Sample Preparation

PVDF in pellets form (SOLEF 1008) and metal chlorides $CuCl_2$ and $MnCl_2$ were obtained from the Aldrich chemical company. Films of PVDF filled with $(x)CuCl_2(15-x)MnCl_2$ were prepared by the casting method. Dimethylformamide (DMF) was used to dissolve these materials. Mixture of the dissolved polymer with mixed halides were cast in a glass dish and kept in a dry atmosphere at 343 K for two weeks to minimize the solvent traces. Different concentrations of the fillers were obtained where x = 0.0, 1, 5, 10, 14, and 15 weight percent. The thickness of the films was in the range of 100 to 150 μm.

Analytical Methods

The XRD patterns were obtained using a Siemens type F diffractometer with CuK_{α}- radiation and LiF monochromator. The DTA thermograms were carried out using Shimadzu DTA-50 with measuring temperature range 30–300°C and a heating rate of 5°C/min. UV/VIS absorption spectra were measured in the wavelength range of 200 to 900 nm using a Perkin Elmer UV/VIS spectrometer. An IR spectrophotometer (Perkin Klmer 883) was used for measuring the IR spectra in the wavenumber range of $4000-400\,cm^{-1}$. The dc electrical resistivity was measured using an autorange multimeter (Keithley 175) with an accuracy of 0.2%. The dc magnetic susceptibility was measured using Faraday pendulum balance technique, which provides accuracy better than 3.0%. The ESR spectra were measured with an X-band ESR spectrometer (Bruker, EMX) at room temperature, using standard rectrangular cavity (4102 ST), operating at 9.7 GHz with a 100 kHz modulation frequency.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

The XRD patterns for unfilled and PVDF films filled with various weight fractions of $CuCl_2$ and $MnCl_2$ are plotted in Figure 1. These patterns indicate the presence of a semicrystalline structure. The assignments of these crystalline peaks [14] are listed in Table 1. It is clear that all samples contain α and β crystalline phases. In addition, γ-phase was observed for unfilled and at x = 5, 14, and 15%. Furthermore, there is a small scattering peak at $2\theta = 16.5$ for 14 and 15%. This peak belongs neither to PVDF nor $MnCl_2$ crystals [15]. However, this peak may indicate the appearance of a new crystalline phase related to copper complex. The area under the A_{β} peak can be taken as measure for the degree of crystallinity of β phase. Figure 2 shows the influence of $CuCl_2$ addition on A_{β}. At low copper concentrations, a maximum is observed at x = 1% whereas a minimum value is observed at x = 5%.

Differential Thermal Analysis (DTA)

The DTA thermograms of the present systems are displayed in Figure 3. The thermograms are characterized by: (a) an endothermic peak, T_m, at

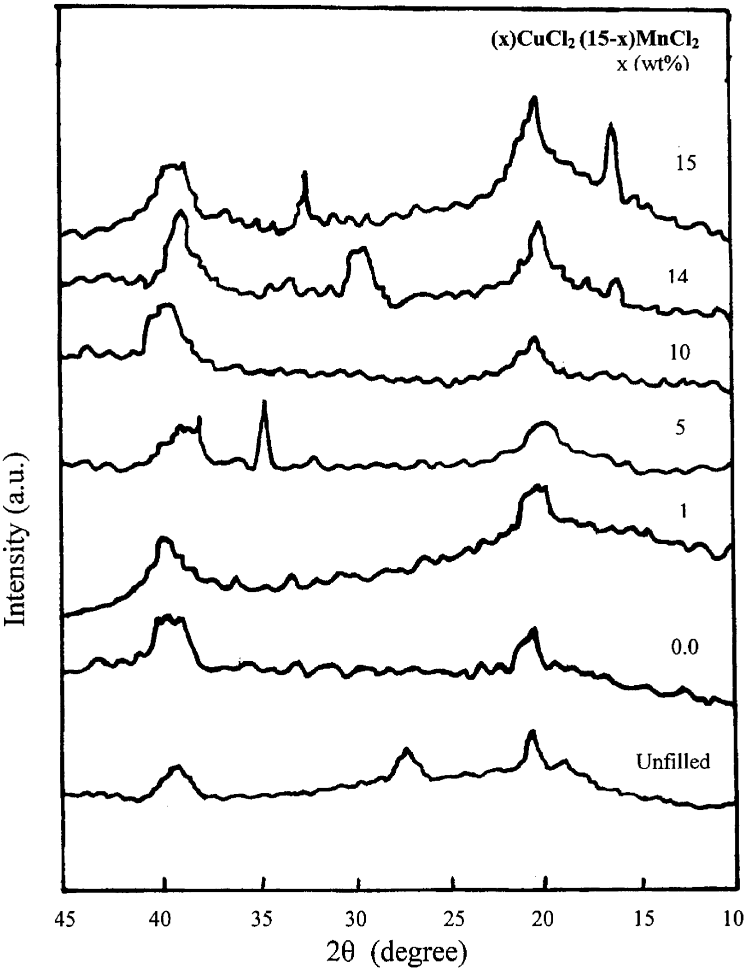


FIGURE 1 The X-ray diffraction patterns of unfilled and filled PVDF films with $(x)CuCl_2(15\text{-}x)MnCl_2$.

about 174°C, which is attributed to the PVDF melting [16], (b) another endothermic peak, T_{m^*}, at about 250°C, for $x = 14$ and 15%, which may be assigned to the melting temperature of γ-phase and/or copper complex [17], and (c) a crystallization exotherm temperature, T_c, of the filled films is visible in the DTA curves at about 88°C. The values of the order of reaction n, at T_m, were calculated using the Kissinger method [18], and the values of n, T_m, and T_{m^*}, are listed in Table 2. It is clear that $n \sim 1$, which indicates that all the reactants are melted at T_m.

TABLE 1 The assigned X-ray Diffraction Peaks Characterizing the Crystalline PVDF Phases

$CuCl_2$ (wt%)	2θ (degree)	Assignments
Unfilled	20.5	$(110)\beta$, $(200)\beta$
	26.8	$(021)\gamma$
	38.8	$(002)\alpha$
0	20.5	$(110)\beta$, $(200)\beta$
	39.5	$(002)\alpha$
1	20.5	$(110)\beta$, $(200)\beta$
	39.8	$(002)\alpha$
5	20.4	$(110)\beta$, $(200)\beta$
	35	$(200)\gamma$
	39.7	$(002)\alpha$
10	20.5	$(110)\beta$, $(200)\beta$
	39.8	$(002)\alpha$
14	20.4	$(110)\beta$, $(200)\beta$
	30.3	$(130)\gamma$
	39	$(002)\alpha$
15	20.5	$(110)\beta$, $(200)\beta$
	32.5	$(200)\gamma$
	39.2	$(002)\alpha$

Optical Absorption

The UV/Vis absorption spectra of the PVDF system with various FLs are shown Figure 4. The observed spectra for $x = 0$ and 1% contain two shoulder-like bands centered at about 319 and 350 nm, which characterize the Mn^{2+} ions in octahedral symmetry [19]. Moreover, the spectra for $x \geq 5\%$ exhibit a strong valley with heigher wavelength edge at $\sim$800 nm. This edge may be attributed to the Cu^{2+} absorption band [13], which appears normally within the range of 689–800 nm. This was assigned to the d–d band of Cu^{2+} due to the transition between ^2E and $^2T_2$ levels origination from the splitting of the 2D ground state of the Cu^{2+} free ion d^9 in an octahedral field. Moreover a shoulder-like band is centered at 415 nm for $x = 15\%$, in Figure 4, due to the presence of binuclear Cu^{2+} complex [16].

IR Transmittance

The IR transmission spectra of various FLs of the present system are shown in Figure 5. The main characterizing peaks of PVDF are observed. The α-phase may be indicated by the peaks at 604, 773, and 480 cm^{-1}. The β-phase may be identified at 840 cm^{-1}. The γ-phase at 970 cm^{-1}. This confirms the XRD implications about the presence of

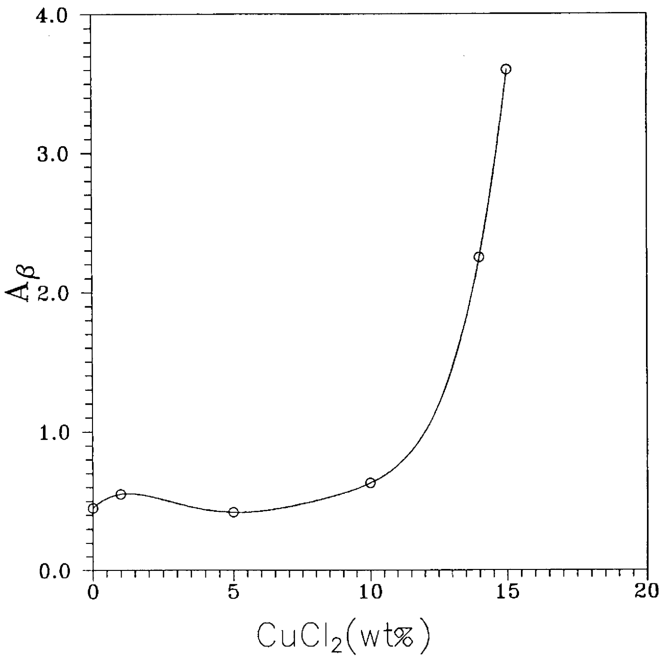


FIGURE 2 The FL dependence of the A_β.

α, β, and γ phases. Moreover, there is an absorption band at 773 cm^{-1}, characterzing the α phase, which is sensitive to head-to-head (h-h) defects. According to the spectroscopic study by Kobayashi et al. [20], this band corresponds to h-h concentration of ~12%. This value is comparable with the 10% obtained by Hasegawa et al. [21] for pure PVDF. Another absorption peak is observed at 1628 cm^{-1}, which is assigned to conjugated double bond C=C stretching in monochlorinated alkenes [22].

The structural disorder can be identified by investigation of the FL dependence of certain IR absorption peaks depicted in Figure 6. The bands at 840 cm^{-1}, characterizing the β-phase, and 1628 cm^{-1}, assigned to C=C stretching, exhibit a minimum value at $x = 5\%$.

DC Electrical Conduction

The dc electrical resistivity, ρ, was measured in the temperature, T, range of 298–403 K. The h-h defects and the conjugated C=C, detected by IR analysis, are considered as suitable sites for polarons and/or bipolarons. Therefore, the present results can be discussed on the

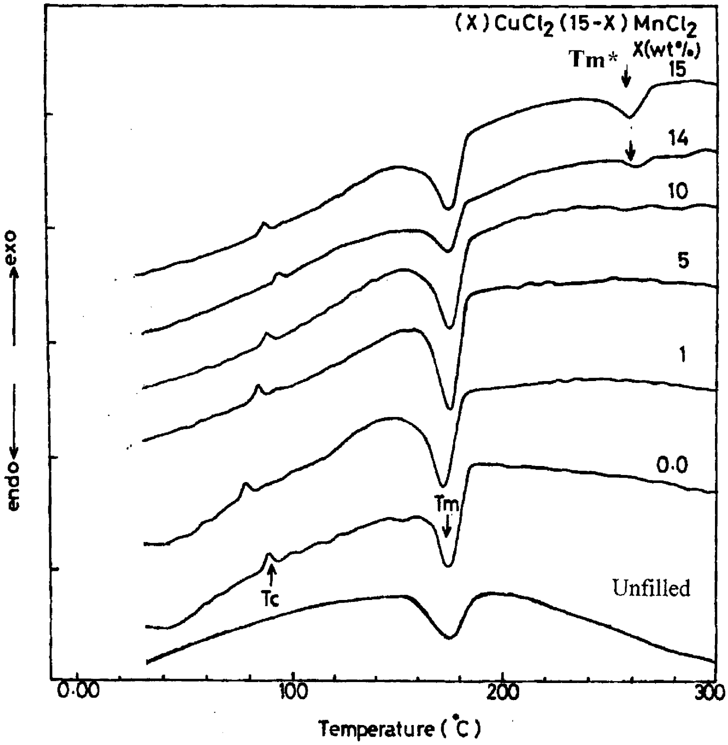


FIGURE 3 The DTA plots of unfilled and filled PVDF films with (x)$CuCl_2$ (15-x)$MnCl_2$.

basis of the Kuivalainen et al. [23] modified interpolaron hopping model, in which the conduction is attributed to phonon-assisted hopping between polaron and/or bipolaron bound states in the polymer. According to this model the electrical resistivity can be

TABLE 2 The FL Dependence of: Crystallization (T_c), Melting (T_m and T_{m^*}) Temperatures and Order of Reaction (n)

$CuC1_2$ (wt%)	T_c (°C)	T_m (°C)	T_{m^*} (°C)	n
Unfilled	—	175.5	—	1.03
0.0	88.27	174.34	—	1.07
1	78.45	172.77	—	1.00
5	84.16	176.03	—	0.939
10	88.22	175.31	—	0.966
14	93.74	174.25	262.9	1.06
15	86.76	175.02	259.4	1.028

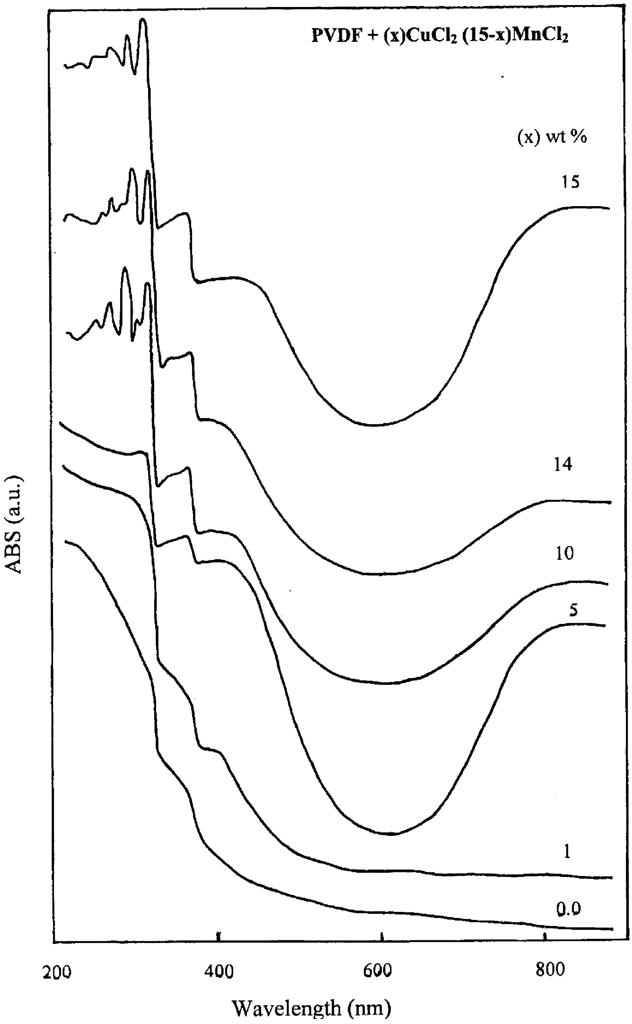


FIGURE 4 The UV/Vis absorption specra of PVDF filled films filled with various FLs.

expressed as

$$\rho = \frac{kT}{Ae^2\gamma(T)^2}\frac{R_0^2}{\xi}\frac{(y_p + y_{bp})^2}{y_p y_{bp}}\exp\left(\frac{2BR_0}{\xi}\right) \tag{1}$$

where A = 0.45; B = 1.39; y_p and y_{bp} are the concentration of polarons and bipolarons, respectively; $R_0 = \left(3/4\prod C_{imp}\right)^{1/3}$ is the typical

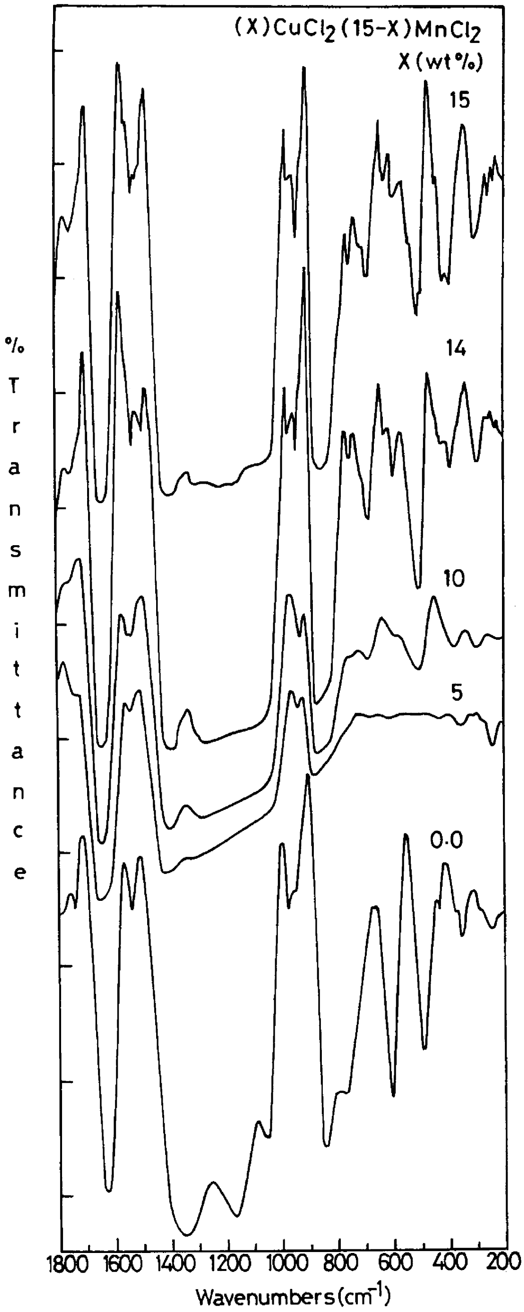


FIGURE 5 The FTIR spectra of PVDF with different FLs.

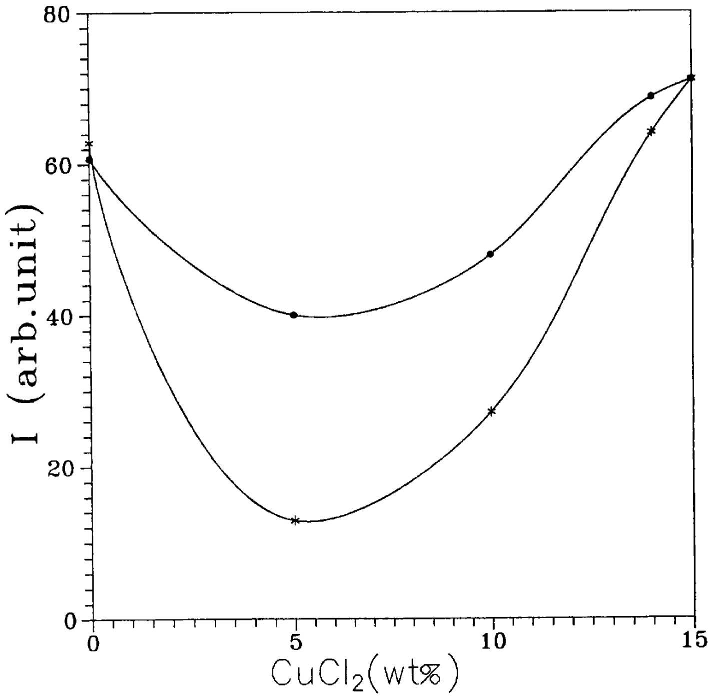


FIGURE 6 The FL dependence of the IR peaks at (∗) 840 cm^{-1} and (●) 1628 cm^{-1}.

separation between impurities whose concentration is C_{imp}, $\zeta = (\zeta_{\|}\zeta_{\perp}^{2})^{1/3}$ is the average decay length of a polaron and bipolaron wave function, $\zeta_{\|}$ and $\zeta_{\perp}$ are the decay lengths parallel and perpendicular to the polymer chain, respectively. Bredas et al. [24] reported that the extension of defect should be the same for polaron and bipolaron. The electronic transition rate between polaron and bipolaron states can be expressed as

$$\gamma(T) = \gamma_0(T/300\,K)^{n+1} \tag{2}$$

where n is a constant ~10 and the pre-factor $\gamma_0 = 1.2 \times 10^{17}\, s^{-1}$ were estimated by Kivelson [25]. Using a computer-aided program, the order of magnitude of ρ in the present system was adjusted with the impurity concentration C_{imp}, which actually was the fitting parameter [27]. The parameter $\zeta_{\|} = 1.06$ nm, whereas $\zeta_{\perp} = 0.22$ nm [28], depends on the inter-chain resonance energy and the inter-chain distance. Taking $y_p = y_{bp}$ for simplicity, which is an acceptable approximation [29], and using Eqs. 1 and 2, the values of the hopping

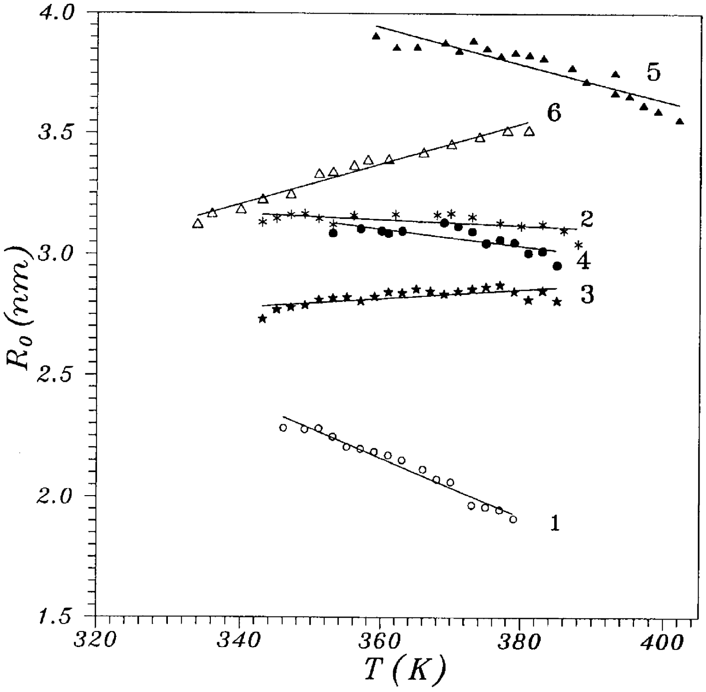


FIGURE 7 The temperature dependence of hopping distances R_0 for various FLs: (1) 0.0, (2) 1, (3) 5, (4) 10, (5) 14, and (6) 15 wt%.

distance R_0 can be obtained. A liner temperature dependence of R_0, for various FLs, is noticed in Figure 7. This indicates that the concentration of thermally activated polarons (acting as hopping sites for the charge carriers) changes as the temperature increases.

Figure 8 shows the dependence of R_0 and $\log \rho$, at $T = 373$ K, on $CuCl_2$ content. The R_0 and $\log \rho$ have: (i) a maximum value at $x = 1\%$ (ii) plateau in the range $5 \leq x \leq 14$, and (iii) sharp decrease at $x = 14\%$. The obtained values of R_0 were in the range of 2.0–3.8 nm, which were 8 to 15 times the monomer length (~0.25 nm [21]). This indicates that the electrical conduction is an intrachian one-dimensional hopping type.

DC Magnetic Susceptibility

Figure 9a,b displays the temperature dependence of the reciprocal dc magnetic susceptibility, χ, measured in the temperature range of 90 to 260 K. These plots exhibit the Curie–Wiess law in which

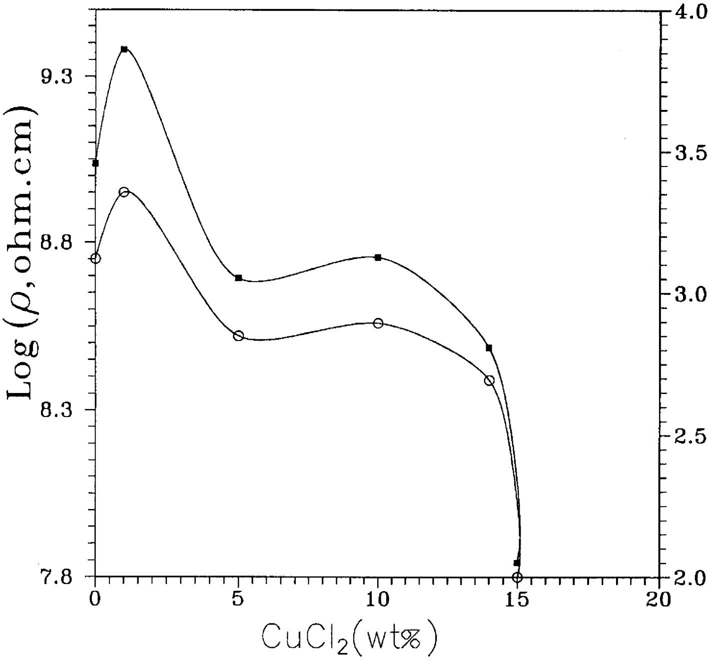


FIGURE 8 The FL dependence of $\log \rho$ (○) and R_0 (●) at temperature $T = 373\,K$.

$$\chi = C/(T - \theta_p), \tag{3}$$

where C is the Curie's constant and θ_p is the paramagnetic Curie temperature. The dependence of θ_p on the content of $CuCl_2$ is shown in Figure 10. It is clear that the observed negative values of θ_p, for $x \leq 1\%$, indicate an antiferromagnetic interaction at lower temperature. On the other hand, the positive values of θ_p, noticed for $x > 1\%$ suggested the predominance of ferromagnetic interaction at lower temperatures. The effective paramagnetic moment, μ_{eff}, at $T = 150\,K$ was calculated using the following equation

$$\mu_{eff} = 2.84[\chi_m(T - \theta_p)]^{1/2}, \tag{4}$$

where χ_m is the molar susceptibility of the used sample. The dependence of μ_{eff} on the $CuCl_2$ content is shown in Figure 10. The nonlinear behavior of the FL dependence of μ_{eff} is noticed. This indicates that the present system does not obey the magnetic dilution mechanism [30]. The behavior of μ_{eff} in the present FL range has two maxima, at $x = 0.0$ and 10%, and a minimum value at $x = 5\%$. Accordingly, one

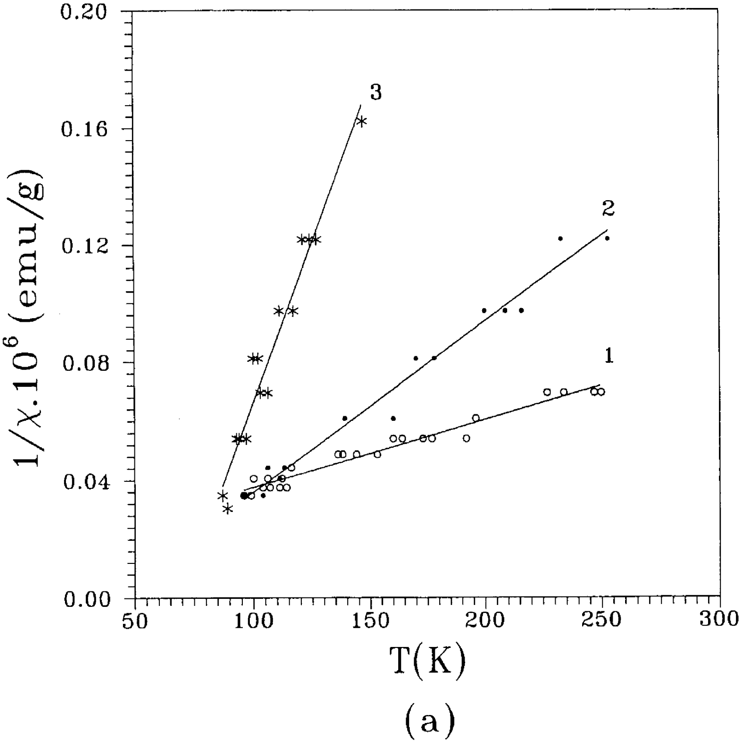


FIGURE 9 The temperature dependence of the reciprocal magnetic susceptibility for variously filled PVDF films: (a) (1) 0.0, (2) 1, and (3) 5 wt% and (b) (4) 10 and (5) 14 wt%.

may imply that the magnetic centers, induced by the filler molecules, are randomly distributed in the noncrystalline regions of the PVDF matrix.

Moreover, the obtained Curie–Wiess behavior indicates that the energy band diagram of the present filled PVDF system is characterized by magnetic localized energy states. This diagram differs from the itinerant one that was found previously for unfilled PVDF films [7].

Electron Spin Resonance

Figure 11 depicts the ESR spectra, measured at room temperature, for samples of x = 0.0, 1, 5, 10, 14, and 15%. The main characterizing features of PVDF, previously reported in Reference [29], are not observed in the present work. Moreover the six-hyperfine lines are not observed indicating the disappearance of isolated Mn^{2+} ions. However, the spectra are characterized by strong Lorentzain signal, located around

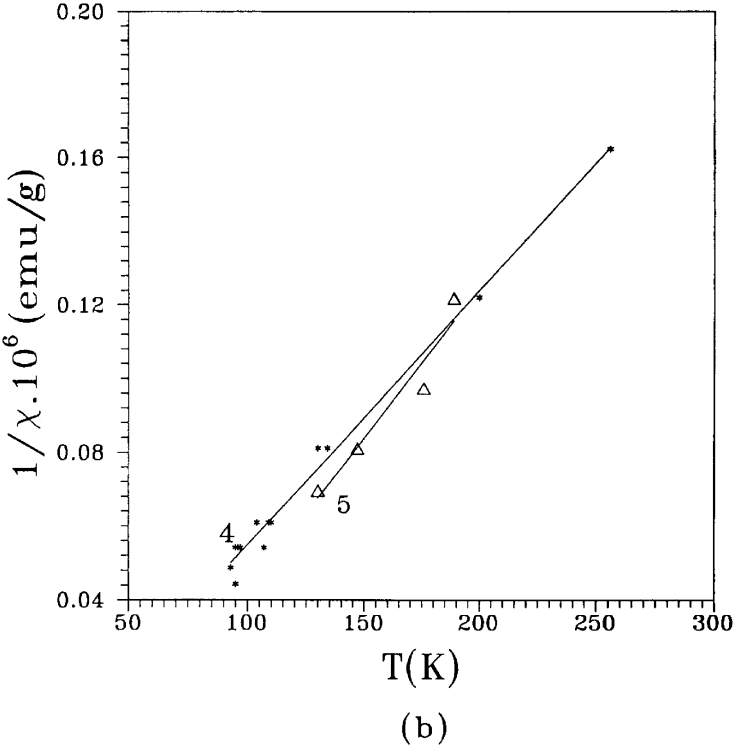


FIGURE 9 Continued.

a Landè factor (g) equal to 2.00, indicating the presence of aggregated Mn^{2+} form. On the other hand, two anisotropic peaks are clearly present for samples at $x = 14$ and 15%. The height of these peaks is sharper for $x = 15$ than for $x = 14\%$, indicating a very large concentration of Cu^{2+} ions in the polymeric matrix. These peaks are due to the aggregated form of the binuclear Cu^{2+} complex [30]. This result supports the findings of the XRD, DTA, and UV/Vis optical spectra.

The FL dependence of the $CuCl_2$ content can be clarified more explicitly with the aid of the peak-to-peak separation (ΔH) of the main ESR Lorentzian signal and the asymmetry factor, A, which is the ratio between the two halves of this signal. Figure 12 shows the dependence of ΔH and A on $CuCl_2$ content. It is clear that A decreases as $MnCl_2$ content increases, according to the following numerical formula

$$A = 0.0099x + 0.83 \tag{5}$$

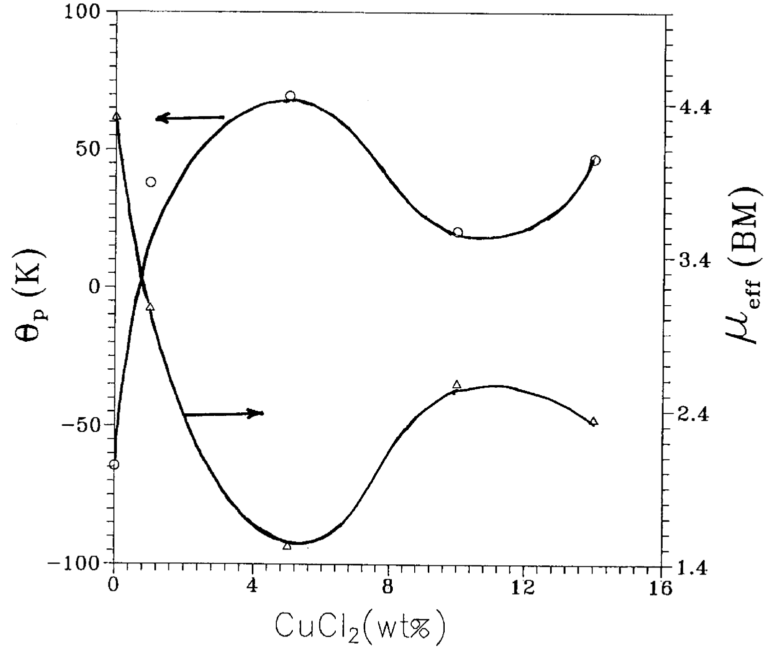


FIGURE 10 The FL dependence of θ_p (○) and μ_{eff} (Δ).

confirming the implication that Mn^{2+} loses its symmetrical distribution as the $MnCl_2$ increases. On the other hand, Figure 12 depicts a monotonic decreases of ΔH as x increases, indicating the decrease of dipolar interaction between the magnetic ions [16].

CONCLUSION

It could be concluded that the present filled PVDF films are characterized by the following features:

- The existence of two main endothermic peaks at 174 and 250°C indicating two melting temperatures as detected by DTA thermograms.
- The presence of semicrystalline structure containing α, β, and γ phases as evidenced by XRD.
- Two shoulder-like bands that were assigned to the splitting of the 2D ground state of the Cu^{2+} free ion $3d^9$ in an octahedral field as well as strong valley that can be attributed to octahedral Cu^{2+} complexes.
- The h-h defects and the conjugated C=C detected by IR analysis are considered as suitable sites for polaron and/or bipolaron. Moreover,

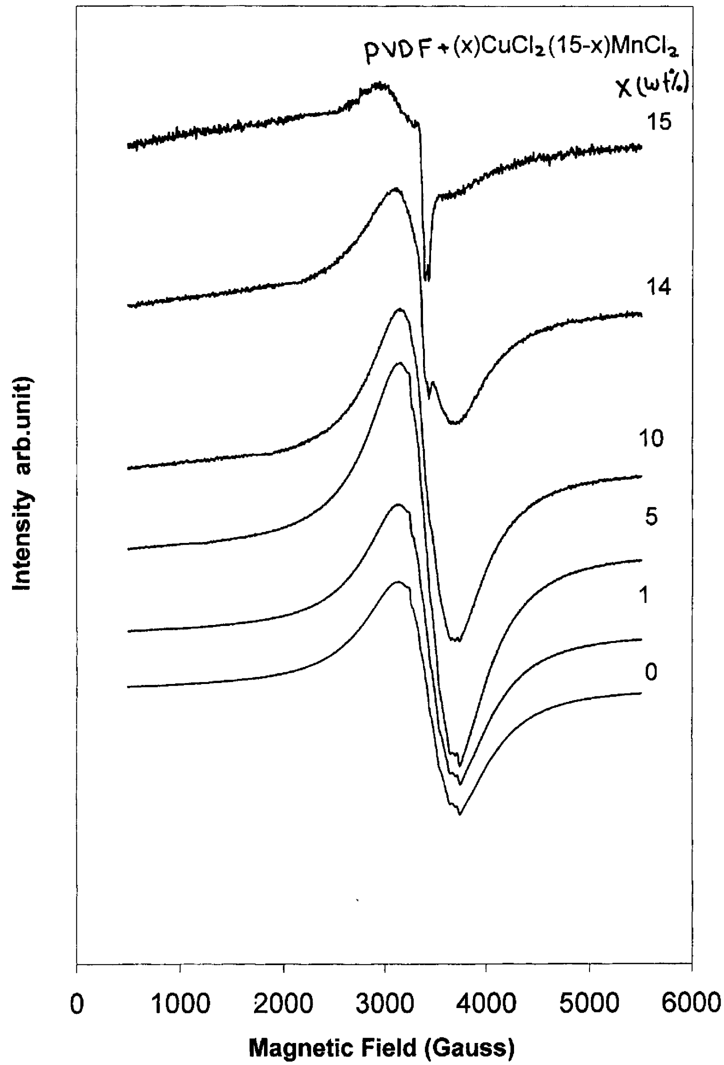


FIGURE 11 The ESR spectra of PVDF filled with (x)$CuCl_2$(15-x)$MnCl_2$.

IR spectra confirmed the XRD implications about the presence of α, β, and γ phases.

- The dc electrical conduction mechanism was of one dimensional intrachain type based on phonon-assisted interpolaron hopping model. The temperature and FL dependence of the hopping distance R_0 were studied.

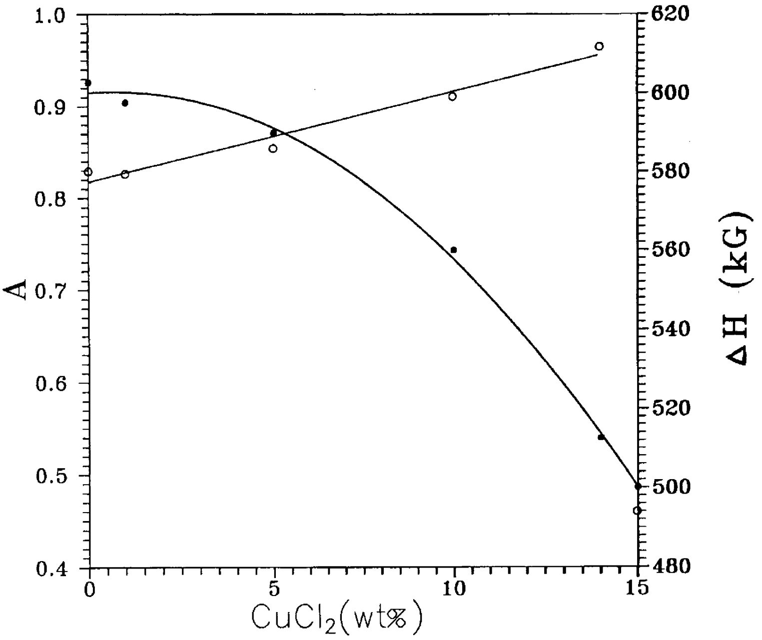


FIGURE 12 The FL dependence of A (O) and ΔH (●).

- The dc magnetic susceptibility data followed the Curie–Weiss law. At $x \leq 1\%$ an antiferromagnetic interaction proceeds at lower temperatures, whereas at $x > 1\%$ ferromagnetic interaction predominates.
- The ESR investigations suggested the existence of aggregated Mn^{2+} at higher values of x where the spectra were characterized by Lorentzian signal, whereas being characterized by unresolved two sharp peaks at lower values of x.

REFERENCES

[1] Hattori, T., Masashi, K., and Hiroji, O., *J. Appl. Phys.* **79**, 2016 (1996).
[2] Bernd, P., Rudolfand, E., and Sieghried, B., *J. Appl. Phys.* **72**, 5363 (1992).
[3] Ohnson, G. E., Blyler, L. L., Crance, G. R., and Gieniewski, C., *Ferroelectrics* **42**, 32 (1981).
[4] Sessler, G. M., *Electronics* **33**, 115 (1981).
[5] Takse, Y. and Odajima, A., *J. Appl. Phys.*, Part 2 **L** **707**, 21 (1993).
[6] Naoto, T., Yashiaki, U., and Tsuyoshi, K., *J. Appl. Phys.* **74**, 3366 (1993).
[7] Tawansi, A., Abdelkader, H. I., Balachandran, W., and Abdelrazek, E. M., *J. Mater. Sci.* **29**, 2001 (1994).
[8] Hughes, S. T. and Piery, A. R., *J. Phys. E.* **19**, 976 (1986).

[9] Valentini, R. F., Vargo, T. G., Gardella, J. A., and Aebischer, P., *J. Biomater. Sci. Polym. Ed.* **5**, 13 (1993).

[10] Tawansi, A., Zidan, A. M., Oraby, A. H., and Dorgham, M. E., *Physica B* **254**, 126 (1998).

[11] Bahri, R., *J. Phys. D: Appl. Phys.* **15**, 1036 (1982).

[12] Tawansi, A., Abdelrazek, H. E., and Zidan, H. M. *J. Mater. Sci.* **32**, 6243 (1997).

[13] Tawansi, A., Ayad, M. I., and Abdelrazek, E. M., *J. Appl. Polym. Sci.* **72**, 771 (1999).

[14] Tawansi, A., Oraby, A. H., Abdelrazek, E. M., Ayad, M. I., and Abdelaziz, M., *J. Appl. Polym. Sci.* **70**, 1437 (1998).

[15] Tawansi, A., El-Khodary, A., Zidan, H. M., and Badr, S. I., *Polym. Testing* **21**, 381 (2002).

[16] Abdelaziz, M. Effect of filling with mixed transition metal chlorides on the physical properties of polyvinylidene fluoride and some of its blends, Ph.D. thesis, Mansoura University, Egypt (2002).

[17] Van Krevelen, D. W. (1990) *Properties of Polymers,* Third Edition, (Elsevier, Amsterdam).

[18] Kissiger, H. E., *Anal. Chem.* **29**, 11, 1703 (1957).

[19] Srinivasa, A., Sreedhar, B., Lakshmana, J., and Lakhman, S. V. I., *Non-Crys. Solids*, **14**, 169 (1992).

[20] Kobayahi, M., Tashiro, K., and Tadokoro, H., *Macromolecules*, **8**, 158 (1975).

[21] Hasegawa, R., Takahashi, Y., Chatwi, Y., and Tadakoro, H., *J. Polym.* **13**, 600 (1972).

[22] Fleming, I. and Williams, D. H. (1966). *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, New York.

[23] Kuivalainen, P., Stubb, H., and Isotlo, H., *Phys. Rev.* **B31**, 7900 (1985).

[24] Bredas, J. L., Chance, R. R. and Silbey, R. *Phys. Rev.* **B26**, 5843 (1982).

[25] Kivelson, S., *Phys. Rev.* **B25**, 3798 (1982).

[26] Mott, N. F. and Gurey, R. W. (1940). *Electronic Process in Ionic Crystals*, Oxford University Press, London.

[27] Tawansi, A., Abdelrazek, E. M., and Zidan, H. M., *J. Mater. Sci.* **32**, 6243 (1997).

[28] Tawansi, A., Oraby, A. H., Bader, S. I., and Abdelaziz, M., *J. Mater. Sci.: Mater. in Electronics* **14**, 135 (2003).

[29] Tawansi, A., Abdel–Kader, H. I., Abdel–Razek, E. M., and Ayaad, M. I., *J. Mater. Sci. Technol.*, **13**, 194 (1997).

[30] Algra, H. A., Jornal, L. J., Huiskamp, W. J., and Corlin, R. L., *Physica*, **923**, 187 (1977).