Effect of Valence Electron Spin Polarization on the Physical Properties of CuCl₂-Filled Poly(vinylidene fluoride) as a Microwave Modulator

A. TAWANSI,¹ M. I. AYAD,² E. M. ABDEL-RAZEK¹

¹ Department of Physics, Faculty of Science, Mansoura University 35516, Mansoura, Egypt

² Department of Chemistry, Faculty of Science, Almenofya University, Shebeen Elkoom, Egypt

Received 4 May 1998; 11 October 1998

ABSTRACT: Infrared and optical spectra, differential thermal analysis, dc electrical resistivity, magnetic susceptibility, electron spin resonance, and microwave response of CuCl₂-filled poly(vinylidene fluoride) (PVDF) films, over the filler mass fraction range $0.05 \leq W \leq 0.4$, were measured. The infrared spectra evidenced the presence of β -phase, for all of the filler levels with main deformations of 20% (for W = 0.25) and 30% (for other filler levels) head-to-head and tail-to-tail units, which were considered as polaron and bipolaron defects. Optical activity was mainly influenced by PVDF structure. Differential thermal analysis revealed dipole relaxation and premelting endothermic peaks. A quasi-one-dimensional interpolaron hopping was thought to proceed in the direct current electric conduction, with a hopping distance less than the distance between two successive head-to-head sites. A temperature-independent Pauli paramagnetic behavior was observed, confirming the presence of induced energy bands due to CuCl₂ filling. Most of the observed electron spin resonance signals were antisymmetric, with superimposed repels due to the hyperfine interactions characterizing PVDF. The obtained linear dependence of the isotropic hyperfine coupling constant (ΔA°), for Cu(II), on average g-factor, implied that ΔA^{\cdot} is a measure of the valence electron spin polarization. An octahedral or distorted octahedral configuration was suggested for Cu(II). The present system is a good microwave modulator. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 771-781, 1999

Key words: CuCl₂-filled PVDF films; IR; optical; DTA; electrical conduction; magnetic susceptibility; ESR; microwaves

INTRODUCTION

Due to its high piezoelectric¹ and pyroelectric activity,² poly(vinylidene fluoride) (PVDF) has been considered a good candidate for the following applications: pressure,³ temperature,⁴ gas,⁵ and electromagnetic wave⁶ sensors. It is an infrared (IR)-to-visible light converter.⁷ It is used in nonlinear optics⁸ and microwave transducers.⁹ PVDF is a water-resistive material; therefore, it is suitable for outdoor and indoor paintings.¹⁰ Moreover, it has important medical applications¹¹ because it is nonrejectable in human tissues.

The foregoing features enhanced vast research aiming to get a more efficient PVDF technical element. In previous work, our research group investigated the physical properties of PVDF films filled with NiCl₂,¹² AlCl₃, ZnCl₂, CoCl₂,¹³ and MnCl₂.¹⁴ These investigations revealed that the used fillers modified the electric and/or mag-

Correspondence to: A. Tawansi.

Journal of Applied Polymer Science, Vol. 72, 771-781 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/060771-11

netic properties of PVDF and helped get a desired crystalline form (with a suitable fraction).

One of the most important applications of PVDF is the microwave transducers and microwave cavities.⁹ It has been evidenced that PVDF films filled with NiCl₂¹² and FeCl₃⁹ are good microwave modulators with different features. Tawansi and colleagues¹⁵ investigated the role of filler ion (Fe³⁺) configuration and spin electron density on the microwave response of PVDF films, using the electron spin resonance (ESR) spectra.¹⁶ The effect of equal amounts of FeCl₃ and CuCl₂ mixed fillers on the ESR, electronic and magnetic properties of PVDF, has been studied.¹⁷ It was found that Lorentzian ESR signal, due to the Fe³⁺ singly filled PVDF system, exhibits a significant deformation in the case of Fe³⁺ and Cu²⁺ multifilled PVDF system.

It seemed important to clarify the role of the valence electron spin polarization of Cu(II) filler on the microwave response of PVDF films. Thus, the present work was devoted to study the effect of $CuCl_2$ filler level (FL) on the structural, electrical, and magnetic properties, and on ESR and microwave responses of PVDF.

EXPERIMENTAL

Samples were made from an α -PVDF resin provided by Solvay (Belgium) and referenced as SOLEF 1008. Dimethylformamide was used as the solvent for the resin, and CuCl₂ was used as a filler. Films were prepared by casting enough of the desired solution onto glass, so that films were $\sim 0.2-0.5$ mm thick after the solvent was removed at 343°K. The maximum filler mass fraction was 40% CuCl₂. The samples were annealed at 393°K for 4 h.

An IR spectrometer type (Perkin–Elmer 1430) was used for measuring the IR spectra in the wavenumber range of $350-4000 \text{ cm}^{-1}$. A (Perkin–Elmer 1800) spectrometer was used for measuring the optical transmittance in the wavenumber range of 1.15×10^4 – $2.95 \times 10^4 \text{ cm}^{-1}$ at room temperature. Differential thermal analysis (DTA) was conducted using a thermoanalyzer type (GDTD16-Setaram) with a measuring temperature range of 20° – 200° C, a heating rate of 2° C min⁻¹, and a sensitivity of $2.5 \ \mu$ V. The direct current (dc) magnetic susceptibility was measured using Faraday pendulum balance, which provides an accuracy better than 3%, provided that diamagnetic corrections are performed.¹⁸

The dc electrical resistivity was obtained, using the normal technique,¹⁹ by measuring the current flowing through the sample using an electrometer of Keithley 175-type with an accuracy of 0.2%.

The ESR spectra were recorded on JEOL spectrophotometer (type JES-FE2XG) at frequency of 9.45 GHz, using 1,1-diphenyl-2-pierylhydrazyl as a calibrant.

The microwave response of the prepared films was detected using a standing wave experiment.⁹ The apparatus was of type KDR-10SA crystal mount (ANDO Electric Co., Japan). Experiments were done in 10 GHz band with the waveguides WRJ-10 and flanges BRJ both according to JIS standards. The sample was connected as a load at the receiving end of the microwave line.¹⁶

RESULTS AND DISCUSSION

IR Analysis

IR analysis (4000–350 cm⁻¹) was conducted for 5, 10, 15, 20, and 25% CuCl₂-filled PVDF films. Spectra are presented in Figure 1. It is noted that most of the obtained peaks are at frequencies characterizing the β -phase²⁰ (most notably at 445, 470, and 510 cm⁻¹) without any shift. The sample of 5% CuCl₂ FL revealed a strong absorption peak at 490 cm⁻¹, belonging to the α -phase.²¹ Hence, this sample contains β -phases and traces of α -phases. The peaks observed at 1,570, 1,638, and 1,735 cm⁻¹ (for 25% FL) may be assigned as: C==C stretching due to ethylene substituting with polar groups



C=C stretching in the monofluorinated alkenes



and C=C stretching in the difluorinated alkines





Figure 1 IR spectra of variously CuCl₂-filled PVDF films.

respectively.²² The peaks noted at 1,950 (1,960), 2,200, 2,290, and 2,470 cm⁻¹ (for 20 and 25% FL) and at 2,780 cm⁻¹ (for 25% FL) may be assigned to the role of dimethylformamide²⁰ with a PVDF chain. It is noteworthy that the frequencies of 700 and 770 cm⁻¹ characterize head-to-head or tail-to-tail linkage concentrations of 20 and 30%,²⁰ respectively.

Thus, the present IR analysis indicated that $CuCl_2$ filler results in a β -phase, with main deformation as 20% (for 25% FL) and 30% (for the other FLs) head-to-head and tail-to-tail units, which may be considered as polaron and bipolaron defects.

Optical Transmittance

Figure 2 shows the optical transmittance spectra of 5, 10, and 15% $CuCl_2$ -filled PVDF films. Sharp absorption bands are observed at 13,300, 13,200, and 13,100 cm⁻¹ for 5, 10, and 15% FLs, respectively. This is evidence of the presence of induced shallow energy bands at depths of 1.65, 1.64, and 1.62 eV for the corresponding FLs, respectively. Other absorption bands are noted at 29,000, 29,000, and 28,500 cm⁻¹ for the respective FL,

indicating deeper induced energy bands at 3.6, 3.6, and 3.5 eV below the conduction band. It is noteworthy that the main features of the present spectra are similar to those of Cu^{2+} doped glasses, where the observed absorption bands within the range of 12,500–14,500 cm⁻¹ were assigned to the d-d band of Cu^{2+} due to the transition between ${}^{2}E$ and ${}^{2}T_{2}$ levels, which originate from the splitting of the ${}^{2}D$ ground state of the Cu^{2+} free ion (d^{9}) in an octahedral field.²³ The absorption band at 28,500–29,000 cm⁻¹ can be attributed to the first allowed electron transfer band.²⁴

DTA

Figure 3 depicts the comparative DTA diagrams of 5, 15, and 40% CuCl_2 -filled PVDF films on an arbitrary scale. Broad endothermic peaks are noted at 333° and 339°K, for 15 and 40% FL, respectively. These peaks are assigned to dipole relaxation due to molecular motion of the filling halide.^{22,25} Endothermic peaks, due to the premelting temperatures,²⁶ are observed at 449°, 446°, and 446°K for 5, 15, and 40% FL, respectively.



Figure 2 Optical transmission of variously $CuCl_2$ -filled PVDF.

dc Electric Conduction

The dc electrical resistivity (ρ) was measured in the temperature (T) range of 299° to 433°K for PVDF films of various CuCl₂ FLs. Figure 4(a,b) displays ln ρ versus ln T plots for this system. A



Figure 3 Comparative DTA diagrams of variously filled PVDF films.

linear character can be noted, in a fair temperature range, for all of the studied films. Therefore, we can use eq. (1), suggested previously by Kuivalainen and coworkers,²⁷ to express the resistivity due to interpolaron hopping as:

$$\rho = [kT/Ae^2\gamma(T)(R_0^2\zeta)] \times [(Y_p + Y_{bp})^2/(Y_{bp})] \\ \times \exp(2BR_0/\zeta), \quad (1)$$

where A is 0.45; B is 1.39; Y_p , Y_{bp} are the concentrations of polarons and bipolarons, respec-



Figure 4 $\ln \rho vis \ln T$ for variously CuCl₂-filled PVDF films.

tively; and $R_0 = (\frac{3}{4}\pi C_{\rm imp})^{1/3}$ is the typical separation between impurities whose concentration is $C_{\rm imp} \cdot \xi = (\xi_{11}\xi_{\perp}^2)^{1/3}$ is the average decay length of a polaron and bipolaron wave function, and ξ_{11} and ξ_{\perp} are the decay lengths parallel and perpendicular to the polymer chain, respectively. According to the calculation of Bredas and colleagues,²⁸ the extension of the defect should be the same for polarons and bipolarons. The transition rate of an electron between polaron and bipolaron states can be expressed as:

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

where $n(\sim 10)$ and $\gamma_0(=1.2 \ 10^{-17} \ \mathrm{S}^{-1})$ was estimated by Kivelson.²⁹ Equation (1) was applied for the quasi-one-dimensional conduction processes between polaron and bipolaron states. Because the distribution of the site energies is narrow, the hopping processes in the model are isoenergetic.

In the present work, the order of magnitude of ρ was adjusted with the impurity concentration, $C_{\rm imp}$, which actually was the fitting parameter. The parameter $\xi_{11} = 1.06$ nm, whereas the value of ξ_{\perp} , which depends on the interchain resonance energy and the interchain distance $b \ (=0.452 \text{ nm})$,³⁰ is not known for PVDF. It was estimated from the relation³¹ $\xi_{\perp} = b/2$. Taking $Y_p = Y_{bp}$ for simplicity, as a reasonable approximation. Using equations (1) and (2), one can obtain the values of the separation between impurities R_0 .

The obtained values of R_0 , at temperature 299°K, are plotted *versus* FL in Figure 5. Up to 25% FL, the following linear formula was obeyed:

$$R_0 = -0.0092W + 0.3698. \tag{3}$$

Beyond 25%, FL R_0 was found to decay exponentially with an increase of W as:

$$R_0 = 13.53 \exp(-0.187W). \tag{4}$$

It is remarkable that $R_0 \leq 0.32$ nm, which is less than the separation between two successive headto-head sides (~ 0.75 nm of three monomer units, corresponding to 30% head-to-head content, implied from IR analysis). Moreover, for FL > 12.5%, the R_0 values are less than the monomer unit length (~ 0.25 nm³²). In such cases, the electrical conduction may proceed through interchain carrier hopping.



Figure 5 CuCl₂ FL dependence of R_0 .

Figure 6(a,b) depicts the temperature dependence of R_0 for various FLs. The solid curves can be fitted by equation:

$$R_{0w} = L \exp(-MT), \tag{5}$$

where the values of the fitting factors L (ligand) and M (metal) are listed in Table I. Figure 7 depicts the FL dependence of the upper temperature limit ($T_{\rm up}$) of eq. (5), which can be formulated as:

$$T_{un} = 453.595 \exp(-0.00792W),$$
 (6)

for $W \leq 35\%$.

dc Magnetic Susceptibility

The dc magnetic susceptibility χ was measured for all the prepared CuCl₂-filled PVDF films in the temperature range of 150°–300°K. The obtained results revealed a temperature-independent Pauli paramagnetic behavior for χ . The FL dependence of χ (measured at 300°K) is shown in Figure 8. It is noted that χ increases with W up to 25% FL, then χ saturates for W > 25%. This implies that: (1) the itinerant character, obtained for the unfilled PVDF, predominates for the CuCl₂-filled cases; (2) the CuCl₂ filler increases the induced density of magnetic states, up to 25%



Figure 6 Temperature dependence of R_0 .

FL; and (3) for further filling, the new induced states are nonmagnetic (i.e., paired electrons). This suggests a different $CuCl_2$ filling mode for W > 25%.

On the other hand, one may assume that the following dismutation reaction proceeds

$$3CuCl_2 + (C_2H_2F_2) = (C_2H_2F_2)_x^+CuCl_4 + 2CuCl.$$
(7)

Table IFitting Parameters of Eq. 5 for VariousCuCl2 FLs

W (wt %)	<i>L</i> (nm)	$M~(\mathrm{K}^{-1})$	
5	0.980	0.0039	
10	3.275	0.0084	
15	8.715	0.0122	
20	35.037	0.0177	
25	162.950	0.0238	
30	2.963	0.0142	
35	0.090	0.0052	
40	0.001	-0.0068	

L, ligand; M, metal.

The following equation can be used to calculate the magnetic susceptibility χ_{i1} for FL ≤ 0.30 :

$$\chi_{i1} = [1/M_p(1 + W)] \\ \times [\chi_p + 0.5WM_p(\chi_1/M_1 + \chi_2/M_2)].$$
(8)

In the present case, M_1 and (χ_1) and M_2 and (χ_2) are the molar mass and (magnetic susceptibility) of CuCl₂ and CuCl, respectively, and $\chi_1 = 1211.6712 \times 10^{-6}$ emu/mol and $\chi_2 = 0.^{33}$ Assume a maximum CuCl₂ insertion level (at $W_c = 0.30$) and a continuous chlorination that follows this limiting intercalation level. Hence, the



Figure 7 $CuCl_2$ FL dependence of the upper temperature.



Figure 8 CuCl_2 FL dependence of the measured $\chi_p(0)$ and calculated χ_{th} (*) susceptibilities.

observed decay of χ arose from the insertion of diamagnetic chlorine instead of paramagnetic CuCl₄, assuming that chlorine forms a covalent bond with the polymer chain and no more CuCl₄⁻ is inserted above W_c . Thus, the following formula can be used for the susceptibility in the high FL $(W > 0.30)^{34}$:

$$\chi_{ih} = \{\chi_p + M_p [0.15(\chi_1/M_1 + \chi_2/M_2) + (W - 0.3)\chi_3/M_3]\}/M_p (1 + W), \quad (9)$$

where χ_3 and M_3 are the susceptibility and molar mass of chlorine ($\chi_3 = -20.1 \times 10^{-6}$ emu/mol.³³ The calculated susceptibility values according to eqs. (8) and (9) are plotted in Figure 8. A clear discrepancy is noted between the experimental and theoretical susceptibility values. This implies that the CuCl₂ filling mode does not obey the dismutation reaction.⁷

ESR

Figure 9(a,b) displays the obtained ESR signals for variously $CuCl_2$ -filled PVDF films. The observed signals are characterized by the following features. Except for the cases of 15 and 20% filler levels, the signals are antisymmetric with superimposed repels due to the hyperfine interactions characterizing PVDF. For the 15% doping level, a sharp signal, with a clear doublet in its second half, is noticed. This signal indicates a predomi-



Figure 9 ESR spectra for PVDF films filled with: (a) 5, 10, 15, and 20% CuCl₂; and (b) 25, 30, 35, and 40% CuCl₂.

W (wt %)	g_{av}	ΔA `	Δg_{11}
5	1.9356	90	0.0681
10	1.9330	85	0.0707
15	1.9317	105	0.0720
20	1.9270	65	0.0767
25	1.9246	60	0.0791
30	1.9246	60	0.0791
35	1.9219	54	0.0818
40	1.9213	74	0.0824

Table II ESR Parameters of Variously $CuCl_2$ -filled PVDF Films

nant role of the filler Cu(II) ions, which are assumed to be located at the head-to-head defects, giving rise to a less folding (or bending) of PVDF chains and a more crystalline form. We think that the 20% head-to-head content, obtained from the IR analysis of the present PVDF films, allows the Cu(II) filler molecules (of 15% level) to occupy only the head-to-head sites. This reveals a more regular order of Cu(II) arrangement along the PVDF matrix. An interesting out-of-phase ESR emission signal is obtained for the 20% FL. This may be attributed to a reversed electronic population pattern (in the energy level diagram), compared with the cases of the other filler fractions.

The possible parameters, calculated by using the obtained ESR spectra, are listed in Table II. The average g-factor vis W is plotted in Figure 10. It is found that the g-factor dependence on W can be fitted with the numerical formula

$$g = g_0 \exp(-0.000214W), \tag{10}$$

where g_0 (=1.9371) is the *g*-factor at W = 0 (i.e., for the unfilled PVDF). The noted shift of g_0 from the electron *g*-factor (=2.0023) is attributed to the orbital contribution.

Figure 11 depicts CuCl_2 FL dependence of the relaxation time τ . It is clear that τ decreases as W increases up to $\sim 30\%$, then τ increases for further increase of W. This behavior is compatible with the assumption that the filler molecules prefer to occupy the head-to-head sites at first resulting in a more regular matrix (of Pauli paramagnetic type) and a smaller τ value. For filler levels beyond 30%, cross-linkage effects lead to an irregular matrix of an increasing τ value.

Symons³⁵ reported that a plot of $A^{(the isotropic hyperfine coupling constant)}$ for the metal ion *versus* g_{av} is nearly linear, moving toward g



Figure 10 $CuCl_2$ FL dependence of the average value of g.

= 2.0023 as A° falls. Symons attributed this behavior to two factors. One is delocalization onto the ligands. Provided spin on the ligands makes no contribution to the net *g*-shift, then the limit of



Figure 11 Dependence of the spin-relaxation time on the CuCl₂ FL.



Figure 12 Dependence of the average value of g on the isotropic hyperfine constant $(\Delta A^{`})$.

zero spin on the metal $g_{\rm av}$ should be \sim 2.0023. However, another important factor is the degree of covalency of the metal-to-ligand σ orbitals. As covalency increases, spin polarization of the σ bonding electrons adds a significant positive contribution of $A^{\,{}^{\,{}^{\,{}^{\,}}}}$. It also increases the d_{xy} – $d_{x^2\!-\!y^2}$ separation and hence reduces Δg_{av} . On the other hand, Cu(II) complexes differ from most others in that the normal trend in the A vis g_{av} plots is reversed. This agrees with the results of the present work. As shown in Figure 12, A` increases in magnitude as g_{av} moves towards freespin. This result already has an explanation in terms of the spin-polarization concept, including a contribution from the valence electrons of covalency-bonded ligands. This is because the unpaired electron is now σ rather than Π , and the sign of the effect is reversed. This result gives strong support to the theory that valence electron spin polarization is indeed a significant factor that changes in A provide a measure of changes in ligand covalency.

Moreover ESR has been quite helpful in the task of elucidating the local structure around the cations. This can be done by plotting ΔA° as a function of Δg_{11} , as shown in Figure 13. It is noted that most of the points fit well with the straight line:

$$\Delta A^{\sim} = 278.207 - 2755.75 \Delta g_{11},$$

of an initial value of $\Delta A^{\sim} = 27.8207$ mT. Another two experimental points lie on another parallel line of an initial value of $\Delta A^{\sim} = 30.0$ mT. These results are in good agreement with the literature³⁵ that favors a distorted octahedral or square-planar structure and rules out the tetrahedral species.

Although, in principle, there seems to be an equal probability of the unpaired electron being in $d_{x^2-y^2}$ or d_{z^2} for distorted octahedral complexes, in practice the built-in or Jan-Teller-induced distortion generally favors $d_{x^2-y^2}^1$, and $d_{z^2}^1$ configurations are rare. Accordingly the ESR (emission) signal, obtained for 20% CuCl₂ FL in the present work, may have arised from the $d_{z^2}^1$ configuration. In such case, the unpaired electrons occupy the $d_{z^2}^1$ state that is higher than the empty $d_{x^2-y^2}^1$ state. It is noteworthy that the observed absorption band $\sim 13,200 \text{ cm}^{-1}$ in the optical transmission spectra of the present system, which was assigned to be the d-d band of Cu^{2+} due to the transition between ${}^{2}E$ and ${}^{2}T_{2}$ levels originating from the splitting of the ${}^{2}D$ ground state of Cu²⁺free ion (d^9) in an octahedral field, supports the present ESR findings. Thus, it could be outlined that Cu(II) in the present CuCl₂-filled PVDF films exhibits an octahedral or distorted octahedral configuration, like the majority of six coordinated Cu(II) complexes.³⁶



Figure 13 Dependence of ΔA on the difference in the parallel *g*-factor.



Figure 14 $CuCl_2$ FL dependence of the phase of the reflected microwave.

Microwave Response

The FL dependence of the phase (Φ) of the reflected microwave is shown in Figure 14. It could be noted that: (1) the phase corresponding to 5% FL is higher than that for the unfilled PVDF, and (2) a broad minimum in the value of Φ exists ~ 25% FL.

On the other hand the FL dependence of the logarithm of the microwave power reflection factor is shown in Figure 15. The obtained behavior is, to some extent, similar to the magnetic susceptibility behavior. This is in good agreement with the results obtained for the previous case of FeCl₃ filling.⁹

Comparing Figure 14 with Figure 15, one may find two differently $CuCl_2$ -filled PVDF films having the same value of Φ but of different power reflection values. Pairs of the present films can be used as similar microwave modulators of different attenuation factors. This is an opposite situation to that found for FeCl₃ filler⁹ in which two different FeCl₃ FLs had led to two different values of Φ , but with the same power reflection value. Therefore, pairs of films of the FeCl₃ filler system were suggested as similar microwave attenuators having different modulator factors. Hence, for a certain desired purpose of application, one may select the suitable type (and mass fraction) of the transition metal halide filler. The suitable fields of application of the present system are microwave guides, modulators, attenuators, and cavity resonators that are essential elements in the magnetic spectroscopy apparatuses and microwave transducers.

CONCLUSIONS

It can be concluded that CuCl₂ filler resulted in a partially crystalline PVDF phase and head-tohead and tail-to-tail deformation content in the range of 20 to 30%. The optical transmittance spectra implied that the FL affects, significantly, the depths of the two induced energy bands. The DTA endothermic peak, due to dipole relaxation, shifts toward higher temperatures as the FL increases. On the other hand, the premelting endothermic peak shifts toward lower temperatures as the FL increases. The calculated hopping distance (R_0) , which is lower than the monomer unit length, suggested the presence of induced hopping sites (differing from the atomic sites) due to the effect of local fields inside the PVDF films. The obtained temperature independent Pauli paramagnetic susceptibility behavior may indicate that the induced deeper energy band is partially filled with spin electrons.



Figure 15 $CuCl_2$ FL dependence of the logarithm of the microwave reflection factor.

The characterizing features of the present CuCl_2 filler PVDF system were explored using ESR implications. The increase in magnitude of A as g_{av} moves toward free-spin was attributed to the electron delocalization onto the ligands and/or the positive contribution of the spin polarization of the σ bonding electrons as the degree of covalency of the metal-to-ligand σ orbitals increases. The present ESR and optical findings suggested that the Cu(II) local structure around the cations is of octahedral or distorted octahedral type.

The microwave results revealed that pairs of the present films can be used as similar microwave modulators of different attenuation factors.

REFERENCES

- Hattori, T.; Masashi, K.; Hiroji, O. J Appl Phys 1996, 79, 2016.
- Bernd, P.; Rudolf, E.; Siegfried, B. J Appl Phys 1992, 72, 5363.
- Johnson, G. E.; Blyler, L. L., Jr.; Crane, G. R.; Gieniewski, C. Ferroelectrics 1981, 32, 43.
- 4. Sessler, G. M. Elektronic 1981, 33, 115.
- Takse, Y.; Odajima, A. Jpn J Appl Phys, Part 2 1982, 21, L707.
- 6. Toda, M. Ferroelectrics 1981, 32, 127.
- Beaulieu, R.; Lessard, R. A.; Clim, S. L. J Appl Phys 1996, 79, 833.
- Naoto, T.; Yoshiaki, U.; Tsuyoshi, K. J Appl Phys 1993, 74, 3366.
- 9. Tawansi, A.; Abdelkader, H. I.; Balachandran, W.; Abdlrazek, E. M. J Mater Sci 1994, 29, 4001.
- 10. Hughes, S. T.; Piercy, A. R. J Phys E 1986, 19, 976.
- 11. Jacobs, J. E.; Remily, S. A. Infrared Phys 1979, 19, 1.
- Abdelkader, M. A. M.Sc. Thesis, Mansoura University, Mansoura, Egypt, 1993.
- 13. Elhefnawy, S. A. Ph.D. Thesis, Mansoura University, Mansoura, Egypt, 1995.
- Tawansi, A.; Oraby, A. H.; Abdelrazek, E. M.; Ayad, M. I.; Abdelaziz, M. J Appl Polym Sci, 70, 1437 (1998).

- Tawansi, A.; Ablelkader, H. I.; Elzalabany, M.; Abdelrazek, E. M. J Mater Sci 1994, 29, 3451.
- Tawansi, A.; Abdelkader, H. I.; Abdelrazek, E. M.; Ayad, M. I. J Mater Sci Technol 1997, 13, 194.
- Tawansi, A.; Abdelrazek, E. M.; Zidan, H. M. J Mater Sci 1997, 32, 6243.
- Mulay, L. N. Magnetic Susceptibility; Interscience Publishers: New York, 1963; pp. 1–1835.
- Tawansi, A.; Zidan, H. M.; Moustafa, Y. M.; Eldumiaty, A. H. Phys Scripta 1997, 55, 243.
- Kobayashi, M.; Tashiro, K.; Tadokoro, H. Macromolecules 1975, 8, 158.
- Williams, D. H. Spectroscopic Methods in Organic Chemistry; McGraw-Hill: New York, 1966; pp. 1–56.
- Mehendra, P. C.; Chand, S. J Phys D, Appl Phys 1983, 16 L, 185.
- Baiocchi, E.; Montenero, A.; Bettinelli, M.; Sotgiu, A. J Non-cryst Sol 1981, 46, 203.
- 24. Duffy, J. A. Phys Chem Glasses 1975, 16, 22.
- Latour, M.; Anis, K.; Faria, R. M. J Phys D, Appl Phys 1989, 22, 806.
- Newman, R. C. Infrared Studies of Crystal Defects; Taylor and Francis: London, 1973; pp. 1–89.
- Kuivalainen, P.; Stubb, H.; Isotlo, H.; Yli, P.; Holmstrom, C. Phys Rev 1985, B31, 7900.
- Bredas, J. L.; Chance, R. R.; Silbey, R. Phys Rev 1982, B26, 5843.
- 29. Kilvelson, S. Phys Rev 1982, B25, 3798.
- Zhang, R.; Taylor, P. L. J Chem Phys 1991, 94, 3207.
- 31. Kilvelson, S. Phys Rev Lett 1981, 46, 1344.
- Mott, N. F.; Gurney, R. W. Electronic Processes in Ionic Crystals; Oxford: London, 1940; pp. 1–34.
- Flandrois, S.; Boukhari, A.; Pron, A.; Zagorska, M. Solid State Commun 1988, 67, 471.
- 34. Hudak, O. Czech J Phys 1985, B35, 1303.
- Symons, M. Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy; Van Nostrand Reinold Company: New York, 1978; pp. 1–130.
- Algra, H. A.; Jornal, L. J.; Huiskamp, W. J.; Corlin, R. L. Physica 1977, 92B, 187.