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Discussions of the physical properties of MoO_3–V_2O_5–PbO films

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ABSTRACT

This study reports on the optical parameters of MoO_3–V_2O_5–PbO films. The measured transmittance spectra in the spectral range 300–2500 nm was used for precise calculations of the complex index of refraction (real (n) and imaginary (k) parts) as well as the film thicknesses. With the addition of MoO_3, a blue shift of the absorption edge was represented while the index of refraction (n) was decreased. The decrease of the index of refraction was discussed in terms of the dispersion model. A good correlation between the bulk modulus K_{op}, the optical band gap E_g and the index of refraction was observed. With the help of K_{op}, E_g and n values, the electronic polarizability has been calculated for the films under study. The results well discussed in terms of the density, electronegativity and polarizability changes due to the addition of MoO_3 content.

1. Introduction

The study of the optical, electrical and thermal characteristics of semiconductor materials, especially, that based on transition metal oxides (TMO) has great attention due to their uses in many technological applications such as memory switching and electrochemical batteries [1–3]. The transition metal ions are characterized by the different valence states of their cations and the wide radial distributions of the external d-orbital electron function [4,5]. Therefore, these ions have an interest to probe in different glassy networks. It was reported that V_2O_5 mostly is participating in the glassy network by VO_5 and VO_4 structural units and many of V_2O_5 based glasses behaves as semiconductors where the electrical conductance takes place through the hopping of electrons from V^{+4} to V^{+5} ions [6]. Furthermore, V_2O_5 in glass network can behave as an n-type with a low value of V^{+4}/V^{+5} ratio [6]. Molybdenum ions have highly selective and effectiveness in a chain of oxidation reactivity in many oxide glasses that are good candidates for catalytic studies [7]. MoO_3 has doubly valuable states in the formation of glassy networks; it acts as glass modifiers with MoO_6 and $Mo^{5+}O$ structural units [8]. Glass formation at high contents of MoO_3 is accessible in the present of modifiers as PbO with MoO structural groups [9–11]. Lead oxide, according to its content in the glass, serves as a glass modifier or as a network former [12]. Moreover, The effect of MoO_3 content (mol%) on the structure, thermal and ultrasonic properties of the $xMoO_3$–$50V_2O_5$–$(50 - x)$PbO glasses has been investigated by Saddeek [3].

The electronic polarizability of a material is one of the key parameters for device design in nearly all fields of modern electronics. Moreover, it is of interest and importance to know the behavior of charge carriers, dopants, impurities and defects in insulator and semiconductor. The electronic polarizability problem of individual ions has been the subject of many researchers. The total polarizability may include four contributions: the ionic contribution which is the displacement of charged ions relative to one another; an electronic contribution which is the movement of electrons in the electric field; the dipolar contribution which is due to the alignment of the permanent dipoles in the structure; and interfacial polarization which is the accumulation of charges on surfaces of heterogeneous insulators. The polarizabilities of gaseous ions have been achieved by Pauling [13] based on the theory of the quadratic Stark effect [14–16]. Presently, many attempts have been carried out to understand the electronic polarizability of solids [17–22].

To the author's knowledge, there is no much papers concern with the optical properties of $xMoO_3$–$50V_2O_5$–$(50 - x)$ PbO ($0 \le x \le 25$ mol%) glasses in the form of thin films. Therefore, the present study deals with a high accuracy determination of the complex index of refraction (real (n) and imaginary (k)) based on only their measured transmittance spectra in the spectral range 300–2500 nm. The results are well discussed in terms of the modern theories and that previously published.

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2. Experimental

Different compositions $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ with $(0 \le x \le 25$ mol%) glasses were prepared. The details of preparations of bulk glasses were mentioned in a previous work [3]. The thin films of these glasses were prepared onto cleaned quartz substrates by thermally evaporation technique under pressure $\sim 10^{-6}$ Torr using Denton Vacuum (502 A) system. Denton's model DTM-100 quartz crystal monitor was used to investigate both the film thickness (~600 nm) and deposition rate (10 nm/s). The chemical composition of the films was checked using X-ray fluorescence. Small deviations ($< 0.76\%$) were observed in the elemental compositions between evaporated thin films and initially bulk samples. The amorphous nature of films was confirmed using Philips type 1710 X-ray diffractometer. Jasco-V670 double beam spectrometer free from any glass substrates in reference beam has been used for measuring the transmittance of the film at the normally incidence within the spectrum range 300–2500 nm. To avoid slit-width correction the spectrophotometer was set to 1 nm slit width which is too small compared with the line widths which is simply taken to be the separation of two adjacent interference maxima and minima. Swanepoel's analysis [23,24] has been applied to the film transmittance spectra for precise investigations of the complex refractive index for $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ films.

3. Results and discussion

The amorphous state of the prepared films was confirmed by the absence of any sharp lines or peaks in the XRD patterns shown in Fig.1. Also, the film composition was obtained by energy dispersive analysis (EDX). Table 1 shows the elemental composition of each film. From Table 1 it can say that the EDX results are in agreement with the starting materials with difference doesn't exceed 0.5 mol%.

A clear blue shift of the absorption edge was observed with the replacement of PbO by MoO_3 as shown in Fig. 2. Fig. 3 represents the measured transmittance T(λ), the generated envelopes T_M, T_m and the geometrical mean $T_\varnothing = \sqrt{T_M T_m}$ within the range of the interference fringes [25] for $5MoO_3 - 50V_2O_5 - 45$ films. Based on the T_M, T_m values and following Swanepoel's analysis [24], one can enable to determine the final values of film thickness and the index of refraction in the interference fringes range. Furthermore, the film thickness was confirmed by using the graphical method [26]. According to this method, the main relationship of the interference fringes $(2.n.d = m.\lambda)$ for the consecutive maxima and minima beginning with the high wavelengths side take the form of [26]:

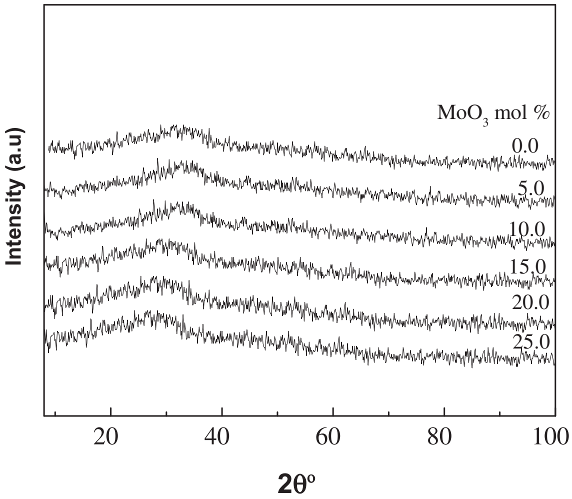

Fig.1. XRD patterns for $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ with $(0.0 \le x \le 25$ mol%) films.

Table 1
EDX Results mol%. $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ with $(0.0 \le x \le 25)$ films.

	Elementary weight (mol%)					
Element	0 MoO_3	5 MoO_3	10 MoO_3	15 MoO_3	20MoO_3	25MoO
Mo	0	3.322	6.765	9.96	13.25	16.812
V	28.01	28.05	27.95	28.03	27.84	27.92
Pb	46.515	41.835	37.12	32.49	27.809	23.12
O	25.475	26.793	28.165	29.52	31.101	32.148
Sum	100	100	100	100	100	100

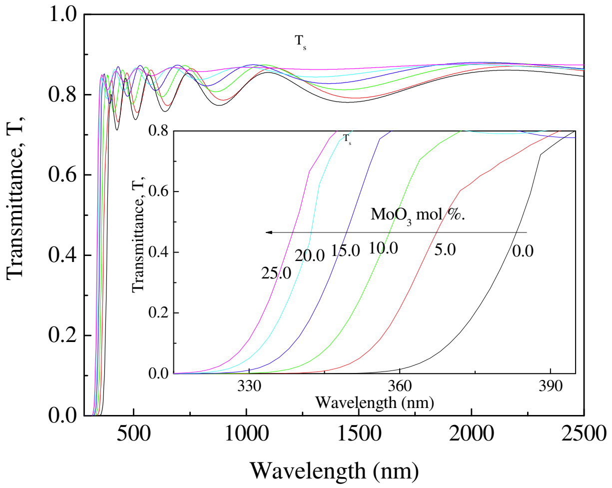

Fig. 2. The measured T(λ) for $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ with $(0.0 \le x \le 25$ mol%) films.

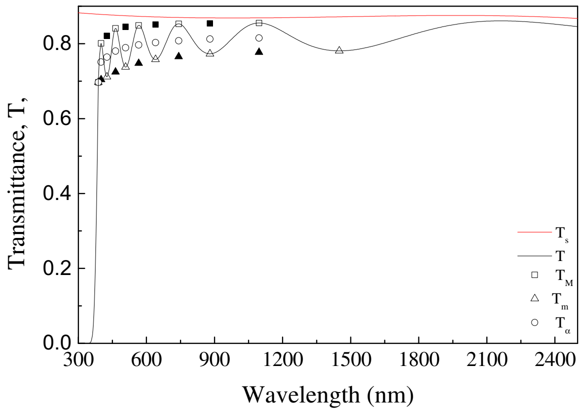

Fig. 3. The measured transmittance T(λ), the generated envelopes T_M and T_m and the geometrical mean $T_\varnothing = \sqrt{T_M T_m}$ in the spectral range with interference fringes for $5MoO_3 - 50V_2O_5 - 45PbO$ film.

$$O/2 = 2d(n.\lambda^{-1}) - O_1 \quad (1)$$

where, $O = 0, 1, 2, \ldots..$ and O_1 is the order number corresponding to $(O = 0.0)$ and it is an integer for maxima and half integer for minima, respectively. In accordance with the above equation, Fig. 4 represents the plots of $O/2$ against $(n.\lambda^{-1})$ for the $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ films. The best fit of each plot yields a straight line whose slope $2d$ and intercept with Y -axis at $-m_1$ value as mentioned in Fig 4. Fig. 5 investigates the final value of the refractive index (symbols) for $xMoO_3 - 50V_2O_5 - (50 - x)PbO$ films while the solid lines correspond to the best fit of the index of refraction according to Cauchy's formula $(n = A + B.\lambda^{-2}$, A and B are constants). The final film thickness, the constants (A, B) for the films under study are listed in Table 2). As one can see, with the addition of MoO_3 at the expense of PbO, the refractive index decreases, which is a result of decreasing the polarizability (P).