Structural and optical properties of high refractive indices lead vanadate thin films

CrossMark

Y.B. Saddeek [a], K.A. Aly [a,b,∗]

[a] Physics Department, Faculty of Science, Al-Azhar University, P.O. 71452, Assiut, Egypt
[b] Physics Department, Faculty of Science and Arts, P.O. Box 80200, 21589 Khulais, King Abdulaziz University (KAU), Saudi Arabia

HIGHLIGHTS

- New xWO$_3$–50PbO–(50 − x)V$_2$O$_5$ films were prepared by using thermal evaporation technique.
- Increasing WO$_3$ content leads to the increase of the average cross-link density.
- Film thickness and complex index of refraction were determined with high accuracy.
- The increase of WO$_3$ content shifts the absorption edge to the long wavelength side.
- xWO$_3$–50PbO–(50 − x)V$_2$O$_5$ films are interesting materials for non-linear optical devices.

ARTICLE INFO

ABSTRACT

Glasses with the chemical formula xWO$_3$–50PbO–(50 − x)V$_2$O$_5$, ($0 \leq x \leq 10$ mol%) were prepared by the usual melt quenching technique. FTIR analysis revealed that, the incorporation of WO$_3$ into the lead-vanadate network increases the number of bridging oxygens, and replaces low-coordinated structural units such as PbO$_4$, and VO$_4$ with higher coordinated structural units WO$_6$ and VO$_5$ which increases the number of bonds and the average cross-link density. Thin films of these glasses onto quartz substrates have been obtained by thermal evaporation technique. Based only on the measured transmittance spectra in the wavelength range 200–2500 nm, both the film thickness and the complex index of refraction have been calculated precisely. The absorption edge was shifted toward the long wavelength side (i.e. red shift of the optical band gap) as the WO$_3$ content increases. The dispersion of the refractive index was discussed in terms of the single oscillator model. The allowed non-direct transitions successfully describe the absorption mechanism in these films. Based on generalized Miller's rule, the third-order non-linear optical susceptibility $\chi^{(3)}$ has been investigated. The obtained values of $\chi^{(3)}$ values are rather large, indicating that the films under study are interesting materials for non-linear optical devices.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Semiconducting glasses can be fabricated from transition metal oxides (e.g. V$_2$O$_5$, PbO, MoO$_3$·Nb$_2$O$_5$...) which constitute a class of non-conventional glass formers [1,2]. The local structure of lead vanadate glasses has been studied by a variety of techniques which concluded that two different forms of metal ion distribution in the glasses in relation to vanadium–oxygen polyhedra, and Pb^{2+} ion occupies the interstitial position. The semiconducting properties of these glasses arises from the transfer of charge carriers (electronic or polaronic) from lower-valence states (V^{4+}) to higher-valence states (V^{5+}) of the vanadium ions. Such a mechanism arises from the redox property of V$_2$O$_5$. Accordingly, the basic structural units were identified as unaffected VO$_5$ trigonal bipyramids as in crystalline V$_2$O$_5$, affected VO$_5$ groups as in crystalline Pb(VO$_3$)$_2$, V$_2$O$_7$ pyro vanadate units and VO$_4$ tetrahedra which are composed of V$_2$O$_7^{4-}$, (VO$_3$)$_n$ single chains, branched VO$_4$, and (V$_2$O$_8$)$_n$ zigzag chains depending on the PbO content [3–18].

Certain studies [10–13] on tungsten oxides confirmed that, WO$_3$ is participated in the glass network with different structural units, such as WO$_4$ (T$_d$) and WO$_6$ (O$_h$) of W^{6+} ions and W^{5+}O$_3^-$ (O$_h$) of W^{5+} ions. Therefore, tungsten ions have an unusual influence on the optical and electrochemical properties of the glasses. However, the concentration of different groups of tungsten oxide present in the glass matrix at a given temperature depends on the quantitative properties of the modifiers, the glass formers, the size of ions in the

∗ Corresponding author. Current address: Physics Department, Faculty of Science and Arts, P.O. Box 80200, 21589 Khulais, King Abdulaziz University (KAU), Saudi Arabia. Tel.: +966 566253734; fax: +966 2135592.
E-mail addresses: kamalaly2001@gmail.com, Kaali5@kau.edu.sa, k_a_ashwal@yahoo.com (K.A. Aly).

glass structure, the mobility of the modifier cation, etc. [14–16]. V_2O_5 based glasses have been studied for possible supercapacitor applications due to their higher energy density [19,20]. Vanadium pentoxide is an important material due to its interesting properties and applications in various fields like batteries, super capacitors, electrochromic devices. V_2O_5 thin films are prepared by various techniques such sputtering [21], vacuum deposition [22], sol–gel process [23] and electrodeposition method [24].

V_2O_5 thin films can be utilized in the fabrication of thermochromic smart windows which are one kind of energy-saving windows. This process can be performed by adjusting the properties of VO_2 to meet the application requirement of smart windows. VO_2 undergoes a first-order semiconductor–metal transition (SMT) at a critical temperature, which is accompanied by a distortion in the crystal structure resulting in severe changes in the optical properties [25]. SMT temperature can be effectively lowered to the vicinity of room temperature for example, through tungsten doping [26].

The current investigation is intended to gain a comprehensive understanding of the influence of the tungsten ions on the structural and optical properties of xWO$_3$–50PbO–$(50 - x)$V$_2$O$_5$, $(0 \leq x \leq 10$ mol%) thin films.

2. Experimental technique

Within the glass forming region, the following particular composition: 50PbO–50V$_2$O$_5$ is chosen for WO$_3$ doping. The details of the compositions used in the present investigation are: xWO$_3$–50PbO–$(50 - x)$ V$_2$O$_5$, $(0 \leq x \leq 10$ mol %). These glasses were prepared by the melting and quenching techniques. The starting materials used for the preparation of the glasses were analytical grade reagents (99.9% pure) of PbO, V$_2$O$_3$ and WO$_3$ powders. The compounds of required compositions to produce 10 g of each glass were accurately weighed, thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible at a temperature 1273 K for about 1 h till a bubble free liquid was formed. The composition given in Table 1 refers to the nominal composition (the starting mixture), where the weight losses were found to be less than 0.5%.

Infrared (IR) spectra for the glass powder were obtained using an IR Fourier transformation spectrophotometer type JASCO, FT/IR-430 (Japan). For this purpose, each sample was mixed with KBr in the proportion of 1:100 (by weight) for 20 min and pressed into a pellet using a hand press. The spectra were recorded in the wave number range of 400–1200 cm^{-1} with a resolution of 4 cm^{-1}, corrected for dark current noise, and normalized. The obtained spectra were fitted [27] to get quantitative values for the band areas of heavily overlapped bands. The curve fitting procedure is based on a least squares minimization which in its turn involves entering the values of the wave numbers of the component bands

(determined by deconvolution) and then a program determines the best estimated parameters of the component curves. The program is Origin version 8. The deconvolution process involves several steps: computation of an interferogram of the sample by computing the inverse Fourier-transform of the spectrum, multiplication of the interferogram by a smoothing function and by a function consisting of a Gaussiane–Lorentzian band shape, and Fourier-transformation of the modified interferogram. The deconvolution procedure is typically repeated iteratively for best results. At iteration, the line shape is adjusted in an attempt to provide narrower bands without excessive distortion. Therefore, each IR spectra has its characteristic peak positions.

Thin films were prepared by thermal evaporation of small ingot pieces onto electronically cleaned quartz substrates. The thermal evaporation process was performed by using a coating (Denton Vacuum 502 A) system, at a pressure of approximately 1.33×10^{-3} Pa during the deposition process. The thickness of the film was determined using a quartz crystal monitor (Denton's model DTM-100). The rate of the film deposition was controlled using the same DTM-100 quartz crystal monitor and it was 10 nm s^{-1}. Chemical compositions of films were confirmed by X-ray florescence. The deviation in the elemental compositions of the evaporated thin films from the initial bulk specimens does not exceed ±0.8 at.%. The amorphous state of these materials was checked using X-ray (Philips type 1710 with Cu as a target and Ni as a filter, $k = 1.5418$ nm) diffractometer. The absence of crystalline peaks confirms the glassy state of the prepared films.

Optical transmittance spectra for xWO$_3$–50 PbO–$(50 - x)$V$_2$O$_5$, $(0 \leq x \leq 10$ mol%) thin films have been measured using a double beam (Jasco-V670) computer controlled spectrophotometer, at normal incidence of light and in the wavelength range 500–2500 nm. The spectrophotometer was set with a slit width of 1 nm and as this was much smaller than the line widths it was unnecessary to make slit-width corrections. The line width is simply taken to be the separation of two adjacent interference maxima and minima. Without a glass substrate in the reference beam, the measured transmittance spectra were used to calculate the optical constants by applying the envelope method suggested by Swanepoel [28].

3. Results and discussion

3.1. Infrared spectral studies

The room-temperature Fourier-transform infrared (FTIR) absorption spectra of all the studied glasses are shown in Fig. 1. All spectra exhibit broad absorption bands in the region of 400–1050 cm^{-1}. In general, the observed broadening of the bands in IR spectra is due to two reasons. The first reason is the distribution of bond-angles, lengths and the fluctuation of the local electronic and atomic environments in the amorphous state which results in spectra similar to the spectra of the crystalline phases. The second reason, according to the bases of the solid state physics is the breakdown of wave vector selection (k-selection) rules in amorphous as a consequence of disorder when compared to crystalline forms, which allows electromagnetic radiation to couple with vibrations other than $k = 0$. As a result, unlike the crystalline case in which narrow well defined lines are observed, broad and diffuse bands representing a continuum of IR absorption result. Even though bands due to individual, localized structural units are observable, the identification of IR spectra of glasses alone is rather difficult unless crystalline spectra are also present [4]. Accordingly, the broad band of amorphous state is the overlapping of some individual bands with each other. Each individual band has its characteristic parameters such as its center (C), which is related to some

Table 1
Deconvolution parameters of the infrared spectra of xWO$_3$–50PbO–$(50 - x)$V$_2$O$_5$, $(0 \leq x \leq 10$ mol%) glasses. C is the component band center (cm^{-1}) and A is the relative area (%) of the component band.

x (mol%)									
0	C	449	502		646	764	835	912	962
	A	2.1	16		40	5.9	25	8.6	1.9
2.5	C	452		564	679	763	846	914	967
	A	1.2		19	25	20	25	7.5	2.5
5	C	423		568	666	791	899	952	987
	A	0.4		6.7	29	40	14	7.7	1.7
7.5	C	439	542	583	659	759	870	960	988
	A	0.6	5.1	12	16	37	29	1	0.3
10	C	425	448	570	688	752	859	968	992
	A	0.8	0.7	5.3	37	19	35	1.4	0.4