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ScienceDirect

Journal of Taibah University for Science 10 (2016) 363–368

Journal of Taibah University for Science

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# Optical properties of amorphous $Li_2O$–$WO_3$–$B_2O_3$ thin films deposited by electron beam evaporation

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Available online 7 April 2015

**Abstract**

Thickness dependencies of the optical properties of as-deposited amorphous $30Li_2O$–$10WO_3$–$60B_2O_3$ thin films prepared by electron beam evaporation on glass substrates at a base pressure of $9 \times 10^{-7}$ Torr were studied. Glancing angle X-ray diffraction studies were performed to confirm the amorphous nature of the prepared films. The absorption coefficient $\alpha$ (and therefore the extinction coefficient $k$) was determined from the reflectance and transmission spectra in the strong absorption region. The dispersion of the refractive index is discussed in terms of the single-oscillator Wemple–DiDomenico model. The optical constants, such as optical band gap, Urbach energy, the average excitation energy $E_o$ and the dispersion energy $E_d$, of the thin films were determined. The optical data revealed the existence of allowed indirect transitions.


*Keywords:* Thin films; Amorphous; Optical band gap; Indirect transitions; Urbach energy; Refractive index

## 1. Introduction

Transition metal ions (such as tungsten) containing borate glasses are suitable for optoelectronic devices because they exhibit nonlinear optical absorption, photochromism, electrochromism and thermochromism properties that can be used for technological applications [1,2]. The $B_2O_3$ glasses are well-known due to their large photo-induced second-order non-linear optical effects, which have strong bearing on the luminescent efficiencies of these glasses [3]. Alkali borate glasses are well-known, due to their high transparency, low melting point, high thermal stability, and good rare earth ion solubility [4,5]. However, interest in these glasses as laser hosts is limited due to their high phonon energy. Nevertheless, the addition of certain transition metal oxides, such as $WO_3$, to $Li_2O$–$B_2O_3$ glass makes them more moisture-resistant; also, the phonon losses can also be minimised to a large extent. Tungsten-containing glasses have been studied due to the favourable properties of tungsten ions, such as high electro-negativity, polarisability, large ion radius, and changeable valence [6,7].

Glassy thin-film electrolytes are materials of considerable technological interest. Such thin films are used in the design of modern solid state batteries,

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Peer review under responsibility of Taibah University

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jtusci.2015.03.012

electrochemical sensors, super capacitors, and electrochromic devices. The optical characterisation of thin films often requires the use of highly refined computer numerical techniques applied to both optical and reflection spectra [8,9]. In contrast, a relatively simple and straightforward method for determining the optical constants using only their transmission spectra has been used for obtaining the optical constants [10].

The optical properties of oxide glasses, for example, excellent transmittance in the infra-red region, continuous shift of the optical absorption edge, and values of refractive index ranging between 2.0 and 3.5, as well as the strong correlation between the former properties and the chemical composition, explain the growing interest in these glassy materials for the manufacture of filters, anti-reflection coatings, and a wide range of optical devices [11–14]. This interest underlines the importance of the characterisation of these glassy materials through the determination of their optical constants, refractive index and extinction coefficient, as well as the corresponding optical band gaps.

The optical, microhardness and structural properties of thin films of borate based glasses were investigated by many authors [15–18]. Thin amorphous films of lithium borate [19] and sodium borate glass systems were prepared by RF magnetron sputtering [20]. Tungsten–tellurite [$(100\text{-}x)TeO_2$–$xWO_3$ ($5 \geq x \leq 30$ mol.%)] thin films doped with $Er^{3+}$ prepared by radio-frequency magnetron sputtering have been studied using Raman scattering and photoluminescence techniques [21,22]. Recently, Ismail et al. [23] reported the optical properties of tungsten-tellurite amorphous thin films prepared by electron-beam deposition. Thin films of binary and ternary tungstate glasses were prepared by electron beam evaporation [24,25]. The influences of the thickness and heat treatment on the photochromic effect of the doped and undoped $WO_3$ films were studied by Avellaneda and Bulhoes [26].

Recently, the authors reported the optical and structural properties of bulk $xLi_2O$–$(30\text{-}x)Na_2O$–$10WO_3$–$60B_2O_3$ glasses [27]. The optical energy band gaps for various indirect and direct (allowed and forbidden) transitions were determined. In the present work, we report the optical properties of lithium boro-tungstate amorphous thin films prepared by electron-beam deposition. The refractive index, absorption coefficient (therefore the extinction coefficient) and optical band gaps were determined from the reflectance and transmission spectra. To determine the refractive index, the film thickness of the samples must be sufficiently high.

## 2. Experimental

Bulk glass samples of composition $Li_2O$–$WO_3$–$B_2O_3$ were mixed at a molar ratio of $Li_2O$:$WO_3$:$B_2O_3$ of 30:10:60 using reagent-grade $Li_2CO_3$, $H_3BO_3$ and $WO_3$ powders as the starting materials. These materials were weighed according to the atomic weight percentages to obtain the intended composition. These materials were subsequently milled together in an agate mortar for approximately 30 min. The milled mixtures were later placed into a porcelain crucible and subsequently melted in air in a preheated furnace with the temperature maintained in the range of 1100–1150 °C for approximately 60 min. These conditions were found to produce good homogeneity of the glass. Once complete fusion was achieved, the melt was quenched between two stainless steel plates pre-heated to approximately 200 °C. Later, the samples were annealed below their respective glass transition temperatures for approximately 24 h followed by slowly cooling them to laboratory temperature. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction analysis.

Thin films of the bulk glass composition $30Li_2O$–$10WO_3$–$60B_2O_3$ of different thicknesses (500, 1000 and 1500 nm) were prepared using the electron-beam evaporation technique. A 3-kW electron gun (Telemark model 528) was used. To ensure good quality deposited films, Thermo Scientific glass microscope slides (19 mm × 25 mm × 1 mm) used as substrates were pre-cleaned using an ultrasonic hot bath, distilled water and pure acetone. Before depositing the films, the graphite boat containing the fragments of bulk glass was heated slowly at approximately 200 °C to release most of the moisture imbedded within the glass. After the oxygen release, the vacuum chamber was evacuated to a base pressure of approximately $1.2 \times 10^{-4}$ Pa. During the deposition process, the substrates were kept at room temperature (300 K). The deposition rate was adjusted to be 5 nm/s. To obtain homogeneous and smooth films, the substrates were rotated at a constant speed. The thickness of the produced films was monitored during the deposition process using a quartz crystal thickness monitor to an accuracy of 5 nm. A Hitachi S-900 high-resolution, field-emission scanning electron microscope was used to confirm the thickness of the films. A direct pull test was used to measure the adhesion between the thin film and the substrate. The film thicknesses were checked independently after removal from the chamber using a F20 profile meter.

The amorphous character of the deposited films was examined via X-ray diffraction studies using a Brucker