Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

The correlation between the structural, optical, and electrical properties in mixed alkali fluoroborate glasses containing vanadium ions

Samir Y. Marzouk[a], Ahmed H. Hammad[b,c,*], H.M. Elsaghier[d], W. Abbas[a], Nehad A. Zidan[d]

[a] Basic and Applied Science Department, College of Engineering and Technology, Arab Academy for Science, Technology, and Maritime Transport, Cairo, Egypt
[b] Center of Nanotechnology, King Abdulaziz University, Jeddah, Saudi Arabia
[c] Electron Microscope and Thin Films Department, Physics Division, National Research Centre, 33 ElBuhouth St., Dokki, Giza, Egypt
[d] Engineering Physics and Mathematics Department, Faculty of Engineering (Mataria), Helwan University, Cairo, Egypt

ARTICLE INFO

Keywords:
Borate glass
V_2O_5
Optical band gap
Infrared properties
Electrical properties

ABSTRACT

Lithium sodium fluoroborate glasses doped with vanadium ions were prepared by melt annealing technique. The structural investigation shows the formation of probable BO_3, BO_4, BO_2F, and BO_3F structural units. Moreover, vanadium ions are mostly presented in such glasses as V^{4+} state and it may form non-bridging oxygens (NBOs). The decreasing in the optical band gap values as a function in the glass composition or vanadium content approves the formation of NBOs. The refractive index is estimated directly from the optical band gap values by using the Dimitrov-Sakka relation. Density, molar volume, molar refraction, and metallization criterion were studied and explained in terms of the structural changes obtained by the impact of the vanadium ions. Thermal activation energy is explained by the formation of Non-bridging oxygens and the effect of V_2O_5 dopant.

1. Introduction

Borate glass (B_2O_3) is another famous glass network former after silicate glass. Hence silicate glass (SiO_2) has only the building units of SiO_4 tetrahedrons linked by their corners to make 3D network as described by Zachariasen [1]. On the other hand, the structural units of B_2O_3 network are quite different than silicate glass. It can be triangular BO_3 units, tetrahedral BO_4 units or both depending on the main composition of the borate glass [2–5].

The conversion process between BO_3 and BO_4 units is strongly dependent on the ratio of the glass modifier such as alkali/alkaline oxides [6–8]. Hence, lithium borate glass can be used in electrochemical application, solar energy converter and high density energy batteries [9–11]. Moreover, borate glasses containing rare earth ions are promising materials for solid state lighting application [12]. When the fluorine ions embedded to the borate network, some structural change or modification should cause in which some BO_3 and BO_4 units tend to modify to be BO_2F and BO_3F structural units, respectively [13,14]. So, consequently this enforces the physical and the structural properties of borate glass.

The incorporation of vanadium pentoxide in borate glasses promotes these glasses as coloring semiconducting glass used in memory/switching application [4] and for radiation shielding effect [15,16]. Vanadium ions can present in different states such as V^{3+}, V^{4+}, and V^{5+} states [4,15,17]. However V^{5+} state has d^0 configuration and not given any visible bands in the UV–visible spectrum [15,18]. V^{3+} and V^{4+} states give greenish and bluish color due to the vanadium exists in distorted octahedral coordination with oxygen's and vanadyl (VO^{2+}) ions, respectively [18]. The conduction mechanism in such glasses is attributed to the electron hopping between V^{4+}, and V^{5+} states [4].

The present work is focused on the structural studies of mixed alkali (Li and Na) fluoroborate glass containing different ratios of vanadium pentoxide as dopant. How the presence of vanadium ions as well as the fluorine ions can modify the borate glass network. How the concept of non-bridging oxygens can be formed and explained in terms of infrared, optical, density, and electrical properties.

2. Experimental details

2.1. Preparation

The mixed alkali fluoroborate glass samples of composition 0.05 NaF – 0.2 Li_2O – (0.75-x) B_2O_3 – x V_2O_5 in mole fraction which x varied in the range from 0 to 0.02 in mole fraction were prepared. The chemicals used to synthesis the glass are high purity orthoboic acid (H_3BO_3), lithium carbonate (Li_2CO_3), Sodium Fluoride (NaF), and vanadium oxide (V_2O_5). Table 1 describes the chemical composition of the prepared glasses. The composition batch of the raw materials was 30 g

* Corresponding author permanent address: Electron Microscope and Thin Films Department, Physics Division, National Research Centre, Dokki, Giza, Egypt.
E-mail addresses: ah.hammad@nrc.sci.eg, ahhhassan@kau.edu.sa (A.H. Hammad).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.08.031
Received 7 August 2017; Received in revised form 25 August 2017; Accepted 27 August 2017

Table 1
Alkali fluoroborate glasses compositions in mol% doped with V_2O_5.

Sample Symbol	Li_2O	NaF	B_2O_3	V_2O_5
Base	20	5	75	0
0.5 V	20	5	74.5	0.5
1 V	20	5	74	1
2 V	20	5	73	2

melted in crucible porcelain at 1200 ± 10 °C for 2 h. The melts were shacked and rotated every 20 min to obtain the homogeneity and to be free bubbles from the melts. Then, the melts poured into preheated stainless steel molds of dimension 3 cm × 2 cm × 2 mm transferred into another furnace post heated at 400 ± 5 °C. The furnace was switched off to cool from 400 °C to the normal room temperature with rate 30 °C/h after 1 h.

2.2. Infrared absorption measurements

The computerized Fourier transform infrared absorption type Bruker's Vertex 70v FTIR with a resolution of 0.4 cm^{-1} in the wavenumber range of 400–4000 cm^{-1} was used to detect the structural change through the borate glass. The pulverized powder samples were mixed with potassium bromide (KBr) in the ratio 1 mg powder: 100 mg KBr subjected to a pressure of 5 tons/cm^{-1} to obtain clear homogeneous discs.

2.3. Density and molar volume measurements

Archimedes method was used at room temperature (25 °C) to calculate the glass density. Glass samples were weighed in both of air (Wt_{air}) and stable liquid of known density xylene (Wt_{xylene}) (ρ = 0.86 g/cm^3). The density is estimated by the following formula:

$$\rho = \frac{Wt_{air}}{Wt_{air} - Wt_{xylene}} \times 0.86 \ \text{g/cm}^3 \quad (1)$$

Moreover, the glass molar volume (V_m) is expressed by $V_m = MWt/\rho$ which MWt is the molecular weight of the glass sample. Each sample was repeated 3 times for deducing the uncertainty of the measurements. The deducing errors in the density values come from the measured value containing both the average value and the uncertainty in the mean ($\rho_m = \rho_{avg} \pm \Delta\rho_{avg}$) where $\rho_{avg} = \Sigma\rho/N$ (number of trials), and $\Delta\rho_{avg} = (\rho_{max} - \rho_{min})/(2\sqrt{N})$. The uncertainty of the molar volume $\Delta V_{m\text{-}avg.}$ measurements was obtained by $MWt \times \Delta\rho_{avg}/\rho^2$.

2.4. Optical absorption measurements

Single monochromator UV–Visible-Near Infrared (NIR) spectrophotometer (type JASCO, V-770, JAPAN) with a resolution of 2 nm in the wavelength range of 190–2500 nm was used to measure the optical absorption spectra of the samples.

2.5. Electrical measurements

For determining the electrical conductivity σ of glass samples, a two point probe method was used for measuring the resistance R where $\sigma = \frac{d}{R \times A_r}$, in which A_r and d represent the glass surface area and the glass thickness, respectively.

Electrical conductivity measurements have been performed inside a pyrex sealed chamber and under vacuum. The measurements were carried out in the temperature range 333–483 K. The electrical resistance R was measured by means of a high impedance electrometer (10^{19} Ω) type, Keithely 6517 B.

Disc shaped sample forms were measured with approximately diameter of 9 mm and thickness of 3 mm. An electrical contact on the glass surface was obtained by conductive silver paste. The specimens were fixed on a sample holder inside a sealed Pyrex glass cell evacuated to 10^{-3} mbar.

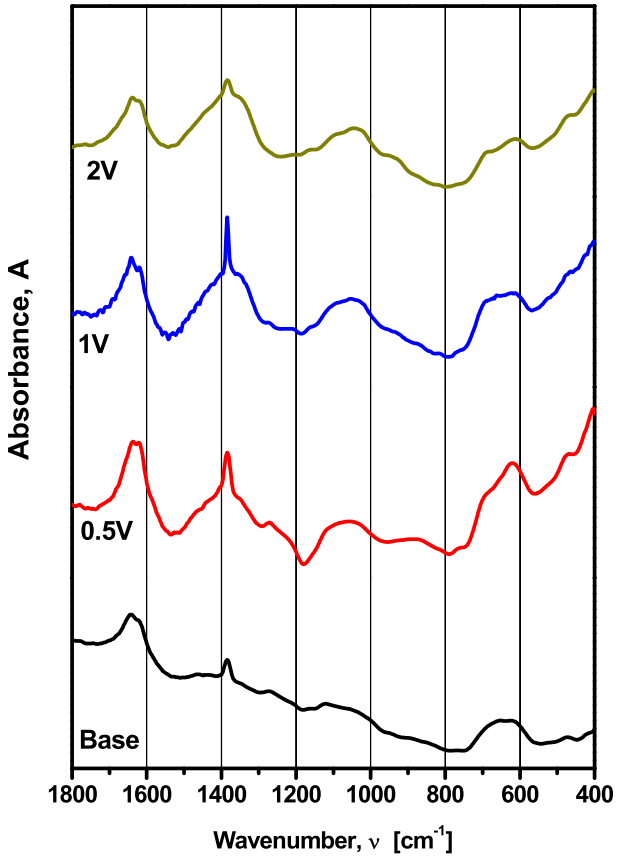

Fig. 1. Infrared absorption spectra of Li_2O-NaF-B_2O_3:xV_2O_5 glasses.

3. Results and discussion

3.1. Structural investigation

Fig. 1 shows the structural changes in lithium sodium borate glasses when doped with V_2O_5 up to 2%. Several bands and peaks are noticed and observed through the spectrum of the base glass (without vanadium content) as follows:

The observed peak at 472 cm^{-1} is attributed to the vibration of the alkali cations like lithium and sodium ions [19,20].

A medium broad band from 550 to 770 cm^{-1} is ascribed to the B—O—B bending vibration or deformation modes of various borate units [3,4,21].

A widely broad unsymmetrical band from 800 to 1200 cm^{-1} having wide shoulder from 800 to 960 cm^{-1} can be explained in terms of the vibrations of BO_4 units [22,23].

The stretching modes of BO_3 units is also observed from the medium broad band located from 1200 to 1600 cm^{-1} containing two peaks at 1270 cm^{-1} and a strong intense narrow one at 1384 cm^{-1} [21,24].

The prominent band in the range of 1500–1750 cm^{-1} with intense peak at 1640 cm^{-1} is also related to the boron-oxygen bond in BO_3 units [20,24].

The present glass contains fluorine content in the form of NaF (5%). Therefore, it is believed that fluorine content can participate in the boron- oxygen network [25] and strongly affect the formation of BO_3F units which equivalent to BO_4 units by replacement of BO_4 tetrahedra units with BO_3F tetrahedral units [26–29]. On the other hand, the formation of BO_2F linkage is also assumed rather than BO_3 units