Study the effect of alkali/alkaline earth addition on the environment of borochromate glasses by means of spectroscopic analysis

CrossMark

F. Ahmad *

Physics Department, Faculty of Science, Alazhar University (Girls Branch), Nasr City, Cairo, Egypt

ABSTRACT

Glassy samples of composition xSrO–$(30 − x)$Li$_2$O–65.5B$_2$O$_3$–0.5Cr$_2$O$_3$ (x = 0, 5, 10, 15 and 20 mol%) were fabricated by using the melt quenching technique method. The investigated glass samples have been examined using powder X-ray diffraction (XRD) technique. FT-IR spectroscopy, density, optical absorption in UV–VIS range and the calculated optical basicity and EPR spectra were recorded. The obtained results of the XRD spectra of all the samples confirmed the amorphous nature of the prepared glasses. The spectrum of FT-IR reveals that, the BO$_4$ units decrease with increasing SrO content and the non bridging oxygen's increase. The obtained density and the molar volume exhibit linear increase with increasing SrO content. Optical measurements show a decrement of optical band gap energy and steepness parameter as well as an increment of the Urbach energy and refractive index. The ligand field parameters calculation shows that, the values of the crystal field strength and the degree of covalency between ions increase as well as the interelectronic d–d repulsion Racah parameters decrease. The increase of the (Dq/B) ratio with increasing SrO content which reaches to 2.58 for x = 20 mol%, suggesting that strong crystal field strength. An increase of the electronegativity by replacing Li$_2$O by SrO, causes a decrease of the glass matrix basicity. The obtained EPR parameters indicate that the increasing of Cr^{3+} signal intensity and spin density. The analysis of the results indicated that, the chromium ions are present in trivalent covalent in the octahedral coordination are more predominate.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In recent years alkali/alkaline earth borate glasses containing various transition metal ions have been under extensive investigation due to their potential application. The study of the optical properties of these materials shows an obvious feature about their application in electronic devices [1–7]. Furthermore, it was found that glasses doped with transition metals have potential applications in solid state lasers, luminescent solar energy concentrator, optical fibers for communication devices and various scientific applications [8–11]. Borate glasses are the main glass-formers which are suitable optical materials with high transparency, low melting point, high thermal stability, good rare-earth ions solubility [12–16]. The effect of addition alkali and alkaline earth oxides on borate glasses has been studied in order to improve optical and physical properties as well as the thermo-mechanical properties of these glasses [17]. The strontium oxide has been extensively used as a component ensuring an improvement of a number of physiochemical properties of glasses [18].

The transition metal ions are being greatly used to know the information about amorphous local environment in the glasses

since their outer d-electron orbital function have a broad radial distribution due to their high sensitive response to the changes in the surrounding actions [1,7]. Chromium ion exists in different oxidation states: Cr^{+3} acts as modifier with CrO$_6$ structural units, Cr^{+5} and Cr^{+6} acting as network former with CrO$_4^{3−}$ and CrO$_4^{2−}$ structural units, respectively. It is well known that the Cr^{3+} ions preferentially occupy octahedral sites in glasses as indicated by their large site stabilizing energy [1,5,19]. The different states of chromium in glass matrices depend on the surrounding environment as the glass formers and the properties of modifiers (the size of the ions in the glass matrix, the electrostatic charge and the mobility of the modifier cation) [20]. Chromium ion is a paramagnetic transition metal ion, when dissolves in glass matrix even in very small quantities makes the glasses colored depends on electron structure and the chemical composition and it has a strong influence over the physical properties of the glasses [21,22]. These results have been interpreted based on ligand field theory [19,21,23]. The transition metal ions of various ionic radii can easily be incorporated in the glass host owing to a much looser and relaxed glass structure than that of crystalline media [21]. The objective of the present work to understand of valence states and the local environment of chromium ions in alkali/alkaline earth borate glass network, by means of spectroscopic studies.

* Tel.: +2001113022588.
E-mail address: F.Ahmad378@yahoo.com

2. Experimental technique

Alkali/alkaline earth borate glass of composition xSrO–(30 − x)Li$_2$O–65.5B$_2$O$_3$–0.5Cr$_2$O$_3$ (x = 0, 5, 10, 15 and 20 mol%) were prepared by melt quenching technique. The batches were placed in porcelain crucibles and then melted in an electrical furnace at 970 °C for ∼2 h. The melts were stirred to ensure homogeneity and then quenched at room temperature in air between two well polished copper plates in order to obtain bubble free glasses and smooth surface. X-ray diffraction was used to investigate the amorphous state of the materials. The measurements of XRD are performed on Philips X'Pert X-ray diffractometer with a Cu Kα radiation of wavelength λ = 1.54056 A° for 2θ angles between 4° and 70°. Infrared absorption spectra were obtained using FTIR (Perkin Elmer) in the range 2200–400 cm^{-1}, the sample powder were mixed with KBr of high purity. The densities of the prepared samples were measured by applying Archimedes principle using carbon tetrachloride as the immersion liquid. Optical absorption spectra of glasses were recorded in the wave length range 190–1100 nm by using UV–VIS spectrophotometer (JenWay-6405). All measurements were recorded at room temperature. The EPR spectra were obtained by EPR spectrometer (EMXBruker) operating in X-band frequency.

3. Results and discussion

3.1. X ray diffraction

Fig. 1 shows the obtained XRD patterns of the glassy system, which clearly illustrates the absence of sharp peaks of the investigated samples. Moreover, the patterns exhibit abroad diffuse scattering hump at low angles (2θ ≈ 23–26), which is a typical feature of borate glass, instead of crystalline peaks confirming along range structural disorder characteristic of amorphous network. The degree of amorphousity of the prepared samples is approximately unchanged due to the X-ray counts of the same order [24].

3.2. FT-IR spectroscopy

Borate glasses are very interesting materials according to their specific properties; these glasses are particularly interesting model systems as they exhibit a variety of structural and physical properties with change of the environments [2,14,21,24]. The alkali borate glasses have two main groups of bands; one is due to trigonal BO$_3$ units and the other is due to the tetrahedral BO$_4$ units [2,24,25]. The obtained IR spectrum of all glassy samples under investigation is shown in Fig. 2, which presents quite similar band shapes. Generally, spectrum shows three main bands assignment to boron formation, the first band located in the range 750–580 cm^{-1} attributed to the B–O is due to bending vibration of boron atoms perpendicular to O$_3$ plane. The second band located in the range 1200–750 cm^{-1} is probably due to the B–O stretching and rocking motion vibration of the BO$_4$ units. The third band located in the range 1600–1200 cm^{-1} is usually assigned as the B–O stretching vibration of the BO$_3$ units. However the spectrum

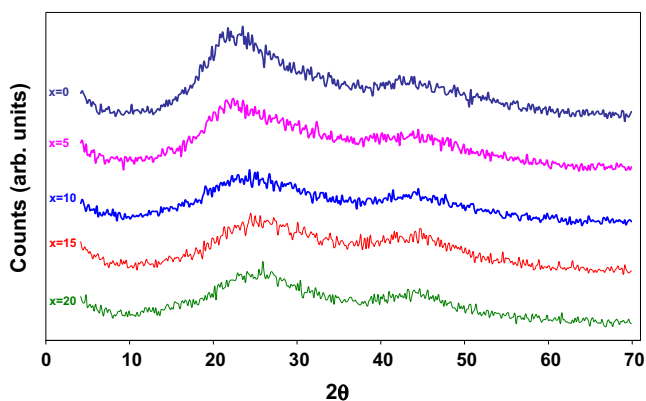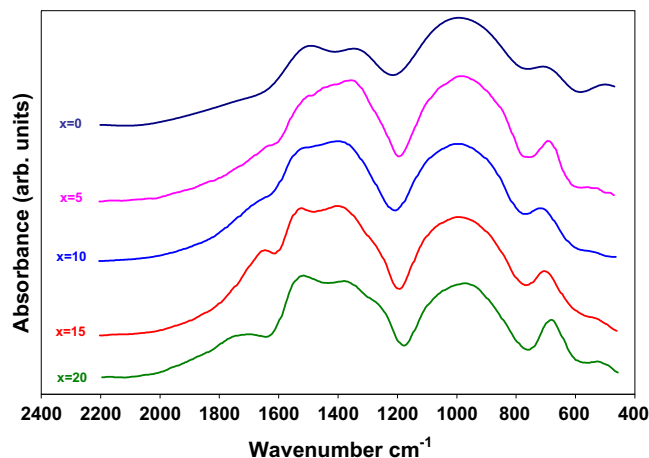**Fig. 2.** FT-IR absorption spectra for all investigated samples.

shows overlap shoulder around ∼1650 cm^{-1} with the triangles BO$_3$ band is due to the −OH bending vibration. Moreover there is weak band around 470 cm^{-1} which is most likely attributed to the vibration of lithium ions [7,24–28]. As modifiers, alkali and/or transition metal, enter the borate network breaking up local symmetry and introduce coordinated defects. When the modifier ions are present in a small amount, the number of the BO$_4$ units increases over the number of BO$_3$ units. With further addition of modifiers, four-coordination of boron reaches a saturation point and the cations are breaking bridging oxygen bonds of the glass backbone to form non-bridging oxygen's (NBO's) by known as dangling bonds in these glasses and residing in sites interstitial to the tetrahedral network in the vicinity of the negatively charged NBO's [21,24,25,28,29].

To get the quantitative information about the structural groups in the investigated samples, the spectra are deconvoluted into the minimum number of bands using Gaussian line shapes. The integrated absorption of the characteristic band envelopes between tetrahedral BO$_4$ and triangular BO$_3$ borate species, were calculated. The quantities N$_4$ reflect the relative population of borate species where N$_4$ can be estimated by the equation [16,24]:

$$N_4 = \frac{\text{concenteration of } BO_4}{\text{concenteration of } (BO_3 + BO_4)} \tag{1}$$

Fig. 3 represents the N$_4$ ratio composition dependence, it is clear that the addition of SrO instead of Li$_2$O causes the fraction of
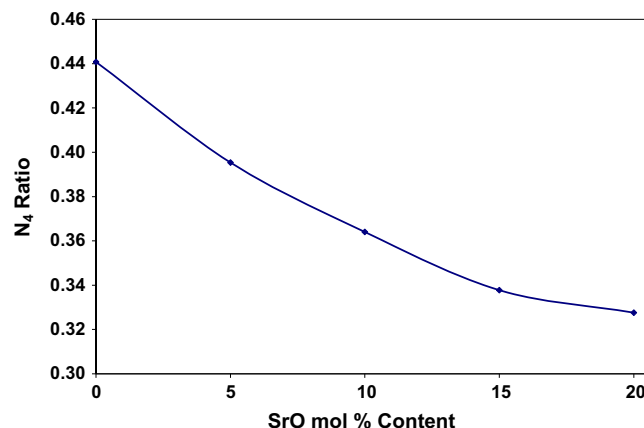
Fig. 1. XRD patterns of the xSrO–(30 − x) Li$_2$O–65.5B$_2$O$_3$–0.5Cr$_2$O$_3$ (x = 0, 5, 10, 15 and 20 mol%) glassy samples.

Fig. 3. N$_4$ ratio as a function of SrO content.