Vibrational Spectroscopy 73 (2014) 90–96

Contents lists available at ScienceDirect

Vibrational Spectroscopy

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

Structural correlations in BaO–PbO–B_2O_3 glasses as inferred from FTIR spectra

H. Doweidar[a,*], G. El-Damrawi[a], E.F. El Agammy[a,b]

[a] Glass Research Group, Physics Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt
[b] Department of Basic Sciences, Faculty of Engineering, Delta University for Science and Technology, Gamasa, Egypt

ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 10 May 2014
Accepted 14 May 2014
Available online 27 May 2014

Keywords:
BaO–PbO–B_2O_3 glasses
Quantitative FTIR analysis
N_4 of borate glasses
Density
Molar volume

ABSTRACT

Infrared spectra of xBaO·(30-x)PbO·70B_2O_3, xBaO·(40-x)PbO·60B_2O_3 and xBaO·(50-x)PbO·50B_2O_3 glasses have been quantitatively analyzed. The fraction of four coordinated boron atoms varies linearly, for each group, between the values of the corresponding binary borate glasses. The data could be used to calculate and follow the composition dependence of the concentration of structural units in all glasses. The results show a linear increase in the ratio of PbO forming BO_4 units to the total content of PbO, with increasing B_2O_3 in binary PbO–B_2O_3 glasses. Similar behavior has been observed for the ratio of BaO forming BO_4 units to the total content of BaO in binary BaO–B_2O_3 glasses. The ratio of PbO forming PbO_4 units to the total PbO content, and that of BaO forming asymmetric BO_3 units to the total BaO content, shows a reversed dependence. The linear change in fraction of four coordinated boron atoms and in density and molar volume suggests that the studied glasses can be treated as mixtures of binary PbO–B_2O_3 and BaO–B_2O_3 matrices.

1. Introduction

The structure of glasses modified by mixed modifier oxides has attracted grown attention over long decades. Various structural studies have been devoted as attempts to explore the mixed-modifier effect in borate glasses. These include spectroscopic investigations, such as infrared [1–4], Raman [5] and NMR [5–11], in addition to neutron diffraction [12] and molecular dynamics simulation [13]. These studies are generally concerned with changes in the spatial distributions of the alkali ions and their environments in mixed-alkali borate glasses, compared to the corresponding single-alkali borate glasses.

NMR investigation on 30($Li_2O + Na_2O$)·70B_2O_3 and 30($Na_2O + K_2O$)·70B_2O_3 glasses (mol%) [7] showed that, with increasing Na_2O content, there is a linear increase of the ^{23}Na isotropic chemical shift in the first series and a linear decrease in the second one. These trends suggest preferential occupation of sites by cations. This means that, regardless the relative proportions of alkali oxides, each type of cations occupies a uniquely selected site. Likewise, no detectable change in the fraction of four coordinated boron atoms (N_4) upon replacing Na_2O for Rb_2O in 20($Na_2O + Rb_2O$)·80B_2O_3 and 30($Na_2O + Rb_2O$)·70B_2O_3 glasses (mol%) [8]. It is concluded that, in those glasses, there is a preference of like-cation interaction. Furthermore, there is no statistical mixing of Na^+ and Rb^+ ions with respect to each other. As a result there would be two domains, each of which has the same ratio of alkali/boron. These conclusions are consistent with a newly presented view of mixed modifier glasses that can be looked as being mixtures of the corresponding single modifier matrices [14]. No change in N_4 has been observed in 33.34($Li_2O + Rb_2O$)·66.66B_2O_3 glasses [12] and 0.4($Li_2O + Cs_2O$)·B_2O_3 glasses [8] when changing the concentration of Li_2O at the expense of the second alkali oxide.

In all the above investigations, it is noted that no attention has been given to the change in distribution of structural units in mixed modifier borate glasses, due to changing the relative concentration of the modifiers. In the present work, a simple technique [15,16] would be applied to fellow the variation in the concentration of structural units in BaO–PbO–B_2O_3 glasses. The applied technique is used to analyze the N_4 data obtained from infrared spectra of the studied glasses. However, it can also be used to treat N_4 data obtained from NMR or neutron diffraction investigations.

2. Experimental

Glasses of the formula xBaO·(30-x)PbO·70B_2O_3 ($0 \le x \le 30$ mol%), xBaO·(40-x)PbO·60B_2O_3 ($0 \le x \le 40$ mol%) and

---

* Corresponding author. Fax: +20 50 2246781.
E-mail addresses: hdoweidar@mans.edu.eg, hdoweidar@gmail.com (H. Doweidar).

http://dx.doi.org/10.1016/j.vibspec.2014.05.003

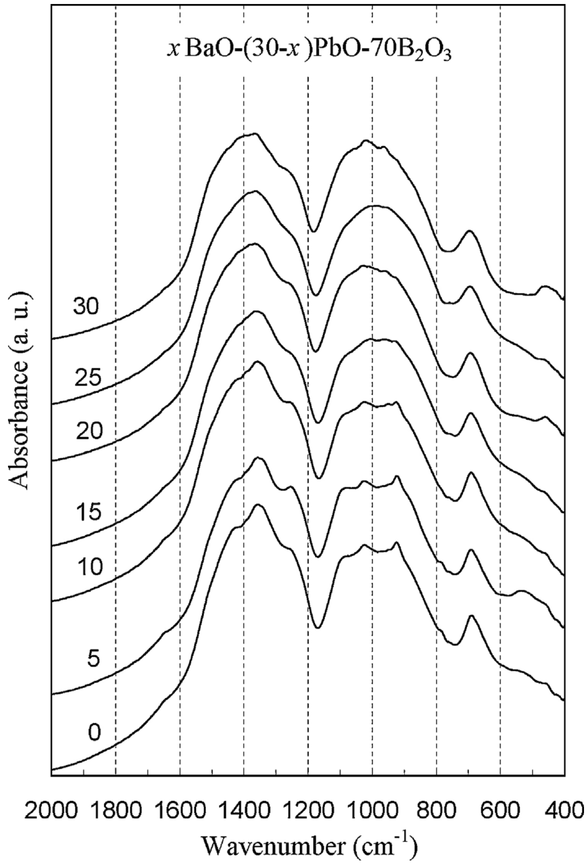

Fig. 1. Infrared spectra of xBaO·(30-x)PbO·70B_2O_3 glasses. Numbers at the plots refer to BaO content (mol%).

xBaO·(50-x)PbO·50B_2O_3 ($0 \leq x \leq 50$ mol%) were prepared by mixing reagent grade $BaCO_3$, PbO and H_3BO_3. The well-mixed mixtures were added in small portions and melted using porcelain crucibles in an electric furnace at a temperature ranging between 900 and 1200 °C, depending on the glass composition. The crucible and its content were kept in the furnace about 20–30 min, during which the melt was swirled frequently. The melt was quenched to room temperature by pressing it between two steel plates. The obtained samples were visually homogeneous and transparent.

The FTIR absorption spectra were obtained, by KBr pellets technique, at room temperature in the range 400–2000 cm^{-1} using Mattson 5000 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. The spectrum of each sample represents an average of 20 scans, which was normalized to the spectrum of blank KBr pellet; i.e. the spectrum of pure KBr was subtracted from each glass spectrum. Also, the spectra were corrected to the background and dark currents using two-point baseline correction. The density (D) of the glasses was determined at room temperature using Archimedes method with xylene as an immersion liquid. Five samples of each glass were used to determine the density. A relative error in these measurements was found as ±1%.

3. Results

The infrared spectra of xBaO·(30-x)PbO·70B_2O_3, xBaO·(40-x)PbO·60B_2O_3 and xBaO·(50-x)PbO·50B_2O_3 glasses are presented in Figs. 1–3, respectively. In all these spectra there is a peak of lower intensity centered at 700 cm^{-1}. In addition, there are two intense absorption envelopes in the regions ~770–1170 cm^{-1} and ~1170–1800 cm^{-1}. Absorption in these regions is related to vibrations of certain structural groups in the borate matrix. Bands in the

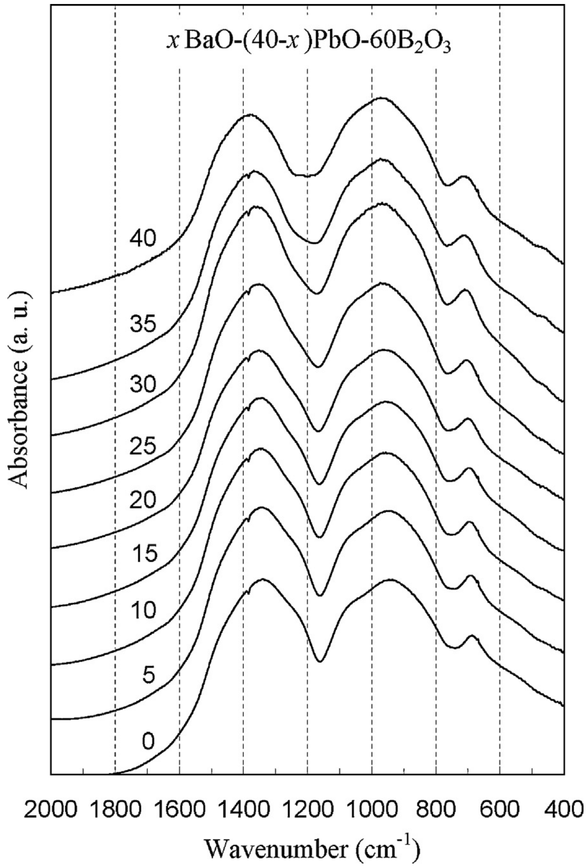

Fig. 2. Infrared spectra of xBaO·(40-x)PbO·60B_2O_3 glasses. Numbers at the plots refer to BaO content (mol%).

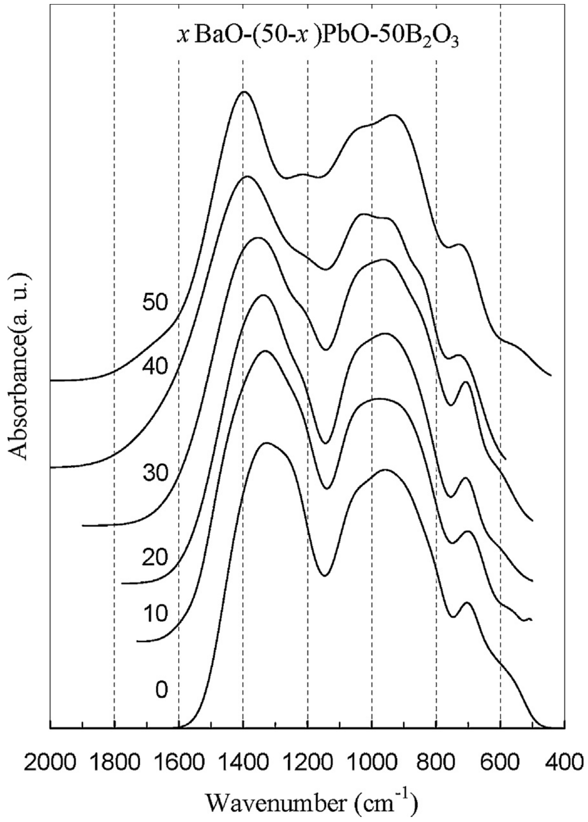

Fig. 3. Infrared spectra of xBaO·(50-x)PbO·50B_2O_3 glasses. Numbers at the plots refer to BaO content (mol%).