# FTIR of binary lead borate glass: Structural investigation

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## ABSTRACT

The glass samples were prepared according to the following formula: $(100-x)$ $B_2O_3 - x$ PbO, where $x = 20-80$ mol% by melt quenching method. The density of the prepared samples was measured and molar volume was calculated. IR spectra were measured for the prepared samples to investigate the glass structure. The IR spectra were deconvoluted using curves of Gaussian shape at approximately the same frequencies. The deconvoluted data were used to study the effect of PbO content on all the structural borate groups. Some structural parameters such as density, packing density, bond length and bond force constant were theoretically calculated and were compared to the obtained experimental results. Deviation between the experimental and theoretically calculated parameters reflects the dual role of PbO content on the network of borate glass.

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## 1. Introduction

Borate glasses are very interesting amorphous materials considering their specific structure and physical properties [1]. They have the phenomenon of so called boron anomaly. A partial explanation of this phenomenon is that with adding small amounts of alkali oxide, some tri-coordinated ($BO_3$) units that exist in pure vitreous $B_2O_3$ are converted to boron tetrahedral structural ($BO_4$) units [2]. Glasses containing non-conventional network formers such as PbO have many extra-ordinary properties such as high refractive index, large density, high non-linear optical susceptibility and excellent infrared transmission [3]. Lead oxide can act dual role in the glass network; as glass former at high lead oxide content and as network modifier at low lead oxide content. Such postulations in the structural role of $Pb^{2+}$ ions would imply significant modifications of its local environment and of its coordination [4]. Lead borate glasses are attractive systems to study the structure composition–property relationship of glasses. They show large glass forming region, which is advantageous for manufacture of structurally and optically different systems, which are strongly depend on $PbO/B_2O_3$. They show a significant variation of atomic structure with composition. Furthermore, spectroscopic studies of these glasses are favorable as the extreme difference between the masses of lead and boron atoms allow for a separation of vibrational modes

of PbO polyhedral and the borate network [5].

In this work $(100-x)$ $B_2O_3 - x$ PbO glass system was prepared, where $x = 20-80$ mol%. Some physical parameters such as density, packing density, bond length and force constant of the structural groups of the studied glass system were theoretically calculated. The effect of PbO on the structure of the studied glass was investigated using FT-IR.
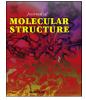
## 2. Experimental methods

### 2.1. Glass preparation

The glass samples were prepared according to the following formula: $(100-x)$ $B_2O_3 - x$ PbO, where [$x = 20-80$ mol%]. Glass samples were prepared by melt quenching method. They were synthesized from lead monoxide (litharge, 99+%, from Strem Chemicals) and boric acid ($H_3BO_3$, 99.5%, from Aldrich). The raw materials were mixed and preheated in an electrical oven from 300 °C to 900 °C at steps of 300 °C for 15 min at each step. They were subsequently melted at 1100 °C for 15 min. The glasses were cast into pre-heated stainless mold at room temperature and then immediately transferred to an annealing furnace between 300 °C and 450 °C, depending on the glass compositions and their respective glass transition temperatures for about 2 h to remove internal stress.

### 2.2. Density measurement

Glass densities of the prepared samples were measured using

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Archimedes' principle using toluene as an immersion liquid at room temperature. The accuracy of the measurements was approximately ±0.015 gm cm$^{-3}$.

### 2.3. IR measurements

All infrared spectra of the investigated glasses were recorded on a FT-IR spectrophotometer type Tensor 27, Brulear over the range of wavenumber 4000–200 cm$^{-1}$ at room temperature. The transmittance spectra were first converted to absorption spectra according to the formula: A = [2 − Log(T%)], then the absorption spectra were deconvoluted using curves of Gaussian shape at approximately the same frequencies to obtain best fitted resolved spectra.

## 3. Results and discussion

The composition of the prepared samples, measured density, molar volume and some theoretically calculated structure parameters such as calculated density, packing density, (B–O) bond length for BO$_3$ and BO$_4$ groups, (Pb–O) bond length and bond force constant are reported in Tables 1 and 2. The packing density V$_t$ of the studied glasses is calculated from the packing factor V$_i$ of its constituents as follow: if the glass has a component $x$ mol% A$_b$B$_c$, where A is the cation, B is the anion, $x$ is the mole fraction, b and c are the valences of the cation and anion, respectively. Then the packing factor is given by Ref. [6]:

$$V_i = \frac{4\pi N_A}{3}\left(b\,r_A^3 + c\,r_B^3\right)$$ (1)

where, N$_A$ is the Avogadro's number, r$_A$ and r$_B$ the ionic radii of the cation and the anion, respectively. Therefore the packing density, V$_t$, is given by:

$$V_t = \frac{\rho}{M}\sum_i x_i\,V_i$$ (2)

where, ρ and M are glass density and its molecular weight, $x_i$ is the mole fraction and V$_i$ is the packing factor which was calculated from Eq. (1) and equals 2.08 × 10$^{-5}$ m$^3$ for B$_2$O$_3$ and 1.28 × 10$^{-5}$ m$^3$ for PbO. The calculated values of V$_t$ are given in Table 1.

The concentration of ions A and B per cm$^3$ of the component A$_b$B$_c$ is given by Ref. [7]:

$$n(A) = \frac{bxN_A}{100\,V_m}$$ (3)

and for ion B it is given by:

$$n(B) = \frac{cxN_A}{100\,V_m}$$ (4)

where V$_m$ is the glass molar volume. Therefore the short separation

distances, r, between identical A or B ions are given by:

$$r = \left(\frac{1}{n}\right)^{(1/3)}$$ (5)

According to Eqs. (3)–(5), the calculated values of r(B–B), r(Pb–Pb) and r(O–O) (nm) of the present glasses are given in Table 2. The values of r(B–B) lie between 0.314 and 0.517 nm, r(Pb–Pb) between 0.629 and 0.411 nm and r(O–O) between 0.276 and 0.341 nm. Therefore, r(B–O) can be calculated for BO$_4$ group by considering the B ions, which are lying in the centre of four oxygen ions. Also, r(B–O) for BO$_3$ group can be calculated by considering the B atom, as occupying the cross-point position of the vertical lines from the vertex of the equal ribs triangle with its vertices are the oxygen atoms [8]. The obtained B–O bond length of the present work (0.257–0.192 nm for BO$_4$ and 0.209–0.156 nm for BO$_3$, see Table 2) agrees with the values for vitreous B$_2$O$_3$ [9].

The average stretching force constant, f, of the studied glass is given by Ref. [10]:

$$f = \frac{1.7}{r^3}\ \text{N/m}$$ (6)

where (r) is the cation − anion bond length (nm), the values of (f) are given in Table 2. Theoretically calculated densities were calculated using the following equation:

$$\rho_{calc.} = \sum_i x_i\rho_i$$ (7)

where $x_i$ and ρ$_i$ are the molar fraction and density of each component, respectively. All these parameters were calculated to help understanding the compositional dependence of the glass structure. According to Table 1, experimentally measured and theoretically calculated densities have the same behavior of increasing with the increase of PbO content. The difference between their values may be due to the minor changes in the chemical composition of the glass during the melting process. The significant change in their values is due to the change of the structural groups of the prepared samples. All these considerations are not taken into account in the theoretical method that was used for calculating the density. The dependence of the measured density and molar volume on PbO content is shown in Fig. 1. The density increases with increasing PbO content. This increase in density is due to the high molecular weight of PbO (223.19 gm) than that of the replaced B$_2$O$_3$ (69.62 gm) content. When The PbO content exceeds 40 mol%, the density shows a lower rate of increasing. The change in the rate of increasing after 40 mol% of PbO may be due to the change in the compaction of the glass structure. This change in the structure compaction is more evident in the curve that shows the behavior of the molar volume of the prepared samples. Molar volume decreases up to 40 mol% of PbO then increases linearly with increasing PbO content, see Fig. 1. This is due to the dual role of PbO in the glass network. At low concentration,

**Table 1**
Composition and some measured and calculated structural parameters for the studied glass samples.

| Sample no. | B$_2$O$_3$ (mol%) | PbO (mol%) | ρ (g/cm$^3$) | V$_m$ (cm$^3$) | ρ$_{calc.}$ (g/cm$^3$) | V$_t$ * 10$^{-6}$ (cm$^3$) |
|---|---|---|---|---|---|---|
| BPb-1 | 80 | 20 | 3.342 | 30.026 | 3.874 | 0.6392 |
| BPb-2 | 70 | 30 | 3.982 | 29.055 | 4.581 | 0.6329 |
| BPb-3 | 60 | 40 | 4.569 | 28.681 | 5.288 | 0.6132 |
| BPb-4 | 50 | 50 | 4.763 | 30.739 | 5.995 | 0.5460 |
| BPb-5 | 40 | 60 | 5.056 | 31.993 | 6.702 | 0.4995 |
| BPb-6 | 30 | 70 | 5.380 | 32.919 | 7.409 | 0.4611 |
| BPb-7 | 20 | 80 | 5.750 | 33.474 | 8.116 | 0.4295 |