



Behavior of bismuth ions in the two glassy systems of 50 LiF-50 P₂O₅ and 50 LiF-50 B₂O₃ (mol %) assessed by optical, FTIR and photoluminescence spectra in addition to thermal expansion properties

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Abstract

Glasses from two varieties of (LiF-B₂O₃) and (LiF-P₂O₅) systems with equal 50 mol % for each partner together with samples doped with 1 or 2% Bi₂O₃ were synthesized by melting–annealing mechanism. Multiple optical, FTIR and photoluminescence spectral measurements were carried out. Optical spectra of Bi₂O₃—doped glasses exhibit UV–near visible peaks owing to the specific absorption of Bi³⁺ ions. FTIR spectra elucidate the presence of characteristic vibrational bands from (LiF-B₂O₃) glass due to (BO₃) and (BO₃F) groups beside (LiF₄) groups while the fluorophosphate glasses (LiF-P₂O₅) show vibrations due to PO₄ and (PO₃F) groups and also the possible sharing of (LiF₄) groups. Photoluminescence spectral data reveal extended emission from about 375 to 700 nm and is more prominent in (LiF-B₂O₃) system than (LiF-P₂O₅) system. The thermal expansion data reveal similar behavior and the derived transition and softening temperatures are slightly lower in (LiF-P₂O₅) glasses than (LiF-B₂O₃) glasses.

Keywords Bismuth · Fluorophosphate · Fluoroborate · Glass · Photoluminescence · FTIR

1 Introduction

The introduction of alkali metal fluorides into any conventional silicate, phosphate, or borate glass results in a blend of different glasses with the good optical properties of fluoride glasses and the higher mechanical and thermal stability of partner oxide glasses (Lucas 1989; Möncke and Ehrh 2019). The term fluoride glass refers to particulate vitreous materials belonging to the general group of halide glasses in which the anions are derived from elements of Group VII of the Periodic Table of the Elements, namely fluorine, chlorine,

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bromine and iodine. Glass materials based entirely on inorganic halides are known to be purely synthetic and their development only started in the mid-1970s (Möncke and Ehrhart 2019). Examples of these fluorides are BeF_2 and ZrF_4 which are known to possess a larger transmission range and are of interest in laser windows, infrared domes, lenses, filters, and laser hosts (Möncke and Ehrhart 2019). Fluoride phosphate glasses (or fluorophosphate glasses) have been studied for their short- and mid-range structures for over 50 years and have been summarized by several glass scientists e.g. (Möncke and Ehrhart 2019; Kondakis et al. 2010; Ehrhart 2015).

Similarly, the interest and progress in fluoroborate glasses have increased since the pioneer and successive studies of Shelby et al. e.g. (Gressler and Shelby 1988; Shelby and Ortolano 1990; Shelby and Baker 1998) on the network building structure and characteristics of these glasses. In such mixed fluorophosphate and fluoroborate glasses, the most accepted additional formed groups; namely (PO_3F) or (BO_3F) are expected to be formed as tetrahedral structural groups.

The introduction of Bi_2O_3 to glasses generally improves their optical properties including the increase of their refractive indices and causes distinct stability against high doses of gamma irradiation due to the heavy atomic mass of Bi_2O_3 which decreases the mobility of free d-electrons during the irradiation process (Dumbaugh and Lapp 1992; Donald 1993; Bishay and Maghrabi 1969; Stehla et al. 1998; ElBatal and Nucl. 2007; ElBatal et al. 2007). Bi_2O_3 can form binary glasses with B_2O_3 or SiO_2 with a high percent reaching 85 wt %. This behavior is very similar to that of PbO and many authors have reached the conclusion that bismuth ions can be existed in glasses both as network modifiers and as network former especially at a high percent of Bi_2O_3 by forming constitutional network BiO_3 units beside BiO_6 groups (Bishay and Maghrabi 1969; Stehla et al. 1998; ElBatal 2007; ElBatal et al. 2007, 2020; Ouis et al. 2020).

The main objective of this study is to prepare varying Bi_2O_3 -doped (1, 2 wt%) within the two host glasses of $(\text{LiF } 50\%-\text{B}_2\text{O}_3 \text{ } 50\%)$ and $(\text{LiF } 50\%-\text{P}_2\text{O}_5 \text{ } 50\%)$ and to find out the behavior of bismuth ions in these two different fluoride glasses through measuring their collective optical, FTIR and photoluminescence spectra. A further study is undertaken to measure the thermal expansion properties of all the prepared undoped and Bi_2O_3 -doped glasses from the two mentioned systems $(\text{LiF}-\text{B}_2\text{O}_3)$ and $(\text{LiF}-\text{P}_2\text{O}_5)$. The collected data would be expected to introduce new data of these two specific fluoroborate and fluorophosphate glass with unfamiliar high LiF content (50 mol%).

2 Experimental details

2.1 Preparation of the glasses

The glasses were synthesized from laboratory chemical reagents. The two hosts studied glass systems include $(\text{LiF } \text{B}_2\text{O}_3)$ and $(\text{LiF}-\text{P}_2\text{O}_5)$ with 50 mol% from each partner. The laboratory chemicals used in the preparation of the studied glasses include: orthoboric acid (H_3BO_3) for B_2O_3 and ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) for P_2O_5 beside both LiF and the dopant oxide (Bi_2O_3) was introduced as such. The melting of the weighed batches was carried out into covered platinum crucibles for the fluoroborate glasses and covered porcelain crucibles for the fluorophosphate to minimize the volatilization of fluoride. The batches were melted at 1000–1050 °C for 60 min under atmospheric conditions in a SiC-heated furnace (Vecstar, UK).

The crucibles were rotated at intervals to reach complete melting and homogeneity. The finished melts were poured into warmed stainless steel molds with the required dimensions. The prepared glasses samples were transferred to an annealing muffle regulated at 285 °C for the fluorophosphate and 320 °C for fluoroborate. The annealing muffle was left to cool after 1 h to room temperature with the glassy samples inside.

2.2 Optical absorption measurements

The UV–visible spectra were measured for polished samples of equal thickness ($2\text{ mm} \pm 0.1\text{ mm}$) using a recording spectrophotometer (type Jasco, Japan) within the range 200–1100 nm.

2.3 FT infrared spectral investigations

The FTIR spectra of the prepared glasses were measured as powders at room temperature within the wavenumber $400\text{--}4000\text{ cm}^{-1}$ using a recording FTIR spectrometer (type Bruker, Vertex 8 V, Germany). The measurements were done with a resolution of 4 cm^{-1} .

2.4 Photoluminescence spectral measurements

PL spectral measurements were recorded at room temperature under different excitation wavelengths in the spectral range 500–700 nm using a fluorescence spectrophotometer (type Jasco-FP-6500, Japan) equipped with a xenon flash lamp as the excitation light source. The scan speed is 0.1 s step⁻¹ with a step wavelength of 0.25 nm and a slight width of 0.2 nm.

3 Results and discussions

3.1 FTIR spectral measurements of the prepared glasses

Figure 1 illustrates the FTIR of the undoped glass as well as the two Bi_2O_3 doped LiF- B_2O_3 glasses. Infrared spectroscopic results show nearly repeating spectral infrared curves, revealing the same characteristic vibrational bands.

The base undoped LiF- B_2O_3 glass reveals an FTIR spectrum composed of the following spectral items:

- (a) A small far-IR peak located at 486 cm^{-1} is identified.
- (b) A second medium band is observed with two connected peaks at 583 and 613 cm^{-1} .
- (c) A broad and highly intense band is identified extending from 800 to 1180 cm^{-1} with several attached peaks at about 920 and 1047 cm^{-1} .
- (d) The second broad and distinct band is observed to be extending from about 1200 to 1550 cm^{-1} with a distinct peak at 1477 cm^{-1} followed by a small curvature at about 1650 cm^{-1} .
- (e) The rest of the IR spectrum reveals small peaks at 2000 , 2500 , 2850 , and 2930 cm^{-1} and succeeded by a broad medium near IR band showing two peaks at 3440 and 3569 cm^{-1} .

Fig. 1 FTIR spectra of base (LiF-B₂O₃) glass (a) and Bi₂O₃ doped glasses (b, c)

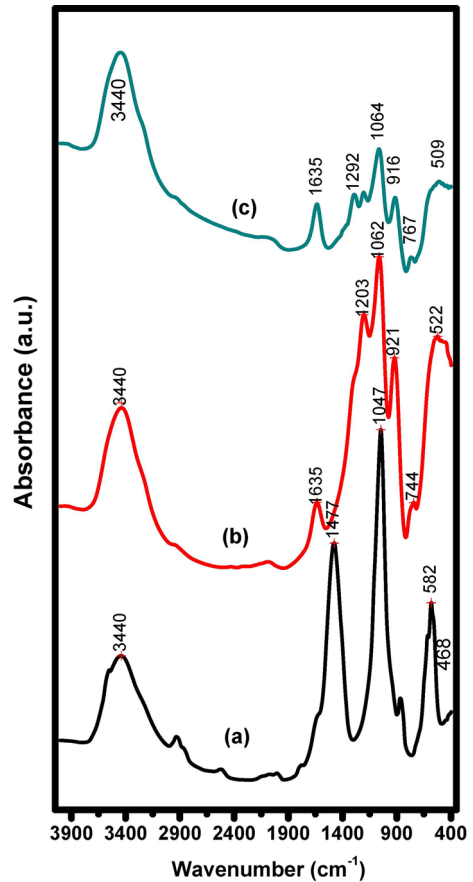


Figure 2 illustrates the FTIR spectra of the glasses from the system (LiF-P₂O₅) consisting of the undoped and the two Bi₂O₃-doped glasses. All the IR curves reveal vibrational condensed peaks within the region 400–1350 cm⁻¹ and followed by separate peaks at about 1640, 2450, and ended by a broad near IR band centered at about 2440 cm⁻¹.

The identified vibrational peaks from the two studied systems due to the unfamiliar composition of the glasses containing high LiF (=50 mol%) are condensed nature due to possible of mixed groups. It is expected that extra or additional groups beside (BO₃) groups and tetrahedral (BO₃F) and (PO₃F) groups besides the formation of some Bi–O units. It has been profitable to conduct a deconvolution process to the IR base glass in each system together with the IR of the highest Bi₂O₃ glass. The deconvoluted spectra will be expected to identify hidden or overlapped IR absorption peaks.

Figures 3, 4, 5 and 6 reveal the deconvoluted IR spectra of the selected glasses from the two systems (LiF-B₂O₃) and (LiF-P₂O₅). Inspection of Figs. 3 and 4 indicates that the common deconvoluted peaks in the two IR curves of undoped and high Bi₂O₃-doped lithium borate glasses are: 405, 486, 494, 563, 598, 613, 711, 902, 912, (1052–1057), 1119, 1188, 1398, 1411, 1488, (1637–1643).

From Figs. 5 and 6 the derived common deconvoluted peaks in the IR curves of undoped and high Bi₂O₃-doped lithium fluorophosphate glasses (LiF-P₂O₅) are: 407, 425,

Fig. 2 FTIR spectra of base (LiF-P₂O₅) glass a and Bi₂O₃ doped glasses b, c

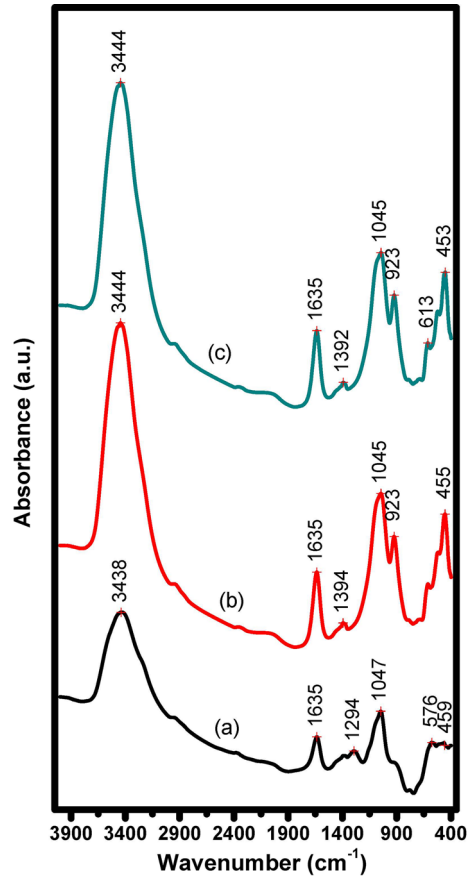


Fig. 3 Deconvoluted spectra of base (LiF-B₂O₃) glass

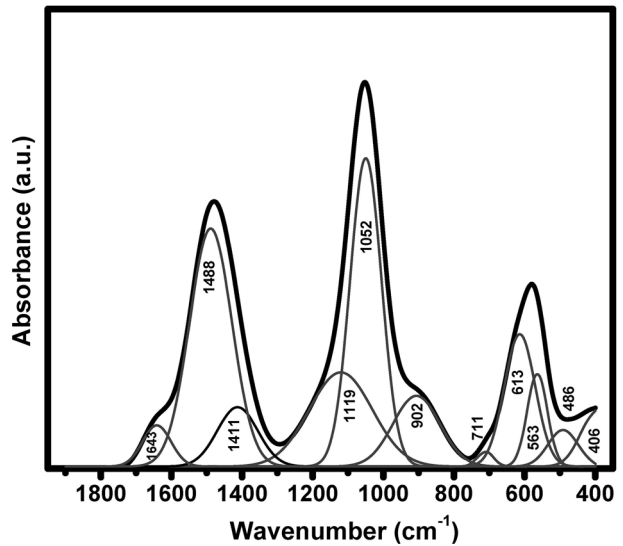


Fig. 4 Deconvoluted spectra of high Bi_2O_3 -doped lithium fluoroborate ($\text{LiF-B}_2\text{O}_3$) glass

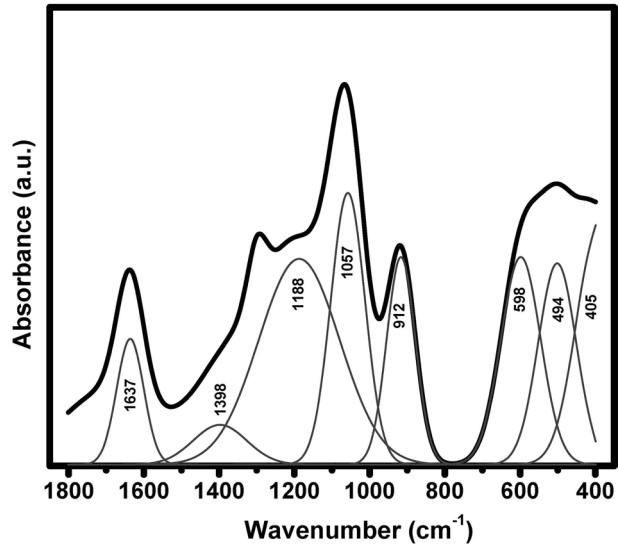
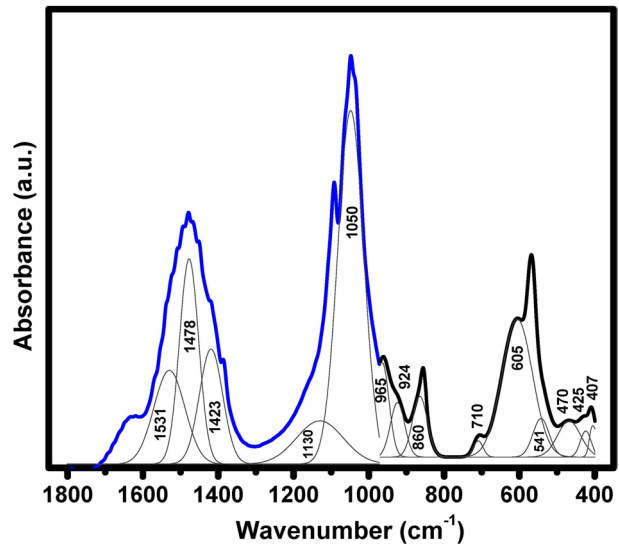


Fig. 5 Deconvoluted spectra of base lithium fluorophosphate ($\text{LiF-P}_2\text{O}_5$) glass

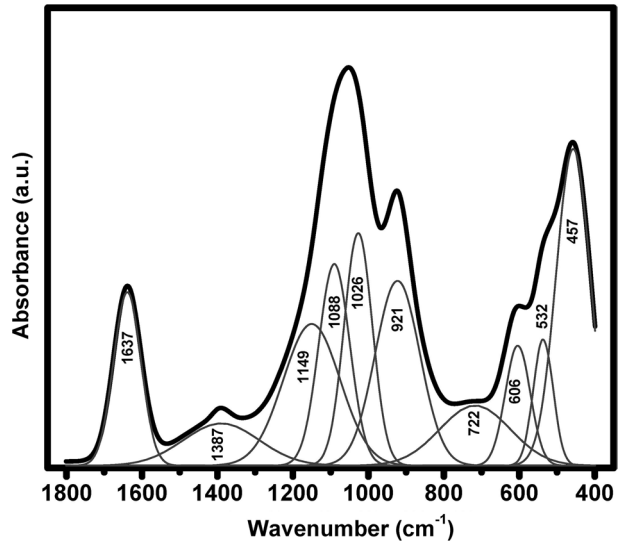


457,532–541,605–606,712–722, 860, 921–924,965,1026–1050, 1088, 1130–1144, 1387, 1423, 1478, 1531, 1637 cm^{-1} .

The specified extended FTIR spectrum of the undoped $\text{LiF-B}_2\text{O}_3$ glass is explained on the following basis (Shelby and Baker 1998; The structure of vitreous and liquid boron oxide 1962; Kamitsos et al. 1990; Kamitsos 2003; Doweidar et al. 2012).

- (a) It is established that the identified vibrational bands and peaks deduced from IR measurements of glasses refer to network structures of such glasses which are originating from the stretching and bending vibrations of the structural building groups which are

Fig. 6 Deconvoluted spectra of high Bi_2O_3 -doped lithium fluorophosphate ($\text{LiF-P}_2\text{O}_5$) glass



dependent or related to the detailed chemical composition and their arrangements or housing within the networks.

- (b) The first glassy system studied is based on the composition of lithium fluoride borate or lithium fluorophosphate ($\text{LiF } 50\text{-B}_2\text{O}_3$ 50 mol %) and the expected formed groups include tetrahedral, fluoro-borate (BO_3F) and triangular borate (BO_3) groups as evidenced in many publications (Möncke and Ehrt 2019; Shelby and Baker 1998; Ouis et al. 2020; Doweidar et al. 2012).

The resultant IR spectra reveal and confirm these previous postulations. Also, they agree with the assumption of the ability of LiF to act in a similar way as Li_2O in the progressive transformation of some BO_3 to BO_3F until a certain percent. Owing to the existence of LiF in measurable equal percent to B_2O_3 (50 mol %) in the host glass, it is to be assumed that the possibility arises from extra LiF to form additional (LiF_4) groups. This postulation is in agreement with the previously published work by Doweidar et al (Doweidar et al. 2012) on $\text{CaF}_2\text{-B}_2\text{O}_3$ glasses. These authors have assumed that at a high percent of CaF_2 (40-45 mol%) the formation of tetrahedral (CaF_4) groups is expected as the same to be identified in crystalline CaF_2 and this behavior stabilizes the glasses containing high fluoride content.

- (c) Regarding the identified IR spectra, it is recognized that the vibrational bands and peaks can be assigned as follows (The structure of vitreous and liquid boron oxide 1962; Kamitsos et al. 1990; Kamitsos 2003; Doweidar et al. 2012):
- (i) The multi-small far IR peaks at $406\text{--}500\text{ cm}^{-1}$ can be correlated to vibrations of monovalent (Li^{4+}) cations in their characteristic sites as derived by many glass scientists (The structure of vitreous and liquid boron oxide 1962; Kamitsos et al. 1990; Kamitsos 2003; Doweidar et al. 2012; Sigel and Ginther 1968; Sigel and in 1977; Duffy 1997; ElBatal and Ouis 2011)
 - (ii) The identified vibrational peaks within the range $600\text{--}750\text{ cm}^{-1}$ are correlated with bending vibrations of different borate groups

- (iii) The observed strong highly intense vibrational peaks within the wavenumber 800–1200 cm^{-1} are attributed to originate from vibrational of tetrahedral fluoroborate (BO_3F) beside the possibility of the sharing of some (LiF_4) groups leading to the higher intensities of such middle absorption region at (800–1200 cm^{-1}).
- (iv) The identified distinct vibrational peaks within the range 1200–1500 cm^{-1} are related to vibrations of triangular (BO_3) groups.
- (v) The rest vibrational peaks in the near-IR region at about 1640 cm^{-1} , 2850, 2950, and 3450–3560 cm^{-1} are related to vibrations of OH, water, and BOH.
- (vi) Regarding the glasses containing small dopants of Bi_2O_3 , several authors (Bishay and Maghrabi 1969; Stehla et al. 1998; ElBatal 2007; ElBatal et al. 2007, 2020; Ouis et al. 2020) have claimed the Bi–O bending vibrations at (460–479) cm^{-1} and 840 cm^{-1} as stretching vibrations of Bi–O (BiO_3).

The identified IR spectra of these glasses can be explained on the following basis (Abdel-Kader et al. 1991; Mostafa and El-Egili 1998; ElBatal 2008; Marzouk et al. 2017):

- (a) The IR bands are originating from the vibrations of the structural groups within the studied glasses.
- (b) The basic host glass consists of ($\text{LiF}50\text{--P}_2\text{O}_5$ 50 mol%) and hence it is found that the structural groups are (PO_4), (PO_3F) and possible additional (LiF_4) groups beside modifier Li^+ ions present in noticeable percent.
- (c) The assignment of the identified IR peaks are assumed to be:
 - (i) The far—IR peaks at 400–450 cm^{-1} can be correlated to vibrations of (Li^+) ions in their characteristic sites.
 - (ii) Peaks at 700–730 cm^{-1} can be attributed to stretching vibrations of P–O–P rings and sharing of vibrations of P–F band in (FPO_3).
 - (iii) The peaks at 860–890 cm^{-1} are assigned to asymmetric stretching P–O–P groups.
 - (iv) The peaks at 1020–1050 cm^{-1} and 1130–1140 cm^{-1} are assigned to asymmetric stretching vibrations of PO_2 groups.
 - (v) The peak at 1250–1275 cm^{-1} is attributed to P=O modes.
 - (vi) The peaks at about 1640, 2850 are related to the stretching of POH water vibrations.
 - (vii) The near IR band located at 3440 cm^{-1} is correlated to vibrations of OH, water, POH.

The addition of a few dopant percent of Bi_2O_3 produces some additional peaks which can be related to Bi–O–Bi in octahedral coordinated BiO_6 within the range 450–500 cm^{-1} and possible BiO_3 vibrations at 820–840 cm^{-1} .

To confirm the assumption of the formation of (LiF_4) group in both studied glasses containing (LiF 50 mol%), we introduce Fig. 7 revealing the vibrational peaks which are expected from (LiF_4) groups from the inspection of IR spectrum laboratory crystalline (LiF) used in the preparation of the two systems.

3.2 Optical absorption spectral measurements of the prepared glasses

Figures 8 and 9 illustrate the UV–visible absorption spectra of both two different fluoroborate and fluorophosphate glasses from the two systems $\text{LiF-B}_2\text{O}_3$ and $\text{LiF-P}_2\text{O}_5$

Fig. 7 FTIR spectrum laboratory crystalline (LiF)

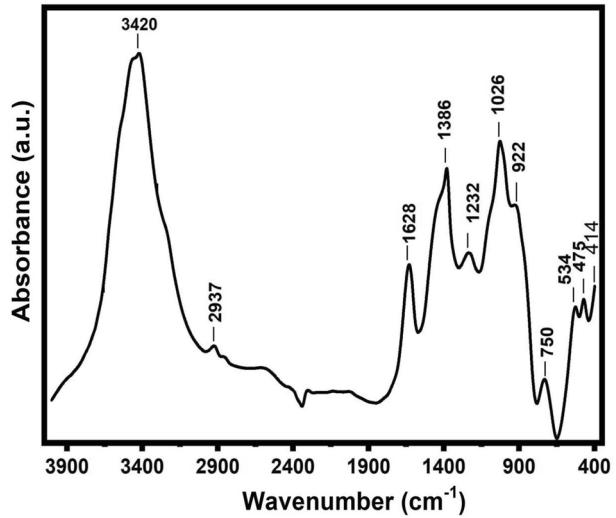
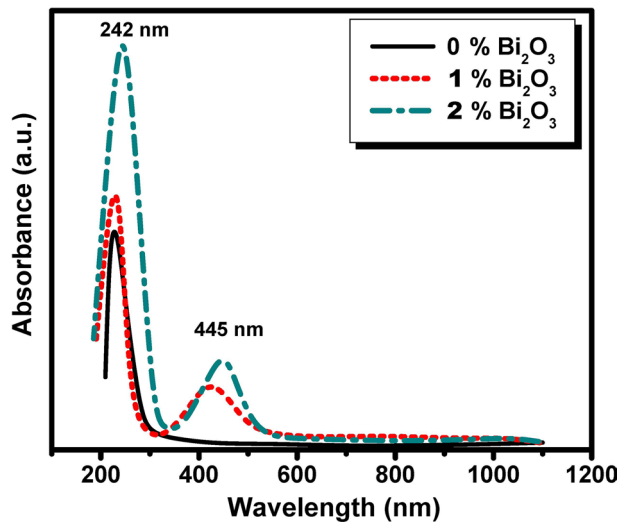


Fig. 8 Optical; (UV–visible) absorption spectra of undoped and Bi₂O₃-doped fluoroborate glasses

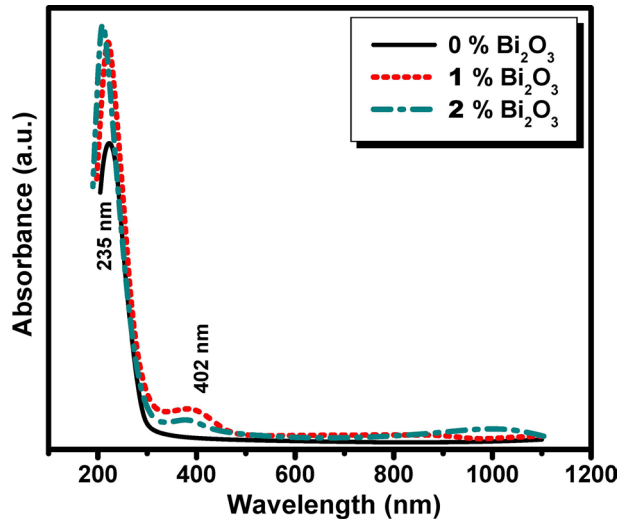


and their dopant samples with Bi₂O₃ (1, 2%). The optical spectra of the two undoped glasses of (LiF-B₂O₃) and (LiF-P₂O₅) reveal distinct UV absorption within the range of 200–270 nm.

The glasses doped with Bi₂O₃ (1,2%) show additional small peaks at 330–350 nm and 400–420 nm for the two systems (LiF-B₂O₃) and (LiF-P₂O₅).

The observed distinct UV absorption identified in the optical spectra of the two undoped fluoroborate and fluorophosphate glasses can be proposed to result from unavoidable contaminated traces of ferric ions exist as contaminants within the laboratory chemicals applied for the preparation of the prepared glasses. This hypothesis is based on the following items:

Fig. 9 Optica; (UV–visible) absorption spectra of undoped and Bi_2O_3 -doped fluorophosphate glasses



- (i) Some glass researchers (Sigel and Ginther 1968; Sigel 1977) early assumed that the appearance of distinct UV absorption bands in the spectra of undoped glasses is due to the contamination of impurities (e.g. Fe^{3+} , Cr^{6+}).
- (ii) Duffy (Duffy 1997) in his reference article on charge transfer spectra in glasses assumed that UV absorption peaks generally observed in the optical spectra of glasses are due to two reasons:
 - (iii) The existence of trace impurities of certain 3d transition metals (e.g. Fe^{3+} , Cr^{6+}) produces distinct UV absorption due to its charge transfer origin.
 - (iv) Duffy (Duffy 1997) also revealed that some other metal ions (such as Ce^{3+} , Tb^{3+} , U^{4+}), as well as $d^{10}s^2$ ions (Pb^{2+} , Bi^{3+}), absorb radiation through electronic transitions involving orbitals essentially of the metal ion only and such UV spectra generally necessitate higher concentrations of the metal ions (Pb^{2+} , Bi^{3+}).

It is therefore presumed that the strong UV absorption bands observed within the range 200–310 nm in the spectra of the two undoped glasses are correlated to trace Fe^{3+} ions present as impurities and the observed small peaks within the range 350–430 nm are related to absorption of Bi^{3+} ions. The same assumptions have been reached by several authors (ElBatal and Nucl. 2007; ElBatal et al. 2007, 2020; Ouis et al. 2020; Marzouk et al. 2017b; Fayad et al. 2022).

3.3 Photoluminescence spectral data

Figure 10 illustrates the PL spectra of the base ($\text{LiF-B}_2\text{O}_3$) glass and two Bi_2O_3 -doped glasses. The emission spectra are observed to extend from 375 to about 700 nm with distinct peaks at 415, 465, 505, 525, 560, and 620 nm. The intensity of the peaks increases with the increase of Bi_2O_3 content. Also, the intensities of the emission peaks decrease with the increase of the wavelength. The excitation peaks reveal two distinct peaks at 266 and 280 nm with the increase of the intensity with increasing wavelength.

Figure 11 reveals the PL spectra of the undoped and Bi_2O_3 -doped within fluorophosphate glasses ($\text{LiF-P}_2\text{O}_5$). The emission spectra show three broad bands with peaks

Fig. 10 Photoluminescence spectra of undoped and Bi₂O₃—doped lithium borate glasses

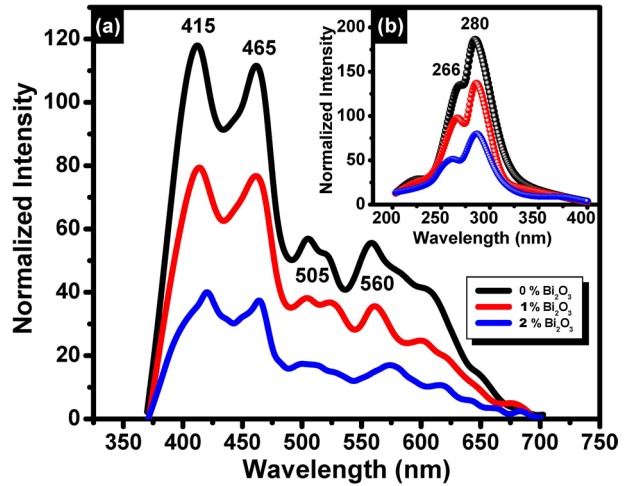
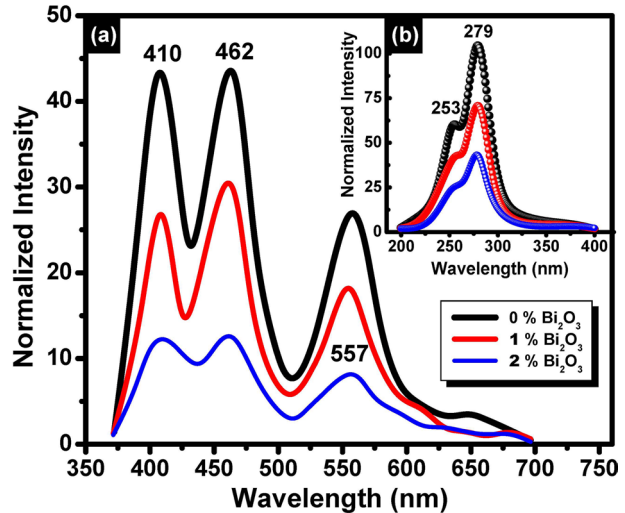


Fig. 11 Photoluminescence spectra of undoped and Bi₂O₃—doped lithium fluorophosphate glasses



at 410, 562, and 557 nm, and the intensities of the first two are nearer while the third peak is lower in intensity. The excitation spectra show two connected bands with peaks at 253 and 279 nm and the latter is more intense than the first peak.

The results shown in Figs. 10 and 11 reveal that the emission spectral peaks identified vary with the type of studied host glass. They show extended emission from about 375 nm to 700 nm in both (LiF-B₂O₃) and (LiF-P₂O₅) host glasses. However, in host borate glass, 6 peaks could be identified while in host phosphate glass only three peaks are observed. The observed excitation peaks within the two host glasses are two but show some variations in their positions, the borate peaks are identified at 266 and 280 nm while the phosphate host glass's peaks are at 253 and 279 nm. The previous results can be explained on the following basis (Singh and Karmakar 2012; Tabaza et al. 2014; Singh et al. 2010; Marzouk et al. 2014; Marzouk 2012);

- (i) It is agreed that the luminescence properties in glasses are generally influenced and affected by the presence of heavy metal and highly polarized Bi^{3+} and Pb^{2+} ions, besides the detailed composition and the structural groupings and their arrangements.
- (ii) The changes in the number and position of the PL peaks can be attributed to different sites for Bi^{3+} ions in different host glasses.
- (iii) The previous postulations agreed with the identified IR and optical spectra for the same glasses. IR spectra of the borate glasses reveal highly intense vibrational bands than phosphate glasses because the boron atom is the lightest glass-forming element and is highly affected to easily shows distinct vibrational peaks.

On the other hand, the optical spectra of phosphate glasses reveal higher intensities of the UV and near-visible bands and this latter visible band is related to vibrations of Bi^{3+} ions

- (iv) The same assumptions can be related to the identified changes in the excitation data which refer to the action of host glass on the intensity of the bands.
- (v) In a recent publication from Xiang et al. (Wu et al. 2020) on the photoluminescence spectra of bismuth in $\text{Na}_2\text{O}-\text{Y}_2\text{O}_3$, B_2O_3 phosphor candidate which refer to the of high-quality white LED lighting applications that can be effectively excited in the near UV region (350–400 nm) and show no reabsorption of Bi^{3+} ions in the visible light region. They have carried out their studies with the ranges (0.05, 0.125, 0.25, 0.5, and 1%) of bismuth ions. They refer that Bi^{3+} has a $d^{10} s^2$ electronic layer structure, the electronic configuration is $[\text{Xe}] 4f^{14} 5d^{10} 6s^2$ and its luminescence characteristics are closely related to the chemical composition of the host material. They added that the spectrum of Bi^{3+} is due to the excitation $^1\text{S}_0$ and the excited state energy levels are $^1\text{P}_1$, $^3\text{P}_2$, $^3\text{P}_1$, and $^1\text{P}_0$ in order of energy.

They concluded that at room temperature, the lowest absorption band of Bi^{3+} luminescence material is due to the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition, while the emission band corresponds to the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition.

In conclusion and based on previous considerations, the distinct changes identified can be related to the difference between the luminescence spectra of bismuth ions in host borate glass and that in host phosphate glass which can be related to change of the sites of bismuth ions. Optical spectra indicate that the bismuth is in the trivalent state from its characteristic near-visible band.

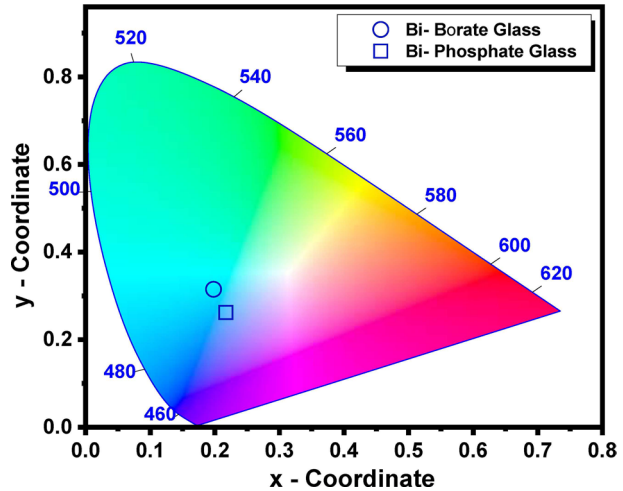
The CIE1931 chromaticity diagram is used to detect the color emitted by a light source using three dimensionless quantities $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$. The tristimulus values for a non-monochromatic light source with spectral relative power $P(\lambda)$ are estimated by Malacara (2011); Mortimer and Varley (2011):

$$X = \int P(\lambda)\bar{x}(\lambda)d\lambda \quad (1)$$

$$Y = \int P(\lambda)\bar{y}(\lambda)d\lambda \quad (2)$$

$$Z = \int P(\lambda)\bar{z}(\lambda)d\lambda \quad (3)$$

Fig. 12 CIE 1931 chromaticity diagram of Bi₂O₃ – doped lithium fluoroborate or lithium fluorophosphate glasses



where X, Y, and Z are the tristimulus values to specify the three primary colors of light, red, green, and blue that are required to match the color P(λ), and from the tristimulus values, the color chromaticity coordinates x and y can be determined using the following expressions (Malacara 2011; Mortimer and Varley 2011);

$$x = \frac{X}{X + Y + Z} \tag{4}$$

$$y = \frac{Y}{X + Y + Z} \tag{5}$$

$$z = \frac{Z}{X + Y + Z} \tag{6}$$

According to Fig. 12, the color coordinates are represented and extended in the blue area under the UV excitations 280 nm for both fluorophosphate and fluoroborate samples. The actual values of CIE color coordinates are (0.198, 0.315) for bismuth borate and (0.217, 0.262) for bismuth phosphate. The observed luminescent blue color is correlated to the presence of heavy metal and highly polarized Bi³⁺ and Pb²⁺ ions in addition to the building structure and attached of trivalent bismuth ions in different sites of the host glasses (Denker et al. 2010).

3.4 Thermal expansion data

Figure 13 illustrates the thermal expansion curves of the undoped LiF-B₂O₃ glass and derived Bi₂O₃—doped samples. The results indicate that the dilatometric transition temperature and softening temperature for the undoped glass are 392 °C and 430 °C and these parameters decrease with the addition of Bi₂O₃ to a noticeable degree but the two Bi₂O₃—doped samples are nearer in their thermal parameters.

Fig. 13 Thermal expansion of undoped and Bi₂O₃-doped lithium borate glasses

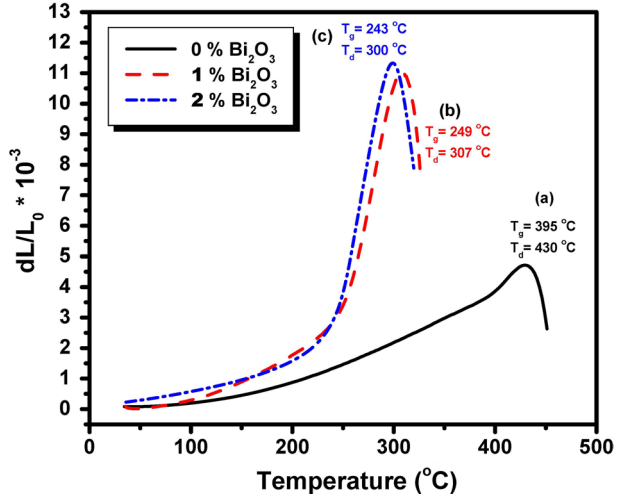


Fig. 14 Thermal expansion undoped and Bi₂O₃-doped lithium fluorophosphate glasses

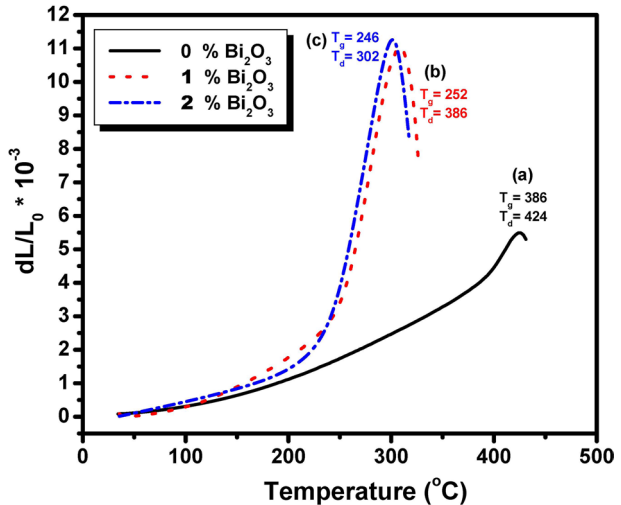


Figure 14 reveals the thermal expansion curves of the undoped and Bi₂O₃-doped LiF-P₂O₅ glasses. The overall behavior is generally similar to that identified with (LiF-B₂O₃) glasses but with slightly lower temperatures.

The collected thermal expansion results can be interpreted on the following parameters (Holloway 1973; Rawson 1980; EzzElDin and ElBatal 1993; Shelby 2005).

- (i) The glass generally expands upon heating like normal solids except few cases. Normal expansion is occurred as a result of the increased extent of the atomic vibrations of the constituents which may include variation in the bond angles and/or bond lengths within the structural groups.
- (ii) The continuous measured increase in the thermal expansion coefficient with temperature is expected and attributed to the collected energy with the temperature rise.

- (iii) The observed lowering of the dilatometric softening temperature with the introduction and increase of Bi_2O_3 is correlated with the known lower melting temperature of Bi_2O_3 and the housing of Bi^{3+} in modifying positions within the parent of doping.

4 Conclusion

Undoped binary lithium fluoroborate ($\text{LiF-B}_2\text{O}_3$) and lithium fluorophosphate ($\text{LiF-P}_2\text{O}_5$) glasses together with samples containing Bi_2O_3 -doped (1 or 2%) were prepared by the normal melting—annealing method. Multiple characterizations of the prepared glasses were carried out through analyzing their optical (UV–visible), FT infrared, and photoluminescence spectra. Optical spectra of the two undoped ($\text{LiF-B}_2\text{O}_3$) and ($\text{LiF-P}_2\text{O}_5$) glasses reveal only distinct UV absorption which is correlated with unavoidable traces of Fe^{3+} ions present as impurities within the chemicals used for the preparation of the glasses. The Bi_2O_3 -doped samples reveal additional near-visible bands which are related to the specific absorption of Bi^{3+} ions. FTIR spectra of the studied glasses reveal vibrational bands which are characteristic for the main structural-forming units (BO_3 , BO_3F) for the borate samples and (PO_4 , PO_3F) groups in the spectra of the ($\text{LiF-P}_2\text{O}_5$) samples. Due to the existence of an unfamiliar high percent of LiF with (50 mol%) in the two host studied glasses, it is assumed that additional vibrational bands of (LiF_4) groups are to be expected in the collected IR spectra. Photoluminescence spectral data indicate the appearance of emission and excitation spectra in connection with the Bi^{3+} ions but are highly defined in host borate than host phosphate glass. This behavior is related to the possible presence of Bi^{3+} ions in different sites. Thermal expansion data indicate that the introduction of Bi_2O_3 decreases the transformation and dilatometric softening temperatures due to the low melting of Bi_2O_3 and the housing of bismuth ions in modifying positions.

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Data availability The authors stated and declare that all data is exist and is available.

Declarations

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval Not applicable.

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