

Study of Structural and Luminescence Properties of Lead Lithium Borophosphate Glass System Doped with Ti Ions

(Struktur dan Sifat Luminesen bagi Sistem Kaca Plumbum Litium Borofosfat Didopkan dengan Ion Ti)

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ABSTRACT

Study of a series of lead lithium borophosphate glass samples was performed to determine the structural and luminescence properties. The glass samples containing the composition of $20\text{PbO-xLi}_2\text{O-30B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5-2\text{TiO}_2$ (where $x = 0, 5, 10, 15, 20$) system were prepared using melt-quenching technique. The $\text{PbO-Li}_2\text{O-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-TiO}_2$ samples were investigated for structural properties using Fourier transform infrared and photoluminescence spectroscopy for studies of luminescence properties. The results from FT-IR showed the presence of trigonal and tetrahedral PO_4 , PO_3 , BO_4 and BO_3 groups within the host network structure. The samples exhibit luminescence emission centered at 420, 482 and 496 nm when excited at 300 nm wavelength. The emission peak at 420 nm were assigned to F center emission and charge-transfer transition of Ti^{4+} ions. The results showed that emission intensity was dependent on lithium contents in Ti-doped lead lithium borophosphate glass composition.

Keywords: Borophosphate glass; FTIR; PL; titanium ions

ABSTRAK

Kajian ini dilakukan ke atas siri sampel kaca plumbum litium borofosfat untuk menentukan struktur dan sifat luminesen. Sampel kaca dengan komposisi $20\text{PbO-xLi}_2\text{O-30B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5-2\text{TiO}_2$ ($x = 0, 5, 10, 15, 20$) telah dihasilkan melalui kaedah sepuh lindap leburan. Sampel kaca telah dikaji dengan menggunakan spektroskopi inframerah transformasi Fourier dan spektroskopi fotoluminesen. Keputusan kajian daripada FT-IR menunjukkan kehadiran kumpulan trigonal dan tetrahedron PO_4 , PO_3 , BO_4 dan BO_3 dalam struktur rangkaian sistem kaca tersebut. Sampel kaca memancarkan luminesen pada 420, 482 dan 496 nm apabila diuja dengan sinaran 300 nm. Puncak pancaran pada 420 nm telah ditakrif sebagai pancaran pusat F dan proses pemindahan caj bagi ion-ion Ti^{4+} . Keputusan kajian menunjukkan bahawa keamatan pancaran bergantung kepada komposisi litium dalam kaca plumbum litium borofosfat dop Ti.

Kata kunci: Kaca borofosfat; FTIR; ion titanium; PL

INTRODUCTION

Borate and phosphate are two of the fundamental network formers in glass sciences. Both phosphate and borate exhibits beneficial physical properties for glass forming such as low melting point, low glass transition temperature and high refractive index. However the fusion of both network formers has been proven to improve the chemical stability of the glass (Jiráček et al. 2007). While extensive studies has been done on borophosphate glass due to its useful properties such as acceptable chemical and physical durability, good transparency and low melting temperature, it has also been researched for optical application as phosphors and laser medium (Kharabe et al. 2008; Sharma et al. 2000). Nonetheless, the hygroscopic nature of borophosphate glass matrices hampered its application and therefore had stimulated further study in incorporating network modifiers using heavy metal and alkali metal. Previous study by Srinivasulu et al. (2012) on $\text{Na}_2\text{O-PbO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ system found this combination to be chemically stable. Other alkali metals such as Li_2O possess the important property for use in fast

ion conductors, waveguides, optical switches and fibers. Meanwhile, heavy metal PbO has been known for its ability to improve chemical and physical durability and also the brilliance of the glasses. Various alkali earth lead borophosphate glass had showed substantial changes in structural and properties of the glasses with compositional change using Raman Spectroscopy and NMR (Mošner et al. 2008). Hence, it is of major interest to study the effects of PbO and Li_2O on borophosphate glass and its influence on structural properties. Such stable glasses are particularly useful in optical glass application. Rare earth doped borophosphate glasses has had successful luminescence and optical properties. But due to scarce supply of rare earth elements, the search for alternative dopant for luminescence enhancement had since been diverted to transition metal ions. Recent studies showed that TiO_2 to be a promising candidate as an activator, emitting photoluminescence in the blue region (Sato et al. 2005). Moreover, the works of Koudelka et al. (2003) proven that TiO_2 increases the bond strength within the glass network hence improving the chemical durability.

The objective of this study was to prepare and analyze a series of $\text{Li}_2\text{O-PbO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glass samples for the purpose of structural and luminescence study due to compositional change, primarily the effect of different Li_2O mol% and P_2O_5 mol%. Structural investigation was carried out using FT-IR spectroscopy, while photoluminescence spectrophotometer is used for luminescence study.

EXPERIMENTAL DETAILS

$\text{PbO-Li}_2\text{O-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-TiO}_2$ glass system with the composition of $20\text{PbO-xLi}_2\text{O-30B}_2\text{O}_3\text{-(50-x)P}_2\text{O}_5\text{-2TiO}_2$ (where $x = 0, 5, 10, 15, 20$) were synthesized in batches of 25 g using conventional melt quenching technique. Reagent grade PbO , H_3BO_3 , H_3PO_4 , Li_2O and TiO_2 were weighed and mixed in porcelain crucibles, Table 1 summarizes the sample composition. Mixtures were then allowed to react before calcined at 350°C for 30 min to remove moisture and then melted in crucible at 1200°C for 15 min in an electric furnace. The obtained melt were immediately quenched by pouring the molten on a stainless steel plate and immediately pressed with second stainless steel plate to form amorphous phased solids. The glass samples were collected and allowed to gradually cool to room temperature.

FT-IR spectra of glass samples were recorded at room temperature in the range of $2000\text{-}400\text{ cm}^{-1}$ using Perkin Elmer Spectrum One IR spectrometer using KBr technique. Before measurement, the powdered samples were mixed thoroughly with IR spectroscopy transparent KBr and then compressed into a homogeneous disc. Photoluminescence were characterized at room temperature using Perkin Elmer LS55 Luminescence Spectrophotometer. Samples were excited at wavelength around 300 nm and emission spectra from 200-900 nm were collected. Emission spectra were corrected to present only emission peaks without excitation.

RESULTS AND DISCUSSION

Homogeneous glass sample were prepared and found to be stable (non-hygroscopic). Clear and transparent sample was observed in lithium-less composition. Samples with lithium content were seen milky white with slight yellowish dye in lithium-rich composition.

Figure 1 shows the infrared absorption spectra of the lead lithium borophosphate glass doped with titanium ions.

Going up the figure are samples with decreasing lithium content and increasing phosphate content. IR spectra show vibrational modes mainly active in three regions around 550 cm^{-1} narrow bands, $850\text{-}1200\text{ cm}^{-1}$ and $1200\text{-}1400\text{ cm}^{-1}$ wide bands. Few confined absorption valley were found along the shoulders of major absorption band around $1635, 1384, 710$ and 450 cm^{-1} . The IR band assignments allocations were comprised of past reports on various borate, phosphate and borophosphate glasses (Almeida et al. 2001; Babu et al. 2012; Carta et al. 2008; Coelho et al. 2012; El-Batal et al. 2012; Mosner et al. 2010; Yew et al. 2012).

IR spectral features of borate is commonly known to show vibration modes around 700 cm^{-1} , $800\text{-}1100\text{ cm}^{-1}$ and $1200\text{-}1500\text{ cm}^{-1}$, which corresponds to the vibrational mode of bridging oxygen in B-O-B groups, tetrahedral BO_4 units and trigonal BO_3 units, respectively. Vibrational broad bands around $1170\text{-}1450\text{ cm}^{-1}$ are assigned to B-O stretching vibrations of BO_3 units in penta-, ortho-, pyro- and metaborate groups. Bands near the $708\text{-}715\text{ cm}^{-1}$ corresponds to the bending vibrations of bridging oxygen in B-O-B bond from pentaborate groups. According to Babu et al. (2012) distinct absorption at 1384 cm^{-1} was associated to the vibrations of bridging oxygen atoms between BO_3 and BO_4 groups. The modes of B-O stretching vibrations of BO_4 unit in di-, tri-, tetra- and pentaborate groups were correlated to the wide absorption bands around $850\text{-}1200\text{ cm}^{-1}$ (Almeida et al. 2001; Coelho et al. 2012; El-Batal et al. 2012). The positions of $850\text{-}1200\text{ cm}^{-1}$ were attributed to the vibration modes of terminal P-O and PO_3 as referred to Carta et al. (2008). Symmetric stretching and asymmetric bending vibrations of Pb-O were assigned to the similar region of 960 and 1090 cm^{-1} as pointed out by Coelho et al. (2012). This implies the sharing vibration between PO, PO_3 , BO_4 and Pb-O units in the $850\text{-}1200\text{ cm}^{-1}$ region. The narrow band in the low frequency region nearby 550 cm^{-1} was assigned to deformation vibration modes of P-O in PO_4 units. As for the weak absorption band located around 710 cm^{-1} , they were correlated to the symmetric stretching vibration of PO in P-O-P bonds (Almeida et al. 2001; Mosner et al. 2010). As reported by Almeida et al. (2001) bands positioned near 1150 cm^{-1} were corresponding to the stretching vibrations of non-bridging oxygen from [P-O]. The presence of lithium cations vibrational modes were detected in the far-infrared band in the range of 450 cm^{-1} (El-Batal et al. 2012). Characteristic feature of bending vibration mode from OH group were associated

TABLE 1. Glass sample composition table

Sample	Glass composition (mol%)				
	B_2O_3	Li_2O	P_2O_5	PbO	TiO_2
Li1	30	20	30	20	2
Li2	30	15	35	20	2
Li3	30	10	40	20	2
Li4	30	5	45	20	2
Li5	30	0	50	20	2

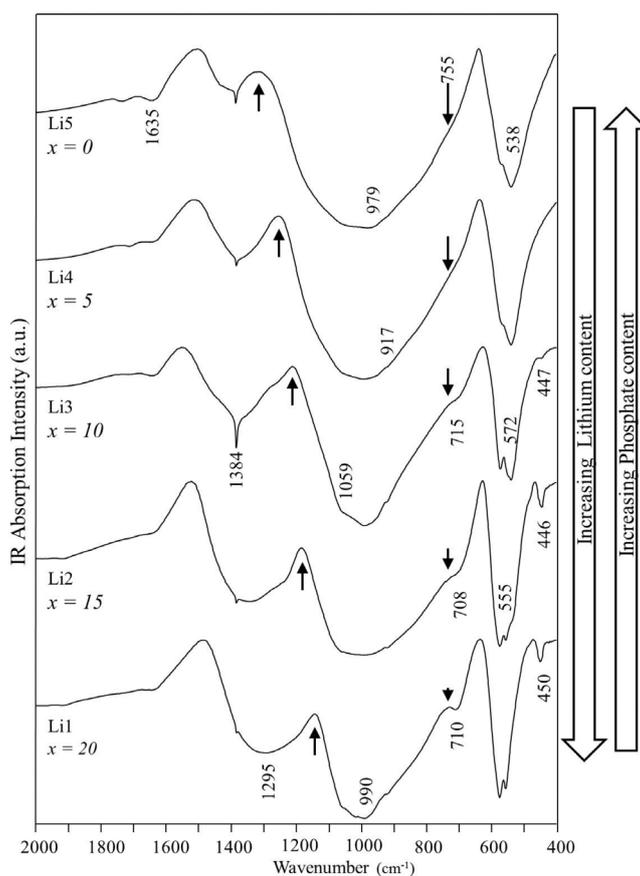


FIGURE 1. IR Absorption spectra

to the vibration mode around 1635 cm^{-1} and the rest of the absorption band extending to 2000 cm^{-1} were also due to water (Babu et al. 2012). Summary of the observed IR absorption spectra and its band assignments are described in Table 2.

It was observed that with increasing phosphate content, broad absorption band $920\text{--}1070\text{ cm}^{-1}$ broaden gradually to $850\text{--}1200\text{ cm}^{-1}$, while the broad band located at $1170\text{--}1400\text{ cm}^{-1}$ narrow steadily to $1380\text{--}1450\text{ cm}^{-1}$. This shifting is illustrated by a left-shifting arrow positioned on the ‘hump’ separating these neighboring broad bands. This suggests phosphate in the form of PO_3 units increases in the network structure while BO_4 units were being replaced, showing dominance of phosphate in the glass structure with higher P_2O_5 content. In conjunction, symmetric stretching vibration of PO in P-O-P bonds assigned to the absorption near 755 cm^{-1} were seen strengthen as phosphate content increased, supporting the postulate that phosphate were taking over the glass network. Based on the data, one could also propose the conversion of BO_3 units to BO_4 unit when phosphate content is increased and borate dominance reduces. This is shown in the weakening of BO_3 bands in $1200\text{--}1500\text{ cm}^{-1}$ while strengthening of BO_4 bands in $850\text{--}1100\text{ cm}^{-1}$. Specific IR valleys detected at 1384 cm^{-1} were typical vibration mode of bridging oxygen atoms between BO_3 and BO_4 groups. The vibration mode were seen weak in sample Li1 and Li2, then strong absorption in

Li3 after which it weakens in Li4 and Li5. This shows the conversion of BO_3 units to BO_4 through bridging oxygen atoms between BO_3 and BO_4 groups, where P_2O_5 content at 40 mol%, the intermediate state of conversion were seen to be the most intense.

IR spectra also exposed the formation of Pb-O bonds in the glass structure. Finally vibration mode in the far-infrared region of 450 cm^{-1} gradually seen as lithium content increases. Such observation suggest the role of Li^+ cations slowly involved in the glass forming network in Li-rich in borophosphate glass system.

Figure 2 shows the typical emission spectra with excitation wavelength at 300 nm of the Ti doped lead lithium borophosphate glass with changing content of lithium and phosphate. The PL spectra displayed two prominent emissions primarily around 420, 482 and 496 nm. Blue-green emission bands in the 482 and 496 nm is associated to the energy transition of $z^4\text{D}^0_{7/2} \rightarrow b^2\text{D}^0_{3/2}$. Also note the blue emissions near 420 nm appear in all samples consistently, it is interesting to note the intensity of 420 nm peak is increasing with lower lithium concentration. Table 3 summarizes energy level transition of the calculated and experimental wavelength.

It was shown by several researchers the blue emission at 420 nm of Ti-doped substance was mainly corresponding to the F defect center. Oxygen vacancy and anions vacancy of host lattice is known to promote recombination process

TABLE 2. Assignments of IR absorption bands

Wavenumber (cm ⁻¹)	FT-IR assignment	Sample				
		Li1	Li2	Li3	Li4	Li5
420-460 (El-Batal et al. 2012)	Vibrations of lithium cations	450	446	447		
550 (Mosner et al. 2010; Almeidaa et al. 2001)	Deformation vibration modes of P-O in PO ₄ units	556	555	539	539	538
700 (El-Batal et al. 2012; Almeidaa et al. 2001; Coelho et al. 2012; Yew et al. 2012)	Bending vibrations of bridging oxygen in B-O-B from pentaborate groups	710	708	715		
700-750 (Almeidaa et al. 2001; Mosner et al. 2010)	Symmetric stretching vibration of PO in P-O-P bonds				755	756
850-1100 (El-Batal et al. 2012; Almeidaa et al. 2001; Coelho et al. 2012)	B-O stretching vibrations of BO ₄ units in various borate rings (di-, tri-, tetra-, pentaborate groups)	920 -1070	850 -1100	920 - 1060	850 - 1140	850 - 1200
900-1100 (Carta et al. 2008)	Vibration of terminal P-O and PO ₃					
960 (Coelho et al. 2012)	Symmetric stretching vibrations of Pb-O					
1090 (Coelho et al. 2012)	Asymmetric bending vibrations of Pb-O					
1150 (Almeidaa et al. 2001)	Stretching vibrations of non-bridging oxygen from [P-O]				1135	1150
1200-1500 (Coelho et al. 2012; El-Batal et al. 2012; Almeidaa et al. 2001)	B-O stretching vibrations of BO ₃ units in various borate chains and rings (Penta-, ortho-, pyro-, metaborate groups)	1170- 1400	1220- 1450	1300- 1450	1300- 1400	1380- 1450
1384 (Babu et al. 2012)	Vibrations of bridging oxygen atoms between BO ₃ and BO ₄ groups	1383	1384	1384	1384	1384
1637 (Babu et al. 2012)	Bending vibration mode of OH group	1635	1637	1635	1639	1647

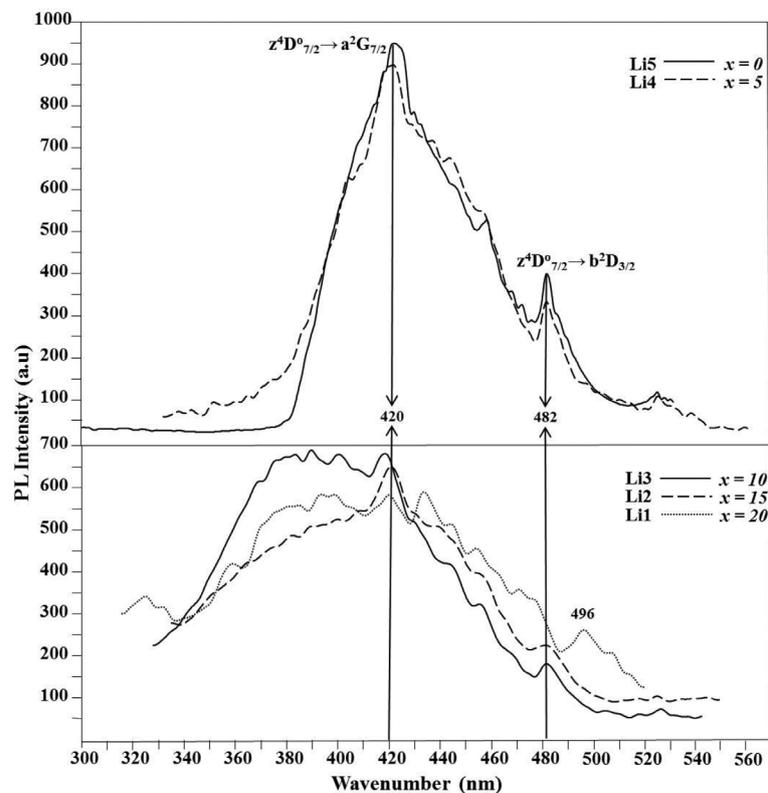
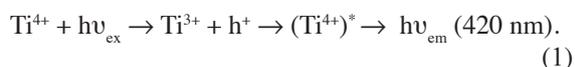


FIGURE 2. Photoluminescence emission spectra

TABLE 3. Calculated and experimental transition energy levels of Ti²⁺ ions in lead lithium borophosphate glass

Transition	Calculated wavelength (nm)	Experimental wavelength (nm)	Sample
$z^4D^o_{7/2} \rightarrow a^2G_{7/2}$	420	420	Li1
		422	Li2
		419	Li3
		421	Li4
		420	Li5
$z^4D^o_{7/2} \rightarrow b^2D_{3/2}$	496	482	Li1
		482	Li2
		482	Li3
		482	Li4
		496	Li5

of electrons trapped in F centers and holes in valence band, causing radiative emissions (Conga et al. 2007; Mikhailik et al. 2011; Tsai et al. 2011). Titanium ions (Ti³⁺, Ti⁴⁺) were reported to create more defect centers and anions vacancy, hence enhances emission. Furthermore, charge-transfer transitions of Ti⁴⁺ were reportedly produce distinct luminescence peak around 420 nm (Sato et al. 2005; Tsai et al. 2011). Explanation adapted over the decades by many researchers (Mikhailik et al. 2011; Molnar et al. 2001; Page et al. 2010) assign the luminescence peak due to excitation through electrons from the valence band is transferred to Ti⁴⁺, creating Ti³⁺ and a hole in the valence band. Followed by the de-excitation of these ions creates the luminescence, according to the sequence below:



FTIR data in Figure 1 shows evidence of Li⁺ involvement in the host lattice increases as the Li content is increased, while the PL peak intensity of 420 nm is decreased. Consequently, presented data permits one to propose that the presence of Li cations reduces the emission at 420 nm which is associated to Ti⁴⁺ charge-transfer transition. We believed that at high Li content above 5 mol%, Li⁺ ions starts to compete oxidation state with Ti⁴⁺. Hence reducing the population of Ti⁴⁺, possibly resulting in less F centers formation and also reduced charge-transfer transition of the model stated above.

CONCLUSION

Glassy samples of lead lithium borophosphate system were successfully prepared using conventional melt quenching method. Infrared absorption and photoluminescence spectra of the samples with increasing Li content were obtained using FTIR and PL spectroscopy. Samples with Li content were found to be milky white coloured with slight yellowish dye as Li content increase. Structural study by FTIR shows evidence of random phosphate and borate groups in the glass structure. IR spectra confirm phosphates

and borates as the main network former in the form of PO₄, PO₃, BO₄ and BO₃ groups. However Pb-O was also detected to be forming the glass structure, as well as Li cations in high Li contained samples. Borates in the glass structure were found to be replaced by PO₃ unit, showing dominance of phosphate in the glass network when phosphate content is increased. Also, boron anomaly effects were exhibited when conversion of BO₃ units to BO₄ units occurs with increasing P₂O₅ content. The Ti-doped samples showed dominant luminescence emission main in 420, 482 and 496 nm. The presence of Ti⁴⁺ ions were identified as the emitting centre for 420 nm through recombination process between F centers and holes in valence band and charge-transfer transition of Ti⁴⁺ ions. Furthermore, variations of Li content in the composition result in change of intensity of the 420 nm emission. The study of this sample series is still on going and is planned for characterization using other spectroscopy technique. Future work of similar host matrix occupying different transition metal element as dopant is recommended.

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