



Structural study on lithium-calcium borophosphate glasses doped with transition metal ions using infrared spectroscopy

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Abstract

This paper reported on the structural properties of Lithium-Calcium borophosphate glasses. The glasses were prepared through melt quenching technique and studied in two compositional series which was $25\text{Li}_2\text{O}:25\text{CaO}:(x)\text{B}_2\text{O}_3:(50-x)\text{P}_2\text{O}_5$ where $0 \leq x \leq 50$ mole % and $25\text{Li}_2\text{O}:25\text{CaO}:30\text{B}_2\text{O}_3:20\text{P}_2\text{O}_5:(y)$ with y was the doped materials (Cr^{2+} , Mn^{2+} and Fe^{2+} ions). The aims of this work were to investigate the vibration mode about the local order around phosphorus tetrahedral structures and the boron coordination changed from trigonal to tetrahedral structures. Their basic properties were determined and their structure was studied by Fourier Transform Infrared spectroscopy (FT-IR). FT-IR spectroscopy analysis of the sample revealed vibration mode related to the characteristic phosphate bonds especially P-O-P, O-P-O and P-O-B. Structural studies were devoted to the investigation of changes in boron coordination in the dependence on changes in B_2O_3 or P_2O_5 ratio in the borophosphate glasses. Besides that, the high frequency bands corresponding to stretching vibration become broader, less distinct and overlap each other with an increasing B_2O_3 content and decreasing P_2O_5 content. The decrease in the strength of the vibrations of the non-bridging PO_2 groups seems to indicate a progressive increase in the connectivity of the glass with increasing B_2O_3 content. It was likely that this connectivity was due to the formation of P-O-B links at 940cm^{-1} , which replaced the vibration mode P-O-P. The glasses doped with Cr^{2+} , Mn^{2+} and Fe^{2+} ions and the undoped glass were almost the same. The addition of doped glasses shows that the band was slightly shifted to the right side compare to the undoped glass. Besides that, it shows that the intensity of the bands described above increased and the position of the main bands shift to the lower frequencies. It was obviously shows that the increasing of B_2O_3 content and decreasing the P_2O_5 content causes the boron coordination changes from trigonal to tetrahedral and the basic units change from BO_3 to BO_4 . The addition of doped Cr^{2+} , Mn^{2+} and Fe^{2+} ions to the glass slightly shift to the right side compared to the undoped glass.

Keywords: Borophosphate glass; lithium; calcium; transition metal ions; fourier transform infrared spectroscopy.

1. Introduction

Glass is an amorphous (non-crystalline) solid material. Glasses are typically brittle, and often optically transparent. B₂O₃ is one of the most common glass forming oxides and has been incorporated with various types of modifier metal oxide in order to attain the desired physical and chemical properties. Borate glasses have the advantageous property of good thermal shock resistance, which can be utilized for sealing to metals.

Recently, phosphate based glasses have been interest due to their several special properties such as large thermal expansion coefficients, low melting temperatures, solubility, etc.[1, 2]. Although phosphate glasses have a wide range of technical applications, it is well known that a pure phosphate network is very hygroscopic and therefore it is not very stable [3]. Therefore, it has been demonstrated that the addition of B₂O₃ to a phosphate network in order to improves the chemical durability as well as the thermal and mechanical stability of pure phosphate glass [4, 5]. The basic units of pure amorphous phosphate glasses are PO₄ tetrahedra linked through covalent bridging oxygen, whereas the basic units of pure amorphous borate glasses are trigonal BO₃ groups. Borophosphate glasses are among the multicomponent glasses studied for some interesting applications. Zinc-calcium borophosphate glasses were studied as candidates for applications as low melting glass solders or glass seals [6]. These glasses are advantages due to their properties can be effectively controlled by changing their composition.

In recent years, glasses doped with transition metal ions have attracted a great deal of attention because of their memory and photoconductivity properties. They find potential applications in solid state laser luminescent solar energy concentrators (LSCS) and fiber optic communications devices [7]. Much research has been done on the optical effects associated with transition elements in glass, primarily because these elements are useful coloring agents.

This paper is devoted to study the interaction with Lithium Calcium borophosphate was investigated in the compositional series of 25Li₂O:25CaO:*x*B₂O₃:(50-*x*)P₂O₅ and sample doped with Cr²⁺, Mn²⁺ and Fe²⁺ ions. The aim of the present work is to investigate the vibrational mode about the local order around phosphorus tetrahedral structures and the boron coordination change from trigonal to tetrahedral structures due to the incorporation of mix alkali and alkali earth cation (Li, Ca) oxide using FT-IR spectroscopy.

2. Experimental Procedure

The investigated Li-Ca borophosphate glasses have the synthetic composition 25Li₂O:25CaO:(*x*)B₂O₃:(50-*x*)P₂O₅ glasses where 0≤*x*≤50 mole % and 25Li₂O:25CaO:30B₂O₃:20P₂O₅ doped with 1 mole % of Cr²⁺, Mn²⁺ and Fe²⁺ ions were prepared from Li₂O, CaO, B₂O₃ and H₃PO₄ (85% liquid) by melt quenching technique. Well mixed powders containing the exact amounts of the raw materials were calcined at 200°C for 30 minutes and 400°C for another 30 minutes to release water and melted in a porcelain crucible at 1100°C for another 15 minutes in an electric furnace. Finally, the melts were then poured onto a stainless steel plate and press quickly with another stainless steel plate.

The structural of the prepared samples were analyzed using analytical tools such as FT-IR spectroscopy. Measurements were carried out using KBr pellets method. The infrared spectra of the glasses had been recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer over the range of wavenumber 400-4000 cm⁻¹ at room temperature using 100 scans at 4 cm⁻¹ resolution.

3. Results and Discussion

Figure 1 shows that the FT-IR spectra of $25\text{Li}_2\text{O}:25\text{CaO}:(x)\text{B}_2\text{O}_3:(50-x)\text{P}_2\text{O}_5$ with x varies in the range $0 \leq x \leq 50$ mole %. The infrared spectrum of the $25\text{Li}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ glass contains 1200 cm^{-1} , 970 cm^{-1} and 940 cm^{-1} . The band at 940 cm^{-1} can be ascribed to the asymmetric stretching vibration of the bridging oxygen atoms in the P-O-P bonds, $V_{\text{as}}(\text{P-O-P})$. Several previous studies [8] have shown that the band corresponding to the stretching vibration of doubly bonded oxygen could be found in the frequency range $1200-1390\text{ cm}^{-1}$. Whereas the other broad band at 1200 cm^{-1} belongs to the asymmetric vibrations, $V_{\text{as}}(\text{PO}_2)$, of the non-bridging oxygen atoms in the phosphate chains. The other band in the infrared spectra at 970 cm^{-1} is ascribed to the symmetrical stretching vibration, $V_{\text{s}}(\text{PO}_2)$. The band at 750 cm^{-1} is assigned to the symmetric stretching vibrations, $V_{\text{s}}(\text{P-O-P})$, of the bridging oxygen atoms. With increasing B_2O_3 content and decreasing P_2O_5 content, a series of changes in the spectra can be observed. The vibrations $V_{\text{as}}(\text{PO}_2)$ at 1200 cm^{-1} become broader and weaker. The decrease in the strength of the vibrations of the non-bridging PO_2 groups seems to indicate a progressive increase in the connectivity of the glass with increasing B_2O_3 content. It is likely that this connectivity is due to the formation of P-O-B links, which replace the P-O-P bonds. The vibrations of the bridging P-O-P groups, $V_{\text{as}}(\text{P-O-P})$, at 940 cm^{-1} decrease and are almost undetectable in the sample with the highest B_2O_3 content. The formation of P-O-B links as B_2O_3 is added is suggested by the broadening of the bands in the region of 940 cm^{-1} (which is due exclusively to the B-O stretching of the BO_4 units) [9]. As the B_2O_3 content increases, new bands appear at around 1100 , 1270 and 1400 cm^{-1} . At around 1100 cm^{-1} is assigned to the vibration of some boron atoms attached to NBO in the form of BO_4 vibration. Whereas at the band 1270 cm^{-1} is representing to the B-O stretching vibration of BO_3 unit in metaborate and orthoborate groups. The band at 1400 cm^{-1} is assigned to the vibration of BO_4 groups.

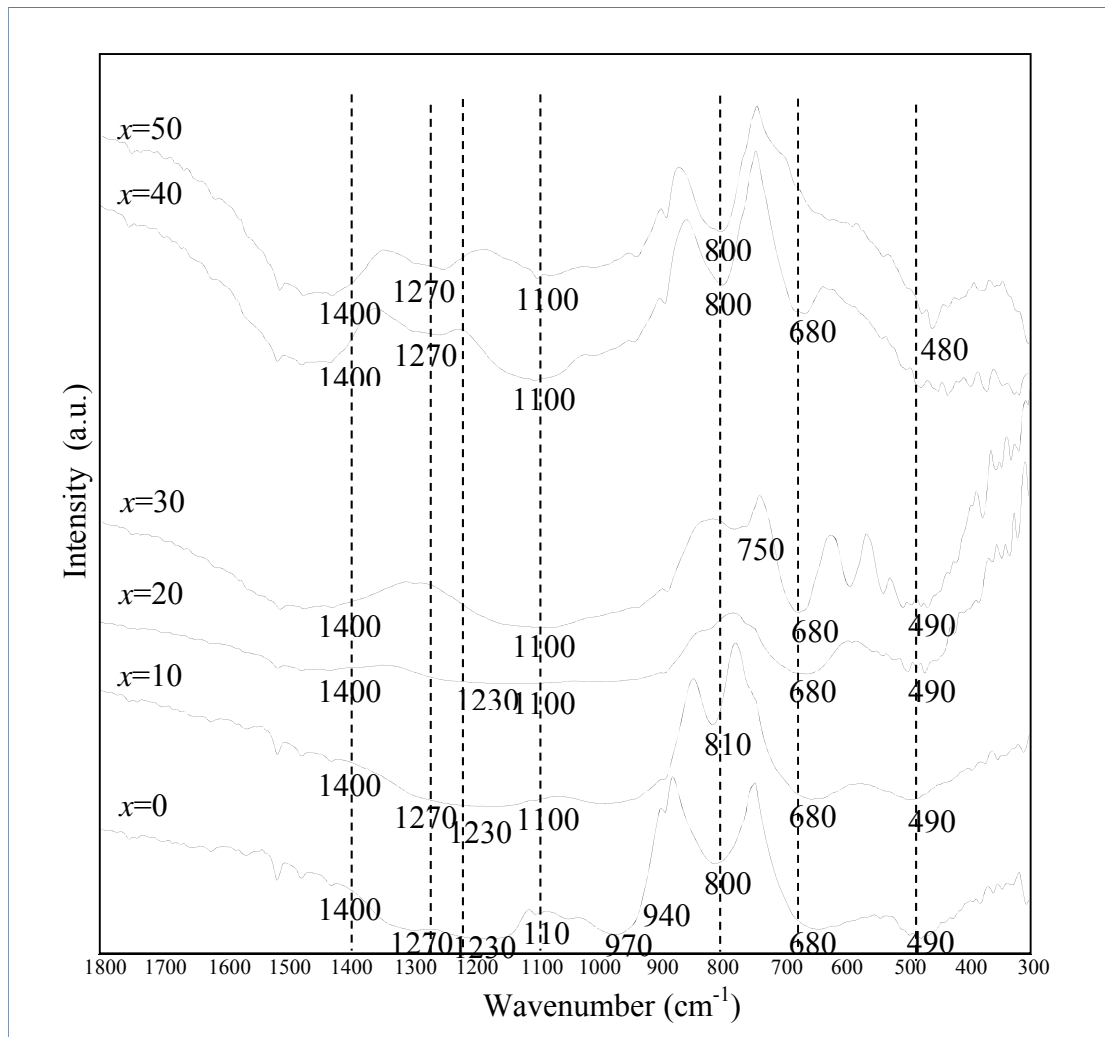


Fig. 1: FT-IR spectra of $25\text{Li}_2\text{O}:25\text{CaO}:(x)\text{B}_2\text{O}_3:(50-x)\text{P}_2\text{O}_5$ with x varies in the range $0 \leq x \leq 50$ mole %.

Fig. 2 shows that FT-IR spectrum of $25\text{Li}_2\text{O}:25\text{CaO}:30\text{B}_2\text{O}_3:20\text{P}_2\text{O}_5:(y)$ with y for Cr^{2+} , Mn^{2+} and Fe^{2+} and $25\text{Li}_2\text{O}-25\text{CaO}-30\text{B}_2\text{O}_3-20\text{P}_2\text{O}_5$ undoped glass. From Fig. 2, the doped and undoped samples are almost the same. There are not many changes for the doped and undoped samples. There is a band at around 510 cm^{-1} for the doped and undoped glass which is assigned to the B-O-B bond bending vibrations, covalent Ca-O bond vibrations. Another band is presence at about 600 cm^{-1} for the doped and undoped glass was attributed to B-O-B bending vibration. The addition of doped Cr^{2+} , Mn^{2+} and Fe^{2+} ions to the $25\text{Li}_2\text{O}-25\text{CaO}-30\text{B}_2\text{O}_3-20\text{P}_2\text{O}_5$ glass matrix shows that the band is a slightly shift to the right side compare to the undoped glass. For the undoped glass, the band at 770 cm^{-1} shift to the lower band (710 cm^{-1}) after doped with Cr^{2+} , Mn^{2+} and Fe^{2+} . This is assigned to the symmetric stretching vibrations, $V_s(\text{P-O-P})$ of the bridging oxygen atoms. The other band in the infrared spectra at 1050 cm^{-1} is ascribed to the symmetrical stretching vibration, $V_s(\text{PO}_2)$. It shifted around 50 cm^{-1} compared to the undoped glass. Besides that, the band for the glass at 1150 cm^{-1} doped with Cr^{2+} , Mn^{2+} and Fe^{2+} ions becomes narrow. The band at 1450 cm^{-1} for the doped and undoped glass is assigned to antisymmetrical stretching vibration with three (NBO_3) of B-O-B groups. The glass doped with Cr^{2+} , Mn^{2+} and Fe^{2+} ions shows that the intensity of the bands described above increase and the position of the main bands shifts to the lower frequencies.

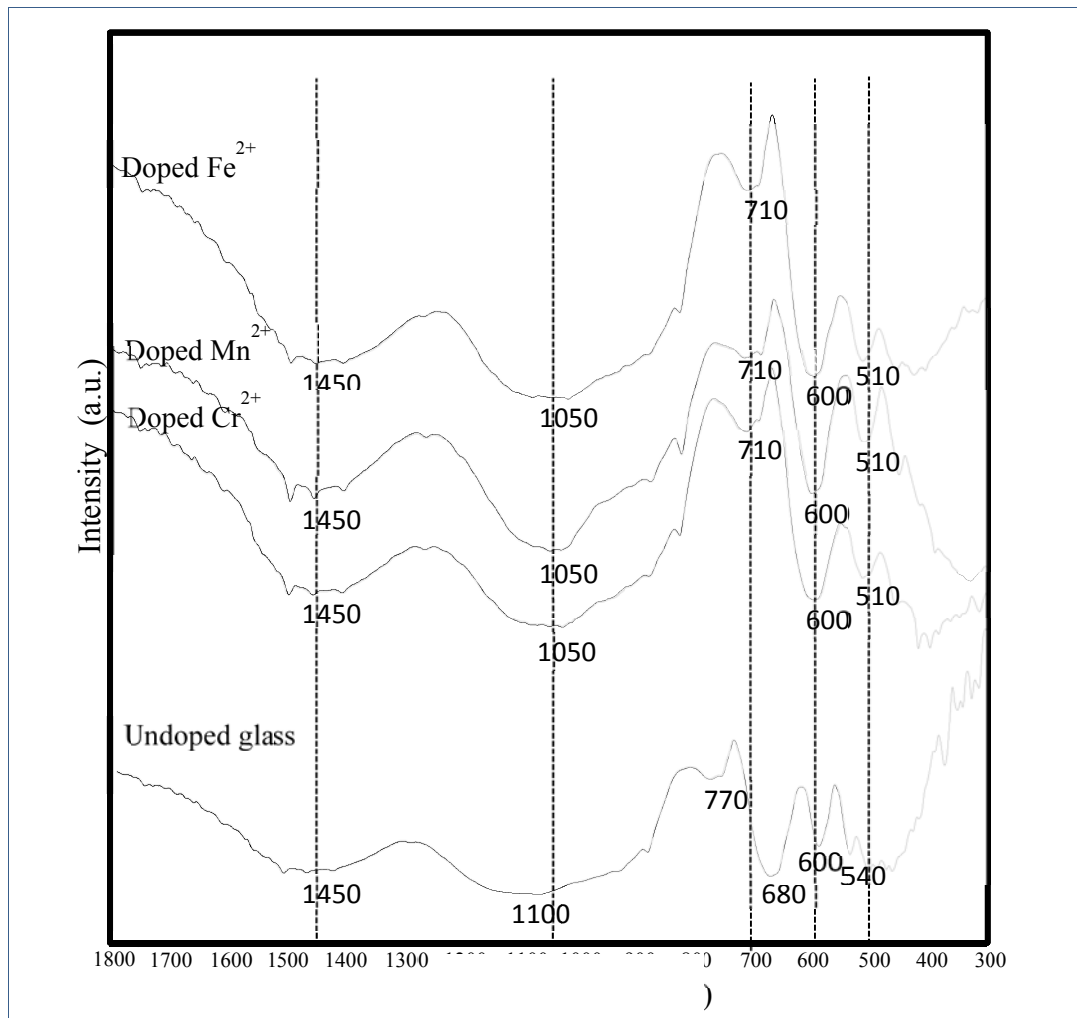


Fig. 2: FT-Infrared spectra of 25Li₂O:25CaO:30B₂O₃:20P₂O₅: (y) with y for Cr²⁺, Mn²⁺ and Fe²⁺ and 25Li₂O:25CaO:30B₂O₃:20P₂O₅ undoped glass.

4. Conclusion

Homogeneous glasses can be prepared in the series 25Li₂O:25CaO:(x)B₂O₃:(50-x)P₂O₅ for x=0 mole % to 50 mole % and 25Li₂O:25CaO:30B₂O₃:20P₂O₅:(y) with y is the doped materials in transition metals such as Cr²⁺, Mn²⁺ and Fe²⁺ ions. Borophosphate glasses offer the possibility of changeable structure and properties according to changing their composition. It shows that the changes in the boron coordination in the dependence on changes in B₂O₃ or P₂O₅ ratio in the borophosphate glasses. Generally, the replacement of P-O-P bonds by P-O-B bonds in the investigated glasses is accompanied by an increase in the chemical durability with increasing B₂O₃ content. Up to a displacement B₂O₃ quantity above 30 mole %, it shows that the structure of the glass consisted of BO₃ and BO₄ tetrahedra. Overall, the high frequency bands corresponding to stretching vibration become broader, less distinct and overlap each other with an increasing B₂O₃ content and decreasing P₂O₅ content.

Acknowledgments

The authors would like to thank Phosphor Research Group, Physics Department, UTM for the preparation of equipment, The Ministry of Higher Education (MOHE), The Ministry of Science, Technology and Innovation (MOSTI) and Universiti Teknologi Malaysia, Research University Grant Project Number Q.J130000.2626.04J29 for their financial support.

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