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Vibrational Studies of Zinc Antimony Borophosphate Glasses Doped Rare Earth

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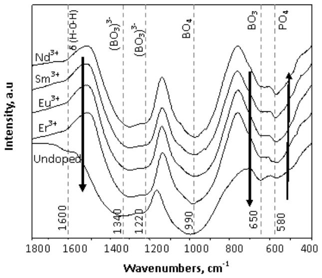
Graphical abstract



Abstract

Zinc antimony borophosphate glasses has been determined for [$10P_2O_5$ $–40B_2O_3$ $–xSb_2O_3$ $–(50-x)ZnO$] and composition of [$10P_2O_5$ – $40B_2O_3$ $–40Sb_2O_3$ $–10ZnO$] has been doped with 1 mol% of rare earth (Eu, Nd, Sm, Er). The functions of compositional changes on their structural features were examined using X-Ray Diffraction (XRD) to detect the amorphousity phase present. While Fourier Transform Infrared (IR) Spectroscopy were used to identify the presences of vibrational modes and band assignments of phosphate, borate, antimony, zinc and Rare earth ion in the system. XRD results expose that crystalline phase changes with different amount of zinc and antimony substitution. Hydroxyl group absorption also vary due to this composition changes and clearly shown in IR spectroscopy in the ranges 1400-4000 cm^{-1}. Result of IR spectroscopy indicated that bands around 1440 cm^{-1} and 760 cm^{-1} was ascribed to the v_{as}(B-O-B) and v_s(P-O-P) vibration respectively. The changes of this vibration indicated that P-O-B linkage was formed near 660 cm^{-1}. The modification of zinc antimony borophosphate glasses with rare earth was studied and showed present of rare earth ion in the glass system does not change the structural features.

Keywords: Glass; borophosphate; quaternary system; infrared spectroscopy; raman spectroscopy

Abstrak

Kaca zink antimoni borofosfat ditentukan bagi [$10P_2O_5$ $–40B_2O_3$ $–xSb_2O_3$ $–(50-x)ZnO$] dan pada komposisi [$10P_2O_5$ – $40B_2O_3$ $–40Sb_2O_3$ $–10ZnO$] kaca telah didop dengan 1 mol% nadir bumi (Eu, Nd, Sm, Er). Kesan dari perubahan komposisi terhadap ciri-ciri struktur sampel telah diperiksa menggunakan Difraktometer Sinar X-Ray (XRD) untuk mengesan fasa polihablur. Manakala Inframerah (IR) Spektroskopi digunakan untuk mengenalpasti mod getaran dalam kumpulan fosfat, borat, antimoni, zink dan ion nadir bumi di dalam sistem. Keputusan XRD mendapati bahawa fasa kristal berubah seiring perubahan komposisi zink dan antimoni. Perubahan terhadap komposisi juga menunjukan perubahan terhadap kumpulan hidroksil dan boleh dilihat dengan jelas dalam spektroskopi IR pada julat 1400-4000 cm^{-1}. Keputusan IR juga menunjukkan bahawa terdapat mod getaran bagi kumpulan vas (BOB) pada frekuensi 1440 cm^{-1} dan kumpulan vs (POP) di sekitar 760 cm^{-1}. Perubahan keamatan mod getaran ini menunjukkan bahawa hubungan P-O-B telah terbentuk berhampiran 660 cm-1. Pengubahsuaian gelas borofosfat zink antimoni dengan nadir bumi telah dikaji dan menunjukkan kehadiran ion nadir bumi dalam sistem kaca tidak mengubah ciri-ciri struktur.

Kata kunci: Kaca; borofosfat; sistem kuatenari; spektroskopi inframerah; spektroskopi raman

■1.0 INTRODUCTION

Considering the advantages of borate and phosphate glass, it can be expected to facilitate tailoring of the physical and chemical properties of interest for specific technological application. Phosphate glasses are important material due to their high thermal expansion coefficient and glass transition temperature make it suitable for solid state batteries and technological application of solid state ionic as electrolytes [1]. Besides, borate glasses can be a great hosts for a glass system because they can accommodate large concentrations of active ions and offer an important range of compositional possibilities such as metaborate, pentaborate, orthoborate, diborate, and pyroborate same as phosphate glasses which also offer an important opportunity to investigate fundamental structural about glass, because their large range of glass forming compositions.

Unfortunately, phosphate and borate alone is not a stable compound for a glass but the chemical durability of phosphate glasses can be improve and stabilize by the incorporation of boron oxide into the structural network as a glass formers and modifier so that borophosphate glasses have acceptable chemical durability compare to pure borate and pure phosphate [2]. The combination of this two glass formers P_2O_5 and B_2O_3 posses a variety of other useful properties. In fact, the presence of P_2O_5 in the borate glasses improves the glass quality when modified with rare earth [3].

Borate and phosphate glasses doped with various rare earths have been studied mainly due to their non linear optical properties in recent years. Its means only a few researches were carried out about borophosphate glasses dope rare earth. One of the primarily spectral studies of doped rare earth oxide in sodium borophosphate glass has been conducted and the result showed interesting features about the split band. In fact, they only focus on ternary borophosphate system. Therefore, the presence study is done in order to know the structural features of antimony zinc borophosphate (ZnO-Sb_2O_3- B_2O_3-P_2O_5) modified by with various rare earth such as Er^{3+}, Eu^{3+}, Nd^{3+} and Sm^{3+} ions. The effect of replacement of ZnO by Sb_2O_3 on the glass structure was also investigated. The information about structural units present in this glass has been obtained from Infrared Spectroscopy and XRD techniques.

■2.0 EXPERIMENTAL

The glass sample in the series of 10 P_2O_5-40B_2O_3-(x)Sb_2O_3-(50-x)ZnO: (x=0, 10, 20, 30, 40, 50) using H_3PO_4, H_3BO_3 acid, Sb_2O_3 and ZnO powder as the raw materials has been successfully prepared by melt quenching technique. Six glass samples were prepared based on 30g batch mixture. However, only one sample with successive physical properties such as high stability and crystal clear borophosphate glass are chosen will be doped with 1% of rare earths such as Eu, Er, Nd, and Sm to study their structure properties.

Based on previous research, they were found that homogeneous glasses were formed on P_2O_5 rich side of the system with 0-30 mol% B_2O_3 but become white after a few hours due to hygroscopic nature of phosphate [4]. Thus, the content of P_2O_5 in the borophosphate glass system for present study was fixed to 10 mol% and B_2O_3 was fixed at 40 mol%.

X-ray diffraction (XRD) is used to identify the phase of the glass sample. For this experiment, the amorphous/crystalline phase of the sample was determined using Siemens Diffractometer D5000 system operating at 40kV, 30mA at room temperature in Faculty of Mechanical Universiti Teknologi Malaysia with CuK_α radiation (λ = 1.54 Å). Diffraction pattern were collected at angle 2θ range from 10^o – 80^o and the steps size is 0.050^o with 2s time per step. In order to reveal the phase compositions, the bulk sample were prepared by grind it into a relatively fine powder form.

Potassium bromide KBr pellet technique was used to study the molecular structure of a glass sample by obtaining their infrared absorption spectra. Bulk sample of glass sample were grind in a clean mortar to a fine powder and has been mix homogenously at ratio of 1:100 with KBr powder before the mixture immediately pressed with a pressure of 5 ton per square inch to yield a approximately thickness of 1.0mm transparent pellet. The samples then examined using a Perkin-Elmer 1710 Fourier Transform Infrared (FTIR) Spectrometer at the Chemical department, Faculty of Science, Universiti Teknologi Malaysia. The examination has done at room temperature and all the infrared spectra of the glasses were record over the range of wavenumber 1800-400cm^{-1} using 100 scans at 4 cm^{-1} resolution.

■3.0 RESULTS AND DISCUSSION

Figure 1 represent the XRD pattern of powdered glass samples measured at room temperature. A broaden diffraction lines reveal typical characteristic pattern for amorphous component. Despite of amorphous component, diffraction line observed for sample containing less than 30 mol% Sb_2O_3 prove the presence of additional polycrystalline related to ZnO phase. Comparing X-ray diffraction pattern for this three composition (x= 0, 10, 20), it shows that the diffraction lines were at the same position but different intensities.

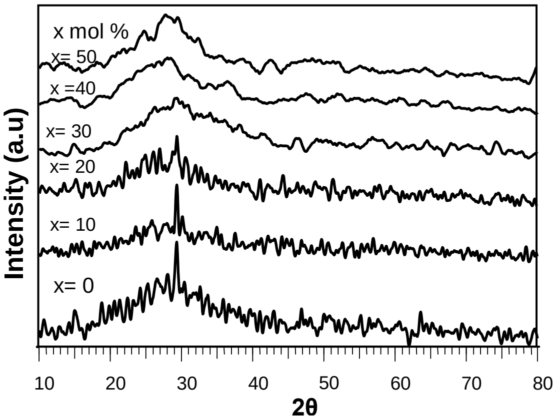


Figure 1 The X-Ray Diffraction (XRD) pattern of $10P_2O_5$ –$40B_2O_3$ –xSb_2O_3 –(50-x)ZnO glasses

The infrared spectra of zinc antimony borophosphate glasses have focus on their low frequency part for identifying further analyzed the functional group of sample. The IR spectra of $10P_2O_5$ –$40B_2O_3$ –(x) Sb2O_3 – (50-x) ZnO [$0 \leq x \leq 50$ mol%] in the range 400 to 1800 cm^{-1} are shown in Figure 2.

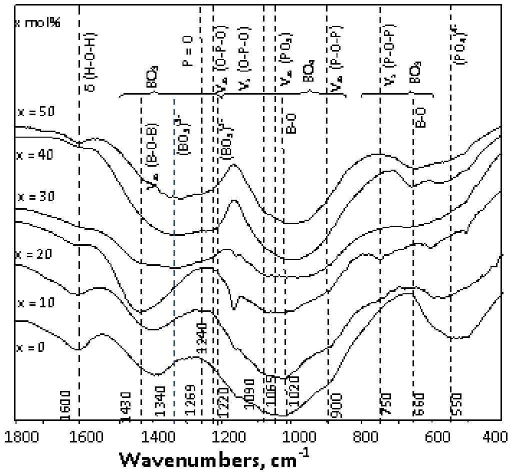


Figure 2 FT-Infrared spectra of $10P_2O_5$ –$40B_2O_3$ –xSb_2O_3 –(50-x)ZnO glasses in the frequency range of 400-1800 cm^{-1}

As modifier, ZnO and Sb_2O_3 will changed the borophosphate glasses system absorption peaks when their concentration was increased and decreased respectively. The infrared absorption bands in low frequency associated with the characteristic vibrational modes of borophosphate. The IR bands assigned in this study are based on the work done by other researchers [4][5][6][7][8]. The vibrational modes of pure borate glasses are mainly active in three infrared spectral regions [9]. The absorption peak around 1200-1500 cm^{-1} is assigned to B-O stretching trigonal BO_3 units, at 850-1200 cm^{-1} is ascribed to the B-O stretching of tetrahedral $(BO_4)^-$ units and the binding vibration of various borate segment is identified at 600-800 cm^{-1}.

Four distinct vibrational bands can be characterized for the pure phosphate composition. The vibration at 1252 cm^{-1} was ascribed to stretching vibration of v_s(P=O) bond in PO_4 structural units with one nonbridging oxygen atom, band at 1206 cm^{-1} is assign to the symmetrical stretching vibrations v_s(O-P-O) group of non bridging oxygen in phosphate chain. The other band at 793 cm^{-1} is due to symmetrical stretching vibration v_s(P-O-P) of the bridging oxygen atoms connecting linking neighboring PO_4 tetrahedra and a distinct band at 500 cm^{-1} is assigned to the deformation vibration of PO_4 units [10].

Significant changes in the the infrared spectra of $10P_2O_5$ – $40B_2O_3$ –xSb_2O_3 –(50-x)ZnO with the composition ($0 \leq x \leq 50$) in the range of 400-1800 cm^{-1} (Figure 2) with increasing content of Sb_2O_3 replacing ZnO manifest the incorporation of Sb_2O_3 into the structural network of parent borophosphate glass. The spectrum of the parent glass $10P_2O_5$ –$40B_2O_3$ –50ZnO borophosphate glass shows a broad complex band appears within range 850-1200 cm^{-1} is composed of several individual bands ascribed to the B-O stretching vibrations of BO_4 tetrahedral at 1020 cm^{-1} and three bands characteristic of P-O stretching vibration of v_s(O-P-O), v_{as}(PO_3) and v_{as}(P-O-P) at 1090, 1065 and 900 cm^{-1} respectively with all the symmetric and asymmetric stretching vibrations observed in the spectra are characteristic of Q^2 and Q^1 groups.

The band at this range obviously become smaller when Sb_2O_3 was increased (x=50 mol%) indicated the change in the coordination of boron atoms from tetrahedral BO_4 to trigonal BO_3 units. Several studies justified the incorporation of Sb_2O_3 into the borophosphate network creates new non-bridging oxygen atoms, which are at the origin of the different BO_4 sites [11]. The formation of BO_4 units into BO_3 units also can be accompanied by the formation of trigonal bipyramidal SbO_4E (E = 5s2 lone pair of electrons) units. The conversion between BO_3 units and BO_4 units can be confirm by the decreases of the band at 1430, 1340 and 660 cm^{-1} characteristic for stretching vibration of v_{as}(B-O-B), B-O bond of $(BO_3)^{3-}$ units in metaborates, pyroborates also ortoborates, and B-O linkage (B-O-B) bond in the borate BO_3 network respectively.

With increasing Sb_2O_3 content, the symmetric stretching vibration of non bridging phosphate atoms in PO_4 units at 550 cm^{-1} assigned to Q^0, orthophosphate group gradually decrease. This result shows, at higher concentration of ZnO, a broad band within range 900-1200 cm^{-1} is owing to stretching vibration of v_{as}(O-P-O) at 1240 cm^{-1} and v_{as}(PO_3) at 1065 cm^{-}1. Both of this vibration is characteristic of the stretching vibration of metaphosphate Q^2 and diphosphate Q^1 respectively. An incorporation of ZnO units into P_2O_5 –B_2O_3 –Sb_2O_3 glasses results in the depolymerisation of phosphate chains. The process of breaking P-O-P bonds to isolated PO_4 units is corresponds to the presence of Q^1 and Q^2 unit in phosphate network.

We assume that, the number of P-O-B bonds increase when the number of P-O-P and B-O-B bonds decrease with increasing Sb_2O_3 content in the borophosphate glasses due to increased number of BO_3 unit. In this way, the shift of the stretching vibration of v_{as}(B-O-B) band at the pure Zn borophosphate glasses $50ZnO$-$10P_2O_5$-$40B_2O_3$ from 1400 cm^{-1} slightly to higher frequencies can be explain. The band at 1400 cm^{-1} can be assigned to the asymmetric stretching vibration of bridging oxygen in borate unit in the glass of this composition.

With replacement of ZnO by Sb_2O_3 the further amount of the cation with higher cationic field strength shifts this band from 1400 cm^{-1} slightly to higher frequency but decrease the number of this band and new band was observed at 1220 cm^{-1} assigned to stretching vibration of B-O bond of $(BO_3)^{3-}$ units involving mainly linkage oxygen connecting different group. Band at 1340 cm^{-1} corresponding to stretching vibrations of B-O bond of $(BO_3)^{3-}$ units in metaborates, pyroborates and ortoborates also arise at higher content of Sb_2O_3 borophosphate glasses.

The IR patterns on antimony zinc borophosphate for both doped and undoped glass samples was shows in Figure 3. Borophosphate glasses doped with various rare earths such as Nd^{3+}, Sm^{3+}, Er^{3+} and Eu^{3+}at the same concentration (1 mol %) were prepared and examined by IR Spectroscopy. The relationship between effects of different type of rare earth in the glass system was study due to their structure in the same host matrices.

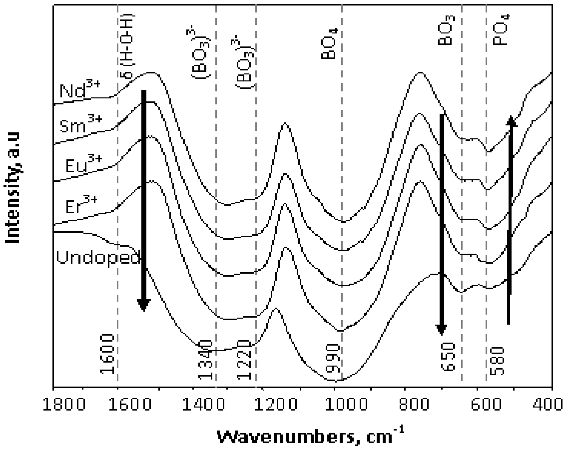


Figure 3 FT-Infrared spectra of and $10P_2O_5$ – $40B_2O_3$ –$40Sb_2O_3$ –10ZnO-1 RE glasses in the frequency range of 400-1800 cm^{-1}

By comparing all of the spectra (Figure 3), it clearly shows no intense changes in the finger print region. It is observed that whole spectrum of each rare earth doped glasses seems to be repetitive to that obtained from base undoped glass. In the sample containing rare earth ion, it is observed that the presence of rare earth ions have only minor effect on the IR spectra of studied glasses. This is maybe due to the low content of dopant, so the structural groups remain unchanged giving their characteristic vibration. A distinct band at 650 cm^{-1} corresponding to B-O linkage (B-O-B) bond in the borate BO_3 network slightly decrease with ionic radii increasing from Er, Eu, Sm to Nd of rare earth series. Previous study by Pisarski on lead borate glasses indicates that rare earth reduce trigonal BO_3 units and suggest that the smaller heavier lanthanides have the most effect on the local structure compare to larger lighter rare earth ones [12]. Completely different situation was observed for band at 500 cm^{-1} due to the deformation vibration of PO_4 units.

Band at 1600 cm^{-1} is attributed to the deformation modes of O-H (δ H-O-H) and usually indicates the water incorporation before glass devitrification unexpectedly decrease with addition of rare earth ions into the glass system even all doped and undoped sample were prepared under the same processing condition such as sample thickness and melting temperature during glass preparation. In particular, sample under investigation does not have H_2O as unit in the glass network but the presence of these bands causing due to reabsorption of water from atmospheric moisture by pellet sample because the infrared spectra were not recorded in situ [6]. In comparison, glass doped Er^{3+} sample shows the most enormously changes towards the OH group. The structural changes proved by the infrared spectroscopy measurement suggest that Er^{3+} ions also can improve the borophosphate glass network by reduces the OH group concentration and play role as modifier in zinc antimony borophosphate glasses at low concentration.

■4.0 CONCLUSION

The X-Ray Diffraction and Infrared Spectroscopy studies on the network structure of P_2O_5 –B_2O_3 –Sb_2O_3 –ZnO glass system doped with various rare earth such as Er^{3+}, Eu^{3+}, Nd^{3+} and Sm^{3+} ions revealed the following discussion: The XRD results of the quaternary samples reveal a change of glass structure and polycrystaline phase was observed for sample containing more than 30 mol% ZnO. At higher ZnO glasses, most of basic coupling unit of P-O bond will affected and the infrared spectra shows that Sb^{3+} enters the glass network by breaking up the B-O-B at higher Sb_2O_3 content. Decreases absorption v_{as}(B-O-B) and v_s(P-O-P) vibration bands indicated that P-O-B linkage was formed near 660 cm^{-1}. Hygroscopic nature of borophosphate glass were minimum at high antimony content and introduction Erbium ions into the zinc antimony borophosphate glass show the most enormously changes towards moisture sensitivity compare to other rare earth ions.

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