Boron and pentavalent vanadium local environments in binary vanadium borate glasses

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ABSTRACT

Vanadium borate glasses containing 5 to 25 mol% vanadium oxide (V2O5) were investigated. Prepared via the melt-quench technique, these glasses were examined by Fourier transform infrared, Raman, ultraviolet-visible and synchrotron-based X-ray absorption spectroscopy. Ultraviolet-visible and X-ray absorption spectra reveal that the only oxidation state of vanadium ions found in these glasses is 5+. Further result shows a subsequent increase in the molar volume of glass as V2O5 rises. This observed relationship indicates the presence of large boron-oxygen frameworks, including loose diborate and pyroborate units, confirmed by Fourier transform infrared and Raman spectra. Non-bridging oxygens of boron network are also formed in all glasses. Moreover, it is found that while four- and five-fold coordinated vanadium are present in all glasses, only five-fold coordinated vanadium show a significant increase following a rise in vanadium content.

1. Introduction

Vanadium-containing glasses is of interest as they are believed to be a promising material used in many applications, e.g. cathode materials in Li-ion battery [1], given the materials' interesting semiconducting properties. These properties arise from unpaired electron hopping between different oxidation states of vanadium, e.g. V4+ and V5+ [2,3]. The oxidation states of vanadium and local environment of vanadium in V2O5 glass and vanadium-containing glasses are very complicated, in which it can be found in various oxidation state (+3, +4 and +5) and in various coordination (four-, five-, and six-fold coordination) depending on glass system and composition. V2O5 glass and vanadium-containing glasses were investigated by various techniques including infrared spectroscopy or Fourier transform infrared spectroscopy (FTIR) [4–7], Raman spectroscopy [8,9], X-ray absorption spectroscopy (XAS) [10–12], solid-state nuclear magnetic resonance (NMR) [4] and electron spin resonance (ESR) [2,6,13]. V2O5 glasses [2,14] and most of the vanadium-containing glasses [4,10,13], prepared at different conditions and compositions, revealed the presence of V4+ and V5+. However, Nassar and Ghoneim [15] reported the possibility of the presence of +3 together with +4 and +5 in vanadium containing alkali borate glasses and +3 and +4 in alkali phosphate glasses. This was also found in less than 10 mol% vanadium containing zinc phosphate glasses [16]. In lead vanadate glasses [4], four-fold coordinated vanadium [VO4]4− and five four coordinated vanadium [VO4]5−, which form various types of units ([V2O7]4− and [V2O8]5− zigzag chain), have been reported. It was also found that in the iron-free glass containing V2O5, V5+ ions are mostly in [VO4]4− environment with a slight [VO5]5− content, whereas 40% of [VO4]4− — 60% of [VO5]5− are in the glasses with iron [17]. Moreover, there is a structure report of zinc vanadium borate glasses that vanadium ion are mainly in [VO4]4− [18].

In general, boron oxide (B2O3) is also a good glass former and have been broadly investigated. Only two types of boron coordination have been reported: three-coordinated boron [BO3]− and four-coordinated boron [BO4]−. Three-fold coordinated boron is solely found in pure B2O3 glass [19]. These units convert to [BO3]− with an addition of alkali oxide, which is a so-called glass modifier, causing a systematic increase in [BO3]− content as the alkali oxide content increases gradually to its maximum level. The number of [BO3]− units then gradually declines as the amount of alkali oxide rises, due to the formation of non-bridging oxygen (NBO). This phenomenon is so-called borate anomaly, which also plays a big role on the properties of glasses [20]. The conversion of [BO2]2− to [BO3]− can be reflected by the changes of boron-oxygen framework or so-called boron superstructural units that contain higher [BO4]− unit in the structure [20–22]. For example changes from boroxol ring to pentaborate, to diborate and to metabolate in potassium borate glasses as the content of K2O content increases [23]. Pentaborate, diborate and metabolate units have the fractions of [BO4]− to overall boron units equal to 0.20, 0.5 and 1, respectively. Similar changes...
were also reported in lead borate glasses [24] showing the dependence of lead oxide (PbO) content on boron superstructure changes (from boroxol ring to pentaborate, diborate, metaborate, and eventually pyroborate) as PbO content increases. The relationships between structures and properties are vital to improve the application of vanadium-containing glasses. Thus, understanding the behaviour of structural change versus glass composition will prove useful for material development. Since the literature on the oxidation state of vanadium and structure of vanadium-containing glasses remain inconclusive, the investigation of binary vanadium borate glasses at various composition is therefore of interest in this article.

Density, molar volume and UV–Vis absorption spectra were monitored in order to obtain the relationship between properties and glass compositions. The oxidation state of vanadium in all glass was also examined using UV–Vis spectroscopy, magnetic susceptibility balance and V–K edge XANES techniques. Moreover, local environments of B and V atoms and bond distances between V and O were also revealed from FTIR, Raman, vanadium K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra. Changes in glass structure as the amount of V2O5 in glasses increases were also proposed in terms of the local environment surrounding B and V atoms, and bond nature in glass network.

2. Experimental procedures

2.1. Sample preparation

Five glass samples with a nominal composition of \(x\text{V}_2\text{O}_5 \cdot (1-x)\text{B}_2\text{O}_3\), where \(x\) ranges from 0.05 to 0.25 M fraction, were produced by the conventional melt-quench method. Vanadium oxide \((\text{V}_2\text{O}_5)\) and boric acid \((\text{H}_3\text{BO}_3)\) were used as raw materials. The calculated batches were mixed in a granite mortar and melted in a platinum crucible at 1000 °C for 150 min using 5 °C/min heating rate from room temperature. The melts were then cooled to room temperature between two stainless steel plates (Splat-quenching technique). Weight change of each composition during melting was also observed to measure volatilisation of vanadium or boron from the melt. Due to the hygroscopic nature of borate glass, the samples were kept in a desiccator until required for measurements. X-ray diffraction was used to ensure the amorphous nature of glass sample.

2.2. Physical properties measurement

The density \(\rho\) of glass samples was obtained by buoyancy technique, in which the weights of samples measured in air and in the liquid were compared. Due to the hygroscopic feature of borate glasses, xylene \((\text{C}_8\text{H}_{10})\) was used as a liquid medium to avoid their reaction with water. The density is then calculated using following equation:

\[
p_{\text{sample}} = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{immersed}}} \rho_{\text{liquid}}
\]

where \(p_{\text{sample}}\) is the calculated density of glass sample, \(\rho_{\text{liquid}}\) is the density of xylene at exact temperature during measurement \((0.8534 \text{ g/cm}^3\) at 28.9 °C), \(W_{\text{air}}\) is the weight of glass sample in air, and \(W_{\text{immersed}}\) is the immersed weight of the sample in xylene.

The density of glass was then used for calculation a molar volume \(V_{R}\) of each glass using equation below:

\[
V_R = \frac{\text{MW}}{\rho_{\text{glass}}}
\]

where MW is the molecular weight of glass calculated using nominal composition.

Magnetism of amorphous samples and commercial vanadium oxide compounds \((\text{V}_2\text{O}_3, \text{V}_6\text{O}_{13}\) and \(\text{V}_2\text{O}_5)\) were implied from a value obtained directly from magnetic susceptibility balance (Sherwood Scientific; \(R\)). In this case, the diamagnetism character of the sample occurs in the sample with a negative \(R\) value.

UV–Vis absorption spectra in the 200–1000 nm region of the solution containing glass sample were obtained using UV–Vis spectrophotometer (Hitachi U-2900), in order to determine an electronic structure of vanadium ion in glasses. A deuterium (D2) lamp and a tungsten wire lamp were used as a light source covering all of the observed regions. Glass samples were digested in 2.4 M sulfuric acid \((\text{H}_2\text{SO}_4)\) and heated to achieve complete dissolution. The concentration of glass solution was constant at 0.1 M.

2.3. Structural investigation

Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were used to investigate the local environment around boron and vanadium atom in glasses. The FTIR spectra of all sample were carried out using FTIR spectrometer (Spectrum RX 1, Perkin Elmer). A HeNe lamp was used as a laser source at the wavelength of 633 nm for sample excitation. The mixture of powdered sample and powdered potassium bromide (KBr) was pressed to make a thin disk for FTIR measurement in the 400–4000 cm\(^{-1}\) range using 4 cm\(^{-1}\) resolution for 32 scans. For Raman spectroscopy, the spectra of the solid sample were examined from Raman spectrometer (T64000, Horiba Jobin Yvon) with 532 nm wavelength solid-state laser in the range from 100 cm\(^{-1}\) to 2000 cm\(^{-1}\). Several areas of measurement were conducted to ensure the consistency of the spectrum.

Moreover, vanadium oxidation states and local environment around vanadium atoms were investigated using synchrotron-based XAS including XANES and EXAFS. The absorption spectra at V K-edge were conducted at the SUT-NANOTEC-SLRI XAS beamline (BL5.2) (electron energy of 1.2 GeV; bending magnet; beam current 80–150 mA; 1.1 to 1.7 × 10\(^{11}\) photon s\(^{-1}\) at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. All spectra were collected in the transmission mode with ionization chamber detectors. For the acquisition of all spectra, a Ge (220) double crystal monochromator with an energy resolution \((\Delta E/E)\) of 2 × 10\(^{-4}\) was used to scan the synchrotron X-ray beam. The normalized XAS data were processed and analyzed after background subtraction in the pre-edge and post-edge region using the ATHENA software which is included in an IFEFFIT package [25,26].

3. Results and discussion

3.1. Glass composition and properties

There are some difficulties in a determination of boron concentration in a glass as boron is very light and sensitive [27]. Thus, to evaluate the difference of the composition of prepared glasses from the designed composition, the weight loss of glass samples were instead monitored. Expected weight loss from the mixture of raw materials used in this experiment was primarily due to the thermal decomposition of boric acid \((\text{H}_3\text{BO}_3)\) to boron oxide \((\text{B}_2\text{O}_3)\). However, the observed loss, reported in Table 1, was approximately 3.1397 ± 0.0001 to 5.0024 ± 0.0001%wt in excess of the expected norm. It is found that the most decremental percentage weight loss is from the VBS sample which contains the least \(\text{V}_2\text{O}_5\) content. The evaporation of \(\text{B}_2\text{O}_3\) liquid phase or \(\text{B}_2\text{O}_3\)-rich liquid phase in glass melt may be accounted for the weight loss of glass sample as an evidence of reduction of a weight loss as \(\text{B}_2\text{O}_3\) content increases as shown in Table 1. Estimated molar fractions of \(\text{V}_2\text{O}_5\) in each glass, listed in Table 1, were calculated based on the assumption that the excess weight loss is solely from evaporation of \(\text{V}_2\text{O}_5\) liquid phase and \(\text{B}_2\text{O}_3\) liquid phase, respectively. This reveals that the deviation of \(\text{V}_2\text{O}_5\) content in glasses from the nominal composition is approximately less than 2%mol. Since there is uncertainty in glass composition, nominal compositions of glass are therefore used throughout the article.
The density of vanadium borate glasses (Fig. 1) is strongly dependent on the content of the higher mass substance; V₂O₅, of which its molar mass is 181.88 g/mol having the density of 3.36 g/cm³, as compared to an amorphous B₂O₃, which has a molar mass of only 69.62 g/mol having density of only 1.82 ± 0.04 g/cm³[28,29]. That is, the densities of glass samples increase from 1.8796 ± 0.001 to 2.1990 ± 0.0004 g/cm³ as V₂O₅ content increases from 5 to 25%mol, respectively. The error estimation values were obtained from a statistical standard deviation of five measurements. These values coincide with the extrapolated trend line (dotted line) obtained from the reported values of vanadium borate glasses at higher V₂O₅ concentration [30]. It is also found that borate anomaly, which is typical in many binary alkali borate glasses [31-37], is nonexistent in the vanadium borate glasses in this study. Calculated molar volumes of glasses also increase as V₂O₅ content increases, which may be due to the presence of the large borate frameworks. Such a large borate framework was also found in phosphorus borate glasses [38] and in lithium borate glass containing thallium oxide (Th₂O₃) [39], in which a large boron-oxygen framework is required in order to accommodate larger phosphorus ions, and Ti⁴⁺ ions respectively. It has also been reported that the existence of non-bridging oxygen (NBO) in borate glass contributes to the increase in molar volumes of glass as reported in sodium borate glasses containing additive TeO₂ [40]. In this case, it is possible that the [VO₄]⁻⁻ unit have the same effect as the previously mentioned larger ions.

Values obtained from magnetic susceptibility balance (R) can be used to state the magnetism of sample, in which an unpaired electron in d-orbital relates to a magnetic moment (µ). A negative value of R implies that there is no unpaired electron in d-orbital so that the material is diamagnetic. This is in contrast with an unpaired electron in d-orbital presenting in paramagnetic materials with positive R value. It is obvious that all glasses is designated to be diamagnetic according to the negative R value as plotted in Fig. 2. The diamagnetic V₂O₅ (V⁵⁺) powder with an empty d-orbital giving no unpaired electron in d-orbital also exhibits negative R value. V₂O₄ (V⁴⁺) and V₂O₃ (V³⁺) substances give positive R values implying that these materials are paramagnetic, as there are one and two unpaired electrons in d-orbital, respectively. It is then reasonable that V₂O₅ has a significantly larger R value (plotted in Fig. 2) as it has a larger number of unpaired electrons in d-orbital comparing with the other two standards. Thus, R values of glasses can be used to imply that vanadium ions in this binary vanadium borate glasses are only in the +5 oxidation state. This contrasts with other multicomponent systems, in which vanadium ions are in the mixed oxidation state (e.g. zinc phosphate [16], barium borate [6], alkali borate, alkali silicate, alkali phosphate [15], Li₂O-MgO-B₂O₃ [41], Li₂O-MoO₃-B₂O₃ [42] and Li₂O-SrO-B₂O₃ glasses [43]).

Fig. 3 illustrates UV–Vis absorption spectra of vanadium borate glass solution in comparison with the V₂O₄ and V₂O₃ oxides solution reveals that the predominant absorption is only in the UV region (between 200 and 377 nm). The absorption spectra are in agreement with the results obtained from 0.2% vanadium doped barium borate glass measured from the piece of glass [44]. Bands appear between 275 and 377 nm can be attributed to the charge transfer band of V⁵⁺ appearing in UV region [15], assuring the presence of only + 5 oxidation state of vanadium in all glass. The d-d transition absorption band of V⁴⁺, which contains one unpaired electron in d-orbital, does not exist in all glasses. This d-d transition band of V⁴⁺ appears at approximately 780 nm, which can be assigned to the transition of electron from 2B₂g stage to 2Eg stage of VO⁴⁺ ions present in Li₂O-MgO-B₂O₃ glasses containing various amount of V₂O₅ [41]. There is a gradual shift of V⁵⁺ spectrum from 340 nm to approximately 346, 350, 356 and 360 nm in 10, 15, 20 and 25%mol V₂O₅-containing glasses, respectively. Moreover, the edge positions of the absorption spectrum clearly confirm the red shift phenomenon in these glasses, which is largely determined by the concentration of vanadium ions in glasses. This shift is also found to be dependent on the concentration of vanadium content in the solution as reported in earlier study [45]. This is in agreement with the study of barium borate glasses containing 2.5 and 5%wt of V₂O₅, in which the edge position moves to the higher wavelength as vanadium content increases [6]. This indicates that the energy gap between valence band and conduction band, which is related to the peak position of UV–Vis spectra in glasses, is smaller in the higher V₂O₅ content glass.
3.2. Boron and pentavalent vanadium environments

FTIR spectra depicted in Fig. 4 provide the structural information of boron and vanadium in glasses containing different V$_2$O$_5$ content. The interpretation of those bands is listed in Table 2, in which the assignments were obtained by comparing the vibrational bands in this study to other FTIR studies of vanadium-containing glasses and other vanadium borate glasses reported in the literature [6, 7, 41–43, 46]. All FTIR spectrum shows a broad band at approximately 3220 cm$^{-1}$, which suggests that a typical moisture attack occurs in these borate glasses, especially in the higher B$_2$O$_3$-containing glasses [47]. However, Hogarth and Ahmed [46] suggested that the IR absorption bands at 550 and 810 cm$^{-1}$ reportedly occur due to the stretching of some boron superstructural units [55]. All small bands at approximately 2300 cm$^{-1}$ have been assigned to the presence of pyroborate superstructural unit in vanadium borate containing ZnO [18] and possibly for the presence of metaborate superstructural unit in various alkali earth borate glasses [52]. Moreover, the shoulder centered at approximately 1386 cm$^{-1}$ corresponds to the asymmetric stretching of B–O bond in [BO$_3$] and [BO$_2$O]$^-$ [6, 44, 52]. The latter unit contains one non-bridging oxygen among two bridging oxygens in the three-coordinated environment. For the information of vanadium, bands at 550 and 810 cm$^{-1}$ reportedly occur due to the stretching modes of an oxygen atom between three vanadium atoms [V$_3$O] [16, 53] and of V=O double bond [9, 11, 46], respectively. This can also be found in V$_2$O$_5$ thin film studies [6, 41, 54]. However, these bands can be assigned for the bending or deformation mode of vibration of some boron superstructural units [55]. A V=O band at approximately 1020 cm$^{-1}$, which has usually been found in various V$_2$O$_5$-containing glasses, also presents in these vanadium borate glasses [6, 7, 41–43, 46]. However, Hogarth and Ahmed [46] suggested that the IR absorption bands at 1010, 810, 650 and 560 cm$^{-1}$ arise from the V=O vibration. In 5 and 10%mol V$_2$O$_5$-containing glasses, a very weak signal appearing at approximately 725 cm$^{-1}$, which has been assigned to the presence of B–O–V–O–B bridge [18, 46], can be observed. In addition, it should be noted that a band at approximately 920–970 cm$^{-1}$, corresponding to an unshared V=O–V bond, does not exist in these glasses. This suggests that V$_2$O$_5$ in this binary system acts as a glass former, forming a bridging oxygen (BO) similar to that of a B$_2$O$_3$ glass former.

Raman spectroscopy was also used to investigate local environments surrounding B and V atoms in amorphous vanadium borate (as illustrated in Fig. 5 and Table 3). A sharp band at 806 cm$^{-1}$, found in only 5%mol V$_2$O$_5$-containing glasses, was assigned for the presence of pyroborate superstructural unit in vanadium borate containing ZnO [18] and possibly for the presence of metaborate superstructural unit in various alkali earth borate glasses [52]. Moreover, the shoulder centered at approximately 1386 cm$^{-1}$ corresponds to the asymmetric stretching of B–O bond in [BO$_3$] and [BO$_2$O]$^-$ [6, 44, 52]. The latter unit contains one non-bridging oxygen among two bridging oxygens in the three-coordinated environment. For the information of vanadium, bands at 550 and 810 cm$^{-1}$ reportedly occur due to the stretching modes of an oxygen atom between three vanadium atoms [V$_3$O] [16, 53] and of V=O double bond [9, 11, 46], respectively. This can also be found in V$_2$O$_5$ thin film studies [6, 41, 54]. However, these bands can be assigned for the bending or deformation mode of vibration of some boron superstructural units [55]. A V=O band at approximately 1020 cm$^{-1}$, which has usually been found in various V$_2$O$_5$-containing glasses, also presents in these vanadium borate glasses [6, 7, 41–43, 46]. However, Hogarth and Ahmed [46] suggested that the IR absorption bands at 1010, 810, 650 and 560 cm$^{-1}$ arise from the V=O vibration. In 5 and 10%mol V$_2$O$_5$-containing glasses, a very weak signal appearing at approximately 725 cm$^{-1}$, which has been assigned to the presence of B–O–V–O–B bridge [18, 46], can be observed. In addition, it should be noted that a band at approximately 920–970 cm$^{-1}$, corresponding to an unshared V=O–V bond, does not exist in these glasses. This suggests that V$_2$O$_5$ in this binary system acts as a glass former, forming a bridging oxygen (BO) similar to that of a B$_2$O$_3$ glass former.

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Table 2

<table>
<thead>
<tr>
<th>Assignment</th>
<th>FTIR bands (cm$^{-1}$)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching mode of an oxygen atom between three vanadium atoms or V=O double bond</td>
<td>550</td>
<td>[16, 46, 53]</td>
</tr>
<tr>
<td>V=O double bond</td>
<td>650</td>
<td>[46]</td>
</tr>
<tr>
<td>Bending or deformation mode of borate units</td>
<td>550–800</td>
<td>[55]</td>
</tr>
<tr>
<td>B–O–V–O–B bridge</td>
<td>725</td>
<td>[18, 46]</td>
</tr>
<tr>
<td>Stretching of V–O–V or V=O double bond</td>
<td>810</td>
<td>[9, 11, 46]</td>
</tr>
<tr>
<td>B–O stretching in [BO$_4$]$^-$ in diborate</td>
<td>890</td>
<td>[6, 44]</td>
</tr>
<tr>
<td>V=O double bond</td>
<td>1020</td>
<td>[6, 7, 41–43, 46]</td>
</tr>
<tr>
<td>Vibration of B–O in [BO$_3$] environment</td>
<td>1200</td>
<td>[23, 49–51]</td>
</tr>
<tr>
<td>Vibration of B–O in [BO$_4$] environment</td>
<td>1230</td>
<td>[23, 49–51]</td>
</tr>
<tr>
<td>Metaborate superstructural unit or pyroborate</td>
<td>1250</td>
<td>[18, 52]</td>
</tr>
<tr>
<td>Asymmetric stretching of B–O bond in [BO$_3$] and [BO$_2$O]$^-$ environments</td>
<td>1386</td>
<td>[6, 44, 52]</td>
</tr>
<tr>
<td>Vibration of B–O in [BO$_3$] environment</td>
<td>1462</td>
<td>[23, 49–51]</td>
</tr>
<tr>
<td>Vibration of CO$_2$ molecules</td>
<td>2300</td>
<td>[47]</td>
</tr>
<tr>
<td>O–H stretching</td>
<td>3220</td>
<td>[47, 48]</td>
</tr>
</tbody>
</table>

Fig. 3. UV–Vis spectra of glass samples and commercial vanadium oxides (inset) in 2.40 M H$_2$SO$_4$ solution.

Fig. 4. FTIR spectra of vanadium borate glasses with different V$_2$O$_5$ content.

Fig. 5. Raman spectra of vanadium borate glasses with different V$_2$O$_5$ content.
V$_2$O$_5$-containing glass, is the characteristic band representing a six-membered boroxol ring, which is a typical structure found in B$_2$O$_3$ glass [56] and some borate glasses [56,57]. Moreover, the low signal at approximately 1220 cm$^{-1}$, which has been assigned to the presence of pyroborate found in high alkali-containing borate glasses [23,52,57], suggests that there are pyroborate superstructural units in glasses even at low V$_2$O$_5$ concentration. The other bands giving the details of boron coordination are a small broad band at approximately 517 cm$^{-1}$ and a broad band ranges from 1400 to 1600 cm$^{-1}$, which correspond to the existing of loose diborate superstructure and NBOs adjacent to boron atom, respectively [23,52,57]. The band at approximately 500 cm$^{-1}$ may also arise from a low energy vibration of V$-$O$-$V [9,58], which overlaps with the previously mentioned boron band. The bands at 661, 871 and 1021 cm$^{-1}$ correspond to the vibration of V$-$O$-$V in [V$_2$O] environment [9], V$-$O stretching in O$-$V$-$O bond [59,56,57] and V$-$O bond of V$^{5+}$ [14], respectively. In this binary vanadium borate glasses, the corresponding O$-$V$-$O band at 871 cm$^{-1}$ is independent of the V$_2$O$_5$ content. This implies that the V$-$O bond length or angle in [VO$_2$]$^+$ or [VO$_3$] environment is very similar in all composition. This band is believed to be shifted to a lower frequency of approximately 900 cm$^{-1}$ found in oxyfluoro vanadate glasses studied by Honnavar et al. [59], due to the difference vanadium environments in these glasses. The other two weak bands at low frequencies may arise from the vibration of vanadium atoms in an environment that no long range order structure is achieved, i.e. in an amorphous state [14].

In alkali borate glasses, the addition of alkali oxide in the boron oxide glass network causes the formation of four-coordinated boron; [BO$_4$]$^-$ from three-coordinated boron; [BO$_3$]. This is relevant to the change in the boron superstructural unit as the alkali oxide increases from boroxol ring (comprises solely of [BO$_3$]) to other borate superstructural units containing more [BO$_4$]$^-$. The presence of those superstructural units depends on the types of alkali oxide and the concentration of alkali oxide [57,61]. Afterwards NBOs are then formed in a very high alkali oxide-containing borate glasses causing the reduction of [BO$_4$]$^-$. In this vanadium borate glasses, there is no evidence that low [BO$_4$]$^-$ content superstructural units, e.g. pentaborate or triborate, is present. NBOs were also observed in these glasses, which can be confirmed by FTIR and Raman spectroscopy results; i.e. the FTIR band at 1390 cm$^{-1}$ and a broad Raman band at 1400–1600 cm$^{-1}$. Moreover, the full width at half maximum (FWHM) of Raman band can be used to inform the information of homogeneity of each unit or each environment corresponding to that band [59]. Therefore, the similar band shape of Raman spectra in this study implies that boron and vanadium environments found in glasses have a narrow bond distance and bond angle distribution.

### 3.3. X-ray absorption spectroscopy study

Normalized V K-edge XANES spectra of all glasses and standard samples; V$_2$O$_4$ (V$^{5+}$), V$_2$O$_4$ (V$^{4+}$) and V$_2$O$_5$ (V$^{5+}$), are presented in Fig. 6. The intensities of the pre-edge peak centered at approximately 5470 eV of these three standard compounds are notably different. It is clear that the intensity reduces as the oxidation state of vanadium reduces from +5 to +4 and +3, respectively. Moreover, the white line position of V$^{5+}$ and V$^{4+}$ also shifts to lower energy of approximately 5475 eV and 5478 eV, respectively, as compared to that of V$^{5+}$ at 5479 eV. This spectra feature coincides with the one reported by Giuli et al. [17] and Wong et al. [62]. The shifts of the white line positions

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**Table 3**  
Raman band lists and their corresponding assignments.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Raman Shift (cm$^{-1}$)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibration of vanadium in short range order structure</td>
<td>154 &amp; 246</td>
<td>[14]</td>
</tr>
<tr>
<td>Low energy V$-$O$-$V vibration</td>
<td>500</td>
<td>[9,58]</td>
</tr>
<tr>
<td>Loose diborate/loose [BO$_4$]$^-$ or low energy vibration of V$-$O$-$V</td>
<td>517</td>
<td>[23,52,57]</td>
</tr>
<tr>
<td>V$-$O vibration in [V$_2$O] environment</td>
<td>661</td>
<td>[9]</td>
</tr>
<tr>
<td>Vibration of B$-$O in boroxol ring</td>
<td>806</td>
<td>[56,57]</td>
</tr>
<tr>
<td>V$-$O stretching in O$-$V$-$O bond</td>
<td>871</td>
<td>[59,60]</td>
</tr>
<tr>
<td>V$^{5+}$=O double bond</td>
<td>1020</td>
<td>[14]</td>
</tr>
<tr>
<td>B$-$O vibration in pyroborate superstructural unit</td>
<td>1220</td>
<td>[23,52,57]</td>
</tr>
<tr>
<td>B$-$O$-$O bond (existing of [BO$_4$]$^-$)</td>
<td>1400–1600</td>
<td>[23,52,57]</td>
</tr>
</tbody>
</table>

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**Fig. 6.** Normalized V-K edge XANES spectra of reference crystalline compounds and vanadium borate glasses.

**Fig. 7.** The Fourier transform of EXAFS spectra of vanadium borate glasses revealing V$-$O bond distances.

**Fig. 8.** The presence of ionic bond (_____ represents ionic bond and —— represents covalent bond in glass network).
are due to the differences in the oxidation state of X-ray absorber atoms and, in particular, the oxygen polyhedral of the absorber atoms [17].

Quantitative analysis of XANES of V environments in glassy materials is very complicated due to the effect of different scattering phenomena and a randomly atomic arrangement in an amorphous state [11]. Thus, only the qualitative analysis of vanadium XANES spectra is proposed in this article. The pre-edge peak at 5470 eV arises from the forbidden transition from 1s state to the combined orbital between transition metal 3d orbitals and oxygen 2p orbitals [63]. The white line position of glasses also appears at 5480 eV. These are very close to the spectrum obtained from V2O5 compound illustrated in Fig. 6. The intensity of the pre-edge peak and the position of the white line, which relate to the oxidation state of vanadium [12,17,62], implies that vanadium ions in these glasses are in their +5 oxidation state. The interpretation of the oxidation state of vanadium is consistent with the UV–Vis absorption spectra of glasses in the acid solution discussed earlier. It can also be seen from the XANES spectra that the pre-edge peak of glasses is slightly broader, i.e. from approximately 2.9 eV in the crystalline V2O5 and vanadium phosphate glasses approximately 0.2–3.7 eV in glass samples, and more intense than that of crystalline V2O5. This is because some vanadium ions are located in a lower coordinated environment, e.g. [VO4]+, as compared to the more [VO5]+ units are formed in the glass as V2O5 decreases [5]. Slight broadening of the pre-edge peak also implies that a higher degree of randomness of vanadium environments in glassy state is achieved. The broadening is governed by the increase in complexity of the mixing state between 3d orbital of vanadium and 2p orbital of oxygen [64]. The change in coordination number of vanadium can also be obtained from the feature and position of edge peak as reported by Guli et al. [17]. The first edge peak of all glass samples appear at higher energy as compared to the one obtained from the standard V2O5. The position of the peak also shifts to lower energy as vanadium content increases approaching the position of the crystalline V2O5. This could be due to the lower quantity of tetrahedrally coordinated vanadium: [VO4]+ in comparison to the quantity of [VO5] in glasses.

The Fourier transform, χ(R), of EXAFS spectra at V K-edge is shown in Fig. 7. It can be seen that the mean bonding distance between vanadium and oxygen of VBS sample, is approximately at 1.33 Å. It must be noted that no phase shift was applied to the χ(R) functions, thus the peak position of χ(R) functions will shift from the actual value by approximately 0.2–0.3 Å (approximately 1.63 Å if the phase shift is included). This obtained distance is shorter than the one found in vanadium germanate phosphate glasses, in which the bond length was reported at 1.75 Å [65]. In higher V2O5-containing glasses (VB20 and VB25), the shorter V−O distance dominates at approximately 1.33 Å including phase shift, causing the broadening of the spectra. The shorter bond could be assigned to the V=O bond, in which the bond length is approximately at 1.35 Å in crystalline V2O5 and vanadium phosphate glasses [65].

3.4. Tentative glass structure

In vanadium borate glasses, there are changes in glass structure depending on the V2O5 content. In the 5%mol V2O5-containing glass (VB5), the boroxol ring remains in the borate network together with loose dioxo in order to accommodate the large unit of vanadium structure. The vanadium in VB5 is in the mixing state between four- and five-fold coordinated vanadium. Moreover, non-bridging oxygens are also found in low-V2O5-content glasses. In higher V2O5-containing glasses, it is believed that the number of [VO5], comprising of one double bond and four single bonds to oxygen, increases. As there is only one oxidation state of vanadium (i.e. +5) found in these glasses, the charge of four-fold coordinated pentavalent vanadium must be positive. The presence of non-bridging oxygen and [BO3]− is then reasonable for the neutralisation of this positive charge from [VO5]+ site. Thus, there should be an ionic bond together with the covalent network between these two types of glass formers, B2O3 and V2O5 as depicted in Fig. 8.

4. Conclusions

Vanadium borate glasses containing 5 to 25%mol V2O5 were investigated. Following the experiment, it is observed that the density values and molar volumes of glasses increase as V2O5 content increases. Such a rise in molar volume implies that the expansion of glass structure is needed to host a large vanadium network. Evidence from UV–Vis absorption spectra, magnetism and XANES spectra, confirm that the oxidation state of vanadium is +5. XANES and EXAFS show that the local environments of this V5+ appear in two forms, [VO4]+ and [VO5]+ with one V=O bond, in which the number of [VO5] units increase as V2O5 increases. Moreover, FTIR and Raman spectra also confirm the presence of these vanadium sites in all glasses. For the boron environment, the network of [BO3] in a form of boroxol ring was observed in only 5%mol V2O5 glass. Loose dioxidate, pyroborate and non-bridging oxygens, which contains various numbers of [BO3] and [BO4] units, are observed in all glasses.

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