



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 (V_2O_5) 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 V^{5+} . Further result shows a subsequent increase in the molar volume of glass as V_2O_5 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.

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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. V^{4+} and V^{5+} [2,3]. The oxidation states of vanadium and local environment of vanadium in V_2O_5 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. V_2O_5 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]. V_2O_5 glasses [2,14] and most of the vanadium-containing glasses [4,10,13], prepared at different conditions and compositions, revealed the presence of V^{4+} and V^{5+} . 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 $[VO_4]^{4-}$ and five four coordinated vanadium $[VO_5]$, which form various types of units ($[V_2O_7]^{4-}$ and $[V_2O_8]_n$ zigzag chain), have been reported. It was also found that in the iron-free glass containing V_2O_5 , V^{5+} ions are mostly in $[VO_4]^{4-}$ environment with a slight $[VO_5]$ content, whereas 40% of $[VO_4]^{4-}$ – 60% of $[VO_5]$ are in the glasses with iron [17]. Moreover, there is a structure report of zinc vanadium borate glasses that vanadium ion are mainly in $[VO_4]^{4-}$ [18].

In general, boron oxide (B_2O_3) is also a good glass former and have been broadly investigated. Only two types of boron coordination have been reported: three-coordinated boron $[BO_3]$ and four-coordinated boron $[BO_4]^{-}$. Three-fold coordinated boron is solely found in pure B_2O_3 glass [19]. These units convert to $[BO_4]^{-}$ with an addition of alkali oxide, which is a so-called *glass modifier*, causing a systematic increase in $[BO_4]^{-}$ content as the alkali oxide content increases gradually to its maximum level. The number of $[BO_4]^{-}$ 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 $[BO_3]$ to $[BO_4]^{-}$ can be reflected by the changes of boron-oxygen framework or so-called boron superstructural units that contain higher $[BO_4]^{-}$ unit in the structure [20–22]. For example changes from boroxol ring to pentaborate, to diborate and to metaborate in potassium borate glasses as the content of K_2O content increases [23]. Pentaborate, diborate and metaborate units have the fractions of $[BO_4]^{-}$ to overall boron units equal to 0.20, 0.5 and 1, respectively. Similar changes

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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 V_2O_5 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 $xV_2O_5 \cdot (1-x)B_2O_3$, where x ranges from 0.05 to 0.25 M fraction, were produced by the conventional *melt-quench* method. Vanadium oxide (V_2O_5) and boric acid (H_3BO_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 (ρ) 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 (C_8H_{10}) was used as a liquid medium to avoid their reaction with water. The density is then calculated using following equation:

$$\rho_{\text{sample}} = \frac{W_{\text{air}}}{(W_{\text{air}} - W_{\text{immersed}})} (\rho_{\text{liquid}}) \quad (1)$$

where ρ_{sample} is the calculated density of glass sample, ρ_{liquid} is the density of xylene at exact temperature during measurement (0.8534 g/cm³ at 28.9 °C), W_{air} is the weight of glass sample in air, and W_{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:

$$V_R = \frac{MW}{\rho_{\text{glass}}} \quad (2)$$

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

Magnetism of amorphous samples and commercial vanadium oxide compounds (V_2O_5 , V_2O_4 and V_2O_3) 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 (D_2) 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 (H_2SO_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 pulverised sample and pulverised 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 (H_3BO_3) to boron oxide (B_2O_3). However, the observed loss, reported in Table 1, was approximately 3.1397 ± 0.0001 to $5.0024 \pm 0.0001\%$ wt in excess of the expected norm. It is found that the most decremental percentage weight loss is from the VB5 sample which contains the least V_2O_5 content. The evaporation of B_2O_3 liquid phase or B_2O_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 B_2O_3 content increases as shown in Table 1. Estimated molar fractions of V_2O_5 in each glass, listed in Table 1, were calculated based on the assumption that the excess weight loss is solely from evaporation of V_2O_5 liquid phase and B_2O_3 liquid phase, respectively. This reveals that the deviation of V_2O_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.

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