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Effect of B_2O_3 content on structure-function of vanadium-lithium-borate glasses probed by synchrotron-based XAS and vibrating sample magnetrometry technique

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ABSTRACT

In this work, vanadium-lithium-borate glasses, $0.5V_2O_5$–$0.5(Li_2O\text{-}xB_2O_3)$ with x = 1.0, 2.0 and 3.0, respectively, were prepared by conventional melt-quench technique. The glass samples were characterized by X-ray diffraction, scanning electron microscopy, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, UV–Visible Spectroscopy and vibrating sample magnetrometry. X-ray absorption near-edge spectra at the V *K*-edge confirmed the presence of the mixing of V^{4+} and V^{5+} oxidation states and X-ray photoelectron spectroscopy were used to quantify and reveal the amount of V^{4+} and V^{5+} in the glass samples with approximately a ratio of 1:4 for V^{4+}:V^{5+}. The paramagnetic behavior were found for the glass samples with x = 1.0 and 2.0 due to the presence of V^{4+}. However, an influence of B_2O_3 content clearly affected to the glass sample with x = 3.0 resulting to a diamagnetic nature of this glass composition. The local structural information around V atoms in all glass samples were addressed using extended X-ray absorption fine structure technique with a mean oxygen coordinated network of 3.50(1). The notable properties of these glasses can be used and applied in the energy storage applications.

1. Introduction

Owing to the various oxidation states of vanadium [1,2], vanadium-based glasses are attractive as promising novel materials in many applications such as cathode in Li-ion batteries [3]. Vanadium based-electrodes have been synthesized by various methods with different starting materials e.g. glass formers [4–6]. For example, V_2O_5-P_2O_5 glass cathodes reported by Sakurai et al. [4–6] demonstrated a drop of the capacity on the first charge (to 350 mAh/g) and cycling properties are not very remarkable for the large potential window.

Generally, one of good glass formers which has been broadly used in many glass-based materials is boron oxide (B_2O_3). Especially in borate-vanadate based glasses with binary, ternary and quaternary glass systems, there have been studied varieties both physical and electrical and electrochemical properties [7–13]. Recently, there has been a report on structure of binary vanadium borate glasses [13]. The V-structure was reported by XAS technique with a mean V oxidation state [13]. However, to the best of our knowledge, their deep information concerning the local structure information around vanadium ions which leads them to the notable properties have not been clearly studied and understood.

In this research work, the vanadium-lithium borate glass systems, V_2O_5-$LiBO_2$, have been introduced with both structural and physical such as scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), UV–Vis and vibrational sample magnetrometry. A very simply synthesis method using furnace melting has been used to synthesize these glasses. Furthermore, the synchrotron-based X-ray absorption spectroscopy (XAS) techniques including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) has been employed to these glasses in order to deeply address the existence of many vanadium oxidation states and local structural information around vanadium atoms in these such prepared glasses.

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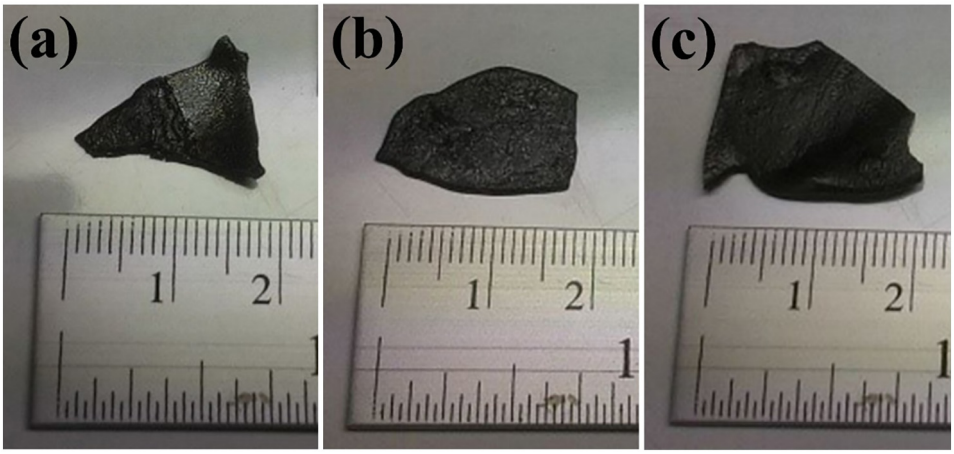

Fig. 1. Feature of $0.5V_2O_5$–$0.5(Li_2O\text{-}xB_2O_3)$ glass samples: (a) x = 1, (b) x = 2, (c) x = 3.

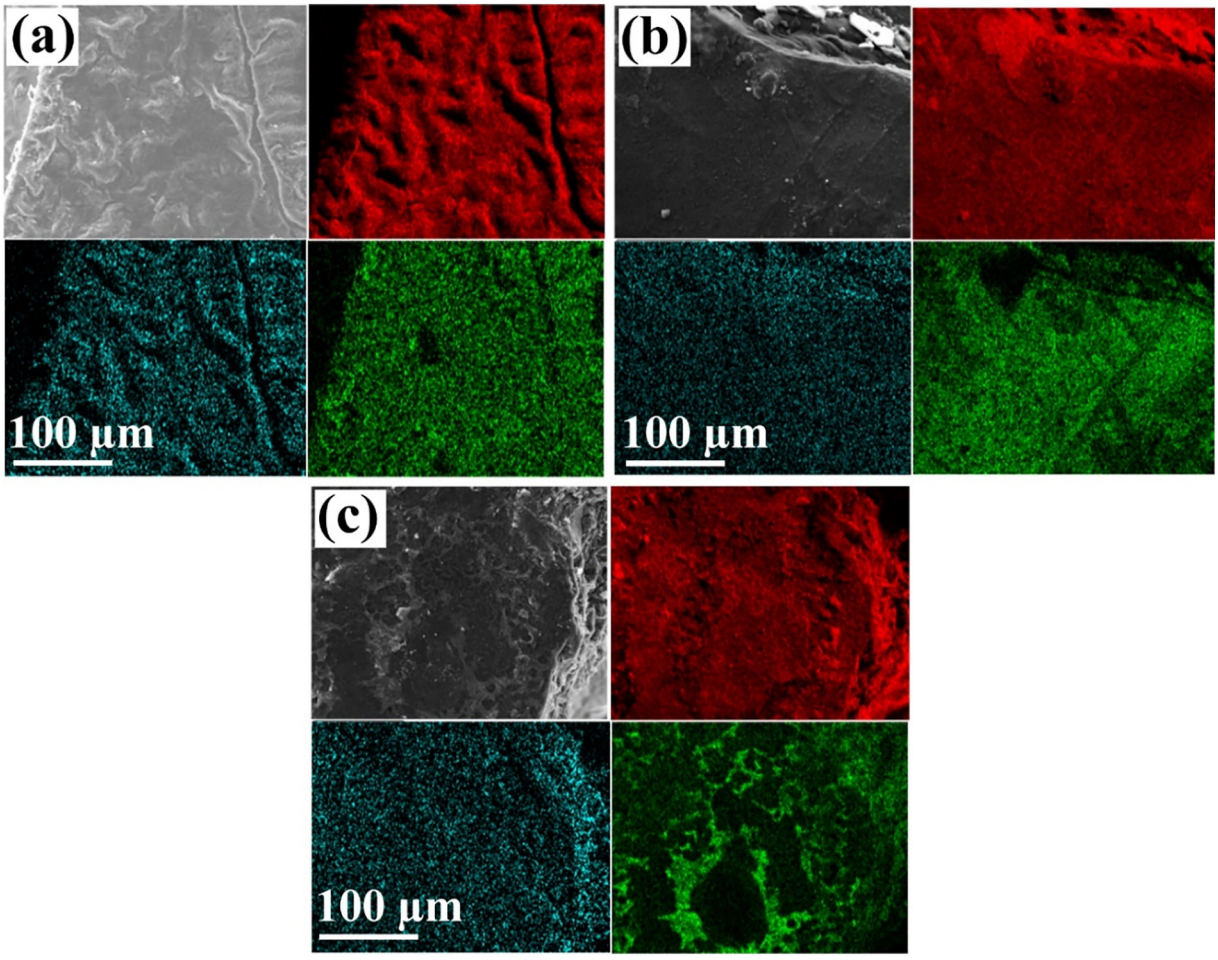

Fig. 2. SEM images and EDS mapping of $0.5V_2O_5$–$0.5(Li_2O\text{-}xB_2O_3)$ glass samples: (a) x = 1, (b) x = 2, (c) x = 3 (samples-grey; O-red; B-blue; and V-green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Density and molar volume of the vanadium-lithium borate glasses.

$0.5V_2O_5$–$0.5(Li_2O\text{-}xB_2O_3)$ Samples	Density (g/cm^3)	Molar volume (cm^3/mol)
x = 1	2.72 ± 0.22	51.64
x = 2	2.25 ± 0.35	78.07
x = 3	2.36 ± 0.01	89.12

2. Experimental procedures

2.1. Sample preparation

The conventional melt-quench method was used to prepare vanadium-lithium borate glass, $0.5V_2O_5$–$0.5(Li_2O\text{-}xB_2O_3)$ glass with x = 1, 2 and 3 glass, which divided into two steps. The first step is lithium borate preparation. The lithium borate were prepared by mixing of the precursor materials of Lithium carbonate (Li_2CO_3, 99%, Himedia) and