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Investigation of vanadium–sodium silicate glasses using XANES spectroscopy

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Abstract

X-ray absorption near edge structure spectroscopy has been used to investigate the electronic and atomic structure of $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ $(x<0.1)$ glasses obtained by melt-quench technique. The results show no sign of metallic clustering of V atoms, but mixed oxidation states (+4 and +5) of V and strong V3d–O2p hybridization in the glasses. Detailed analysis has revealed that the glass samples contain about 15% V^{4+} and 85% V^{5+} and the ligand-field splitting is about 1.6 eV.

Keywords: XANES; Vanadium–sodium silicate glasses; V $L_{2,3}$ edges; O K edge

1. Introduction

Studies on oxide glasses containing transition-metal (TM) ions continue to be of interest due to their semiconducting properties and technological applications [1–3]. The semiconducting nature of these glasses arises from the hopping of unpaired electron(s) between TM ions having multi valence states [4]. The unpaired electron induces polarization around the TM ion and therefore, the conduction process can be described in a polaron model. However, a more detailed modeling of the conduction process is limited due to many factors including the type and concentration of the TM ion, the number of valence states associated with the TM ion, the glass preparation conditions, and the microstructures within the glass matrix. Thus, information on the structure of a glass is imperative for further elucidating our understanding of the glass properties. The concentration and the redox state of polyvalent elements in glasses are of particular interest owing to its influence on manifold properties of glasses such as optical, electrical, and magnetic.

There are a number of methods available which allow determining the valence state of TM ions. However, each method reflects the redox state in a specific way. In this work, the use of X-ray absorption spectroscopy in the near edge region is demonstrated investigating vanadium-sodium silicate glasses. X-ray absorption near edge structure (XANES) spectroscopy is a powerful local probe for the electronic structure as well as the atomic structure of materials. It probes the empty energy bands by measuring transitions from core levels, and does not require a crystalline sample. Element specificity and symmetry selection rules are some of the powerful aspects of the technique. Until recently, the application of XANES to the study of 3d transition metal compounds has largely been limited to 1s absorption (K edge) [5,6]. However, recent advancement in soft X-ray monochromators and synchrotron radiation instrumentation made it possible to probe L absorption edges of 3d TM compounds, as well as O K edge, with high energy resolution [7]. The 2p absorption ($L_{2,3}$ edge) spectrum is dominated by dipole transitions from the core 2p level to empty 3d states, and because of the large coulomb interaction between the two levels, the dipole transition energies and their occurrence probabilities depend on the local electronic structure. Thus, analysis of the $L_{2,3}$ edge structure provides information about the oxidation state (including mixed states), site symmetry, spin state, and ligand-field splitting of the 3d TM ions. Therefore, in this paper we concentrate on the analysis of V $L_{2,3}$ and O K absorption edges of vanadium–sodium silicate glasses.

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Table 1
Nominal and ICP analysed compositions of $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ glasses

x	Nominal			Analysed		
	Na_2O	SiO_2	V_2O_5	Na_2O	SiO_2	V_2O_5
0.025	0.300	0.675	0.025	0.291	0.683	0.026
0.050	0.300	0.650	0.050	0.284	0.668	0.048
0.075	0.300	0.625	0.075	0.293	0.632	0.075
0.100	0.300	0.600	0.100	0.292	0.610	0.098

The relative uncertainty in the ICP results is ±5%.

2. Experimental details

The glass compositions studied have the general formula $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ with nominal x values 0.025, 0.050, 0.075, and 0.100. Analytical grade powders of V_2O_5, Na_2CO_3 (for Na_2O), and SiO_2 in the required stoichiometric ratios were thoroughly mixed and melted in platinum crucibles at temperatures ranging from 1300 to 1400 °C, depending on the composition. The mixture was kept at the melting point for about 2 h and then quenched to room temperature in air. X-ray powder diffraction patterns were taken for the four compositions to check for the presence of crystalline phases and none were detected. After preparation, the samples were stored in a desiccator in order to minimize water absorption. Chemical compositions were determined by inductively coupled plasma (ICP) emission spectroscopy and the results of the analysis are shown in Table 1. The small differences between the nominal and the analyzed glass compositions indicate an evaporation of small amount of starting oxides. Na_2O seems to be more volatile than V_2O_5.

The XANES measurements were performed on beamline 9.3.2 at the Advanced Light Source in Lawrence Berkeley National Laboratory. Finely powdered specimens were used on a double sided carbon tape for the XANES measurements. High-resolution XANES spectra were taken in the V $L_{2,3}$ and O K absorption edge regions, while the monochromator was set at a resolving power of ≥ 4000. The monochromator allows in situ switching of three spherical gratings. Grating G1 (with 100 lines/mm) covers the photon energy range 30–150 eV, Grating G2 (with 600 lines/mm) covers the range 200–800 eV, while Grating G3 (with 1200 lines/mm) covers 400–1500 eV. The Grating G2 was used for our measurements to cover 500–600 eV range. The photon flux at the sample was about 10^{11} photons/s/0.1% bandwidth. The base pressure in the experimental chamber was about 2×10^{-10} Torr. XANES measurements were performed in total electron yield mode by measuring sample current. The beam flux (I_0) signal from a gold grid was used to normalize the spectra.

3. Results

Fig. 1 shows room-temperature XANES data of vanadium–sodium silicate glasses at the V $L_{2,3}$ and O K edge region as a function of vanadium doping. The energy scale was calibrated using absorption peaks of Cr $L_{2,3}$ edges originated from the coatings of monochromator [8]. We normalized the spectra by subtracting a straight line fitted to the region before the peaks (below 515 eV), and adjusting the intensity of the spectra to 1 at 555 eV.

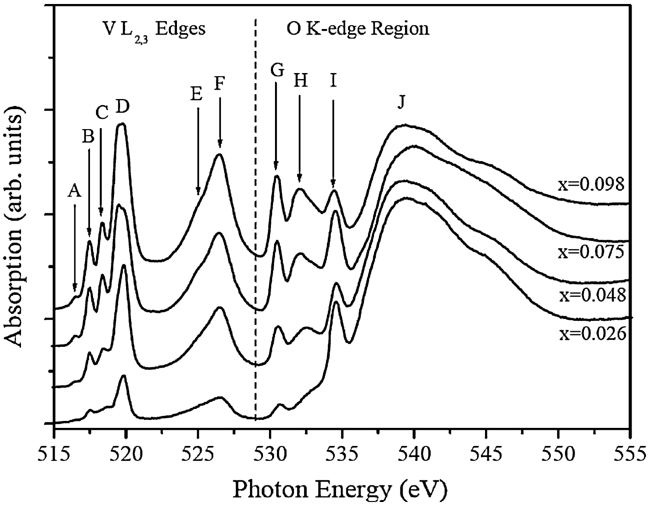

Fig. 1. Room-temperature XANES data of $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ glasses at the V $L_{2,3}$ and O K edge region as a function of vanadium doping.

The V $L_{2,3}$ edge region (515–529 eV) shows a number of interesting features labeled as peaks A through F. The O K edge region (529–555 eV) shows three peaks labeled G, H, and I at about 530.5, 532.1, and 534.7 eV, respectively, in addition to a broad peak (labeled J) centered about 539.5 eV.

4. Discussion

Peak D at about 519.8 eV and Peak F at about 526.5 eV, in Fig. 1, are the main V L_3 and L_2 edges, respectively. The L_3 and L_2 edges are due to electron transition from $2p_{3/2}$ and $2p_{1/2}$ energy levels to V 3d–O 2p hybridized bands. The decrease in the apparent spin-orbit splitting of V 2p level in the absorption spectra (~6.7 eV) as compared to the splitting observed in XPS (~7.7 eV) is a natural consequence of the strong interaction between the 2p core hole and the 3d electrons in the final state [9,10]. These interactions are of the same order of magnitude of the V 2p spin–orbit splitting which causes a large redistribution of the intensity throughout the entire spectra [10]. The peak position of L_3 edge suggests that V is in +5 oxidation state in the glasses [11]. The prepeak B at about 517.5 eV is a signature of electron transition from V 2p into the unoccupied V 4s states [12]. Since the 4s states are occupied in elemental vanadium, the presence of the prepeak implies that V is not in the elemental form in the glasses. In other words, there is no metallic clustering of V atoms in the sample. The peaks labeled A, C, and E at about 516.4, 518.4, and 525.1 eV, respectively, forming another set of prepeak, L_3 and L_2 edges, are assigned to V^{4+} [11]. There is no significant shift in the peak positions as a function of V doping. This observation suggests that the oxidation states of V in the glass remains the same. Note that the peak intensities increase with V doping as expected. The details of the L_2 edge are somewhat blurred, because the intrinsic broadening is larger for L_2 than for L_3 edge, due to the interaction with L_3 continuum [13].

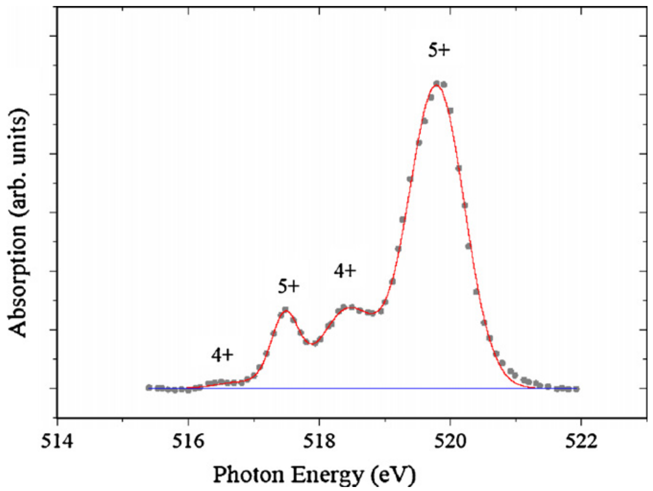

Fig. 2. Fitted V L_3 edge region of $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ glasses for $x = 0.048$.

In order to estimate the amount of V^{4+} in these glasses, the V L_3 edges, along with their prepeaks, that correspond to V^{4+} and V^{5+} (peaks A, B, C and D in Fig. 1) were fitted with Gaussian peaks. Fig. 2 shows such a fit for the sample with $x = 0.048$, as an example. From the ratio of the area under the peaks, we estimate about 15% (with less than 5% uncertainty) of total vanadium is in the +4 valence state in all of the four glass samples. In our earlier work [14], X-ray photoelectron spectroscopy (XPS) did not reveal any V^{4+}, probably due to the poor energy resolution of the spectrometer (~1 eV), which is of the same order as the chemical shift between V^{4+} and V^{5+}. It is also possible that V^{4+} is in the bulk of these glasses rather than on the surface, as the XPS is highly surface sensitive technique (probing depth of less than 10 nm) due to the inelastic mean free path of the photoelectrons. Notice that the probing depth of XANES technique is about 100 nm. The foregoing discussion underlines the power of high-resolution XANES technique for detecting multi valence states of TM ions in glass systems.

The close resemblance of the V-$L_{2,3}$ edge spectral weight of $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ $(x < 0.1)$ glasses to that of V_2O_5 [7] suggests that V in the glasses is in a similar local environment of that in V_2O_5. It means that V atoms are covalently bonded with six nearest-neighbor O atoms in a distorted octahedral structure [15]. This is in agreement with our earlier finding [14] that V is present predominantly in the form of metavanadate units ($V_2O_6{}^{2-}$) in these glasses.

Peaks G (at 530.5 eV) and H (at 532.1 eV), in Fig. 1, are due to transitions from O 1s to the V 3d–O 2p hybridized bands while the broad peak J is assigned to V 4sp–O 2p hybridized bands [9,16]. Based on our X-ray photoelectron spectroscopy (XPS) study [14], we assign the peak I (at 534.7 eV) to O 2p band of bridging oxygen (Si–O–Si). Peaks G and H are attributed to the V 3d(t_{2g})–O 2p and V 3d(e_g)–O 2p hybridized bands, respectively, based on molecular–orbital and crystal-field ideas [15]. V 3d orbital mixes with the O 2p ligands forming unfilled antibonding orbitals $2t_{2g}$ (d_π) and $3e_g$ (d_σ) orbitals [16]. Therefore, O K edge is expected to reflect the unoccupied states that result from the hybridization between V 3d and O 2p states. Thus, the energy separation between the peaks G and H is a measure of ligand field splitting, which is 1.6 eV in our glass samples. Since covalency reduces the number of filled states with O 2p character, the intensity of the peaks is a measure of covalency strength; the higher the intensity the higher the covalency [16]. Notice that covalency increases in the glasses with increased V doping. Defects can also have considerable influence on XANES spectra as they distort the local symmetry and hence affect the amount of hybridization. A detailed discussion of O K edge features would require a symmetry-projected band structure calculation, which is not available to our knowledge.

5. Conclusion

XANES technique has been used to investigate the electronic and atomic structure of $(V_2O_5)_x(Na_2O)_{0.30}(SiO_2)_{0.70-x}$ $(x < 0.1)$ obtained by melt-quench technique. The V $L_{2,3}$ edge spectra show no sign of metallic clustering of V atoms in the glasses. The peak positions suggest that V is in +4 as well as +5 oxidation states in the glasses. Peak fitting procedure estimates about 15% of total vanadium is in the +4 valence state in these glasses. The O K edge spectra reveal strong hybridization between O 2p and V 3d orbitals with ligand-field splitting of about 1.6 eV.

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