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X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility studies of vanadium phosphate glasses

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ABSTRACT

Vanadium phosphate glasses with the nominal chemical composition $[(V_2O_5)_x(P_2O_5)_{1-x}]$, where $x = 0.30$, 0.40, 0.50, and 0.60, have been prepared and investigated by X-ray photoelectron spectroscopy (XPS) and magnetization measurements. Asymmetries found in the O 1s, P 2p, and V 2p core level spectra indicate the presence of primarily P–O–P, P–O–V, and V–O–V structural bonds, a spin–orbit splitting of the P 2p core level, and more than one valence state of V ions being present. The magnetic susceptibility data for these glasses follow a Curie–Weiss behavior which also indicates the presence of some V ions existing in a magnetic state, i.e., a valence state other than that of the non-magnetic V^{5+}. From qualitative comparisons of the abundance of the bridging oxygen or P–O–P sites as determined from the areas under the various O 1s peaks with the abundances of differing phosphate structural groups associated with the presence of different valence states of the vanadium ions, a glass structure model consisting of a mixture of vanadate phosphate phases is proposed for these glass samples. These include V_2O_5, $VOPO_4$, $(VO)_2P_2O_7$, $VO(PO_3)$, and $V(PO_3)_3$ with the abundance of orthophosphate $(PO_4)^{3-}$ units increasing with increasing vanadium content.

1. Introduction

Vanadate and phosphate glasses continue to be of interest because of their unique properties and correspondingly their potential suitability for applications. For example, binary and ternary V_2O_5 glasses can exhibit a semiconducting behavior [1–4] which arises from an unpaired $3d^1$ electron hopping between the transition metal (TM) ions [5–6] when the TM ions exist in two or more valence states, i.e., an electron hopping from a V^{4+} site to a V^{5+} site. On the other hand, the low thermo-optical coefficient and large emission characteristics found in phosphate glasses make them suitable materials for high power laser devices [7]. Furthermore, most biocompatible glasses are based on phosphate glasses. In either glass system, however, information on the structure of a glass is imperative for understanding the glass properties and assessing their suitability for applications.

The basic structure of vitreous phosphate consists of PO_4 tetrahedra connected on the three of the four corners with the fourth corner being occupied by terminal double-bonded oxygen [8]. The introduction of a glass modifier such as RO or R_2O with O/P ratios of less than 3 results in a breaking of the covalent P–O–P bonds with additional terminal oxygen P=O bonds or P–O–R bonds being formed. Depending on the number of remaining bridging oxygen, the phosphate tetrahedra can be classified using the Q^i terminology [8–12], where '*i*' represents the number of bridging oxygen sites per tetrahedron. Thus Q^3 refers to a fully polymerized structure, while Q^2 denotes a two-dimensional structure based on chains or rings which is characteristic of a metaphosphate structure with 2 bridging oxygen and 2 non-bridging oxygen. A PO_4 tetrahedron connected by a corner to another PO_4 tetrahedron as in the pyrophosphate P_2O_7 structure is denoted by Q^1 with 1 bridging oxygen while the isolated tetrahedron with no bridging oxygen as in the orthophosphate PO_4 structure are represented by Q^0.

In comparison, the structure of vanadate glasses is less clear as to the exact nature of the oxygen polyhedra surrounding the vanadium atoms or of the role played by the other glass components. For example, structural studies on alkaline earth vanadate glasses by NMR and IR spectroscopy techniques [13–15] suggest that the local structure of these glasses is basically the same irrespective of the alkaline earth metal and consists mainly of corner-sharing VO_4-tetrahedra. Yet, neutron diffraction investigations on other vanadate glasses [16–17] indicate that the vanadate network is composed of distorted, interconnected VO_5 trigonal bipyramids/tetragonal pyramids with the modifier metal ions being randomly dispersed in holes of the vanadate network. Moreover other

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structural studies have reported that V_2O_5 acts as a network former [18–19] and consists of unaffected VO_5 groups as in vitreous V_2O_5 and affected VO_5 groups with alkaline earth ions. This is in contrast to studies suggesting that the vanadate glasses behave as a conventional network former in which only unaffected VO_5 groups are present [20]. Even in the case of pure V_2O_5 glass it has been reported [21–22] that V^{5+} ions exhibit both fourfold and fivefold coordination states depending upon the sample preparation conditions. Thus the structure of the vanadate glasses may not only be dependent on the network modifier but also on the nature of vanadate network itself.

Structural studies on the vanadate phosphate glass system are even more limited. Early NMR data [23] on a series of vanadate-rich phosphate glasses were interpreted in terms of two types of VO_5 units being present in this glass system, one being similar to that in crystalline V_2O_5 and the other having a VO_5 unit with a PO_4 unit substituted for the apex oxygen. In addition, both NMR and ESR (electron spin resonance) data indicated the presence of both V^{5+} and V^{4+} ions with two V^{4+} sites being formed for each PO_4 unit substituted at the apex oxygen of the VO_5 unit. Another ESR study [24] reported that V^{5+} and V^{4+} ions co-existed for high vanadium oxide content glasses while either lower vanadium oxidation states were produced in smaller concentrated V_2O_5 glasses or V^{4+} ions existed at sites different from those giving rise to a ESR signal. A neutron diffraction study [17] on vanadate-rich P_2O_5–V_2O_5 glasses ($O/P > 5$) concluded that the glass structure was composed of a vanadate chain-like network consisting of distorted VO_5 tetragonal pyramids with these chains cross-linked by PO_4 tetrahedra and having all four P–O bond lengths the same.

Since X-ray photoelectron spectroscopy (XPS) has proven to be an important technique in the study of the local structure of oxide glasses, an XPS study on a series of moderately concentrated V_2O_5–P_2O_5 glasses ($3.5 < O/P < 6$) should be beneficial in further elucidating the nature of glass structure in this system. Distinguishing different types of oxygen sites, e.g., bridging oxygen (BO) versus non-bridging oxygen (NBO) [25–29], as a function of vanadate concentration can be especially important in understanding whether the role of vanadate changes from being a network modifier to a network former. In addition, the valence state of the TM ions in the glass structure can be investigated and their relative concentrations can be determined [30]. Moreover, magnetization measurements combined with inductively coupled plasma (ICP) spectroscopy can provide an independent determination of the ratio of the different valence states of V present in these glasses.

2. Experimental details

2.1. Glass preparation

All glasses were prepared by melting dry mixtures of reagent grade V_2O_5 and P_2O_5 in alumina crucibles to form nominal $[(V_2O_5)_x(P_2O_5)_{1-x}]$ compositions with $x = 0.30$, 0.40, 0.50 and 0.60. Since oxidation and reduction reactions in a glass melt are known to depend on the size of the melt, on the sample geometry, on whether the melt is static or stirred, on thermal history, and on quenching rate, all glass samples were prepared under similar conditions to minimize these factors. Approximately 20 g of chemicals were thoroughly mixed to obtain a homogenized mixture for each V_2O_5 concentration. The crucible containing the batch mixture was then placed in an electrically heated melting furnace and maintained at 1000–1100 °C for about 1-to-2 h under atmospheric conditions during which the melt was occasionally stirred with an alumina rod. The homogenized melt was then cast onto a stainless steel plate mold to form glass buttons and glass rods of approximately 5-mm diameter for XPS measurements. X-ray powder diffraction analysis indicated that the glasses formed were completely amorphous and no alumina was detected within the resolution limits in either the XPS spectra or the compositional analyzes. The actual compositions of the glasses were subsequently determined by inductively coupled plasma spectroscopy (ICP) and are listed in Table 1.

2.2. X-ray photoelectron spectroscopy (XPS) measurements

Core level photoelectron spectra were collected on a VG Scientific ESCALAB MKII spectrometer equipped with dual aluminum–magnesium anodes using Al Kα radiation ($h\nu = 1486.6$ eV) from an anode operated at 130 W. For self-consistency, the C 1s line at 284.6 eV was used as a reference for all charge shift corrections as this peak arises from hydrocarbon contamination and its binding energy is generally accepted as remaining constant, irrespective of the chemical state of the sample. For XPS measurements, a glass rod from each composition was cleaved in the preparation chamber at a base pressure of 2×10^{-9} mbar before being transferred to the analysis chamber where the pressure was maintained at $<2 \times 10^{-10}$ mbar. A non-linear, least-squares algorithm was employed to determine the best fit to each of the O 1s, V 2p, and P 2p spectra with two-to-four Gaussian–Lorentzian curves in order to represent various oxygen bonding sites (e.g., P–O–P, P–O–V, V–

Table 1

Peak positions, FWHM, areas, and relative abundance from the curve fitting of the O 1s and P 2p core levels for various vanadium phosphate $(V_2O_5)_x(P_2O_5)_{1-x}$ glasses. Actual compositions (5%) were determined from ICP measurements.

x (nominal)	x (actual)	O 1s (I) FWHM area abundance	O 1s (II) FWHM area abundance	O 1s (III) FWHM area abundance	O 1s (IV) FWHM area abundance	P 2p FWHM (single-peak)	P $2p_{3/2}$ FWHM area abundance	P $2p_{1/2}$ FWHM area abundance	Ratio of P 2p areas
0.30	0.36	533.10	531.28	529.56	528.43	133.81	133.55	134.45	2.17
		2.27	2.10	1.17	2.05	2.65	1.95	1.95	
		7577	17359	1709	4929		4172	1923	
		0.285	0.652	0.064	–		0.685	0.315	
0.40	0.39	533.08	531.26	529.50	–	133.73	133.40	134.45	2.10
		2.27	2.06	1.23		2.80	2.10	2.10	
		8362	18540	574			4564	2176	
		0.304	0.675	0.021			0.677	0.323	
0.50	0.46	532.99	531.42	–	–	133.65	133.35	134.40	2.11
		2.29	1.94			2.94	2.00	2.00	
		11947	29876				4422	2095	
		0.286	0.714				0.679	0.321	
0.60	0.54	533.18	531.47	–	–	133.97	133.65	134.70	2.05
		2.23	2.09			2.69	2.05	2.05	
		7893	39811				3406	1665	
		0.165	0.835				0.672	0.328	

The uncertainty in the peak positions is ±0.1 eV, FWHM ±0.2 eV, and areas ±10%.