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Role of vanadium ions on structural, optical and electrochemical properties of the vanadate-lead glasses

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ABSTRACT

New different series of $xV_2O_3\cdot(100-x)[4PbO_2\cdot Pb]$ glasses were prepared by melt-quenching method in a wide range of compositions defined by the parameter x = 0–30 mol% V_2O_5. InfraRed (IR) data reveal that by increasing the V_2O_5 content, the glass network was transformed into a mixture of modified $[VO_4]$ structural units, namely pyrovanadate and orthovanadate ones. The UltraViolet–Visible (UV–VIS) spectra show that addition of V_2O_5 produces a gradual shift of the absorption edge towards the higher wavelength side (indicating the increase in concentration of vanadyl species) and a decrease of the gap energy.
The shape of the Electron Spin Resonance (ESR) spectra changes with increasing the V_2O_5 content suggesting that the interactions between vanadium centers strongly depend on x parameter which plays an important role. A hyperfine structure becomes visible in the glass with x = 20 mol% V_2O_5 suggesting modifications of the glass structure caused by the network modifier. If the network is moderately disrupted the formation of Pb^{+2}–V^{+4} pairs was coupled through the oxygen atom or the interactions within V^{+4}–O–V^{+5} chains mask hyperfine structure. The shape of cyclic voltammograms, redox waves and good reversibility of the x = 20 mol% V_2O_5 glassy electrode depends on the electrolyte acidity and electrochemically active species present in the glass network.

1. Introduction

Researches related to the understanding of structural and physical properties of glasses in general and of semiconducting glasses in particular become of considerable interest due to the important potential applications of such materials: switching, memory switching, electrochemical batteries, etc [1].

Glasses containing transition metal ions such as V, Fe, Co, Mo, and W are known to be electronic semiconductors. The electronic conduction is due to the small polaron hopping between different valence state transition metal (TM) ions. Accordingly, conduction in these glasses is explained by the phonon assisted hopping of electrons (small polaron hopping) between the low and high valence states of TM ions. For example, the V_2O_5–PbO glasses are known to contain V^{+4} and V^{+5} ions and the conduction mechanism is attributed to the hopping of a $3d^1$ electron from V^{+4} to V^{+5} [2–4]. Electron hoping in vanadophosphate glasses depends on the distance between the V^{+4} and V^{+5} ions as well as on their concentration [5].

Lead is known to play various structural roles in glasses depending upon the glass-forming systems and their compositions [6–10]. Structural roles of lead in vanadato-lead glasses are particularly interesting because lead is not considered to be a conventional glass former. Previous studies suggested that lead may play a network former role, a charge compensator and also a network modifier role [11–14]. Network forming properties of lead are due to the formation of $[PbO_3]$ and $[PbO_4]$ structural units while network-modifying role is due to the Pb^{+2} ions. The polarizability of Pb^{+2} ions also contributes to network formation by allowing changes in the polyhedral angles.

The main objective of the present work was to provide a study on structural, optical, magnetic and electrochemical properties of the $xV_2O_5\cdot(100-x)[4PbO_2\cdot Pb]$ glasses where x = 0–30% V_2O_5. A second objective was to understand the electronic conduction mechanism based on the electron hopping between the multivalent states of the vanadium ions.

2. Experimental procedure

Glass samples with a general formula of $xV_2O_5\cdot(100-x)[4PbO_2\cdot Pb]$ where x = 0–30 mol% V_2O_5 were synthetized by melt quenching method using as starting materials metallic lead, lead (IV) oxide and vanadium (V) oxide of high purity. The mechanically homogenized mixtures in stoichiometric quantities were melted in sintered corundum crucibles at 950 °C in an electric furnace for 10 min. Then the melts were rapidly quenched onto a stainless steel plate maintained at room temperature.

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The amorphous nature of all samples was confirmed by X-ray diffraction studies performed with a XRD-6000 Shimadzu diffractometer, with graphite monochromator for Cu Kα radiation (λ = 1.54 Å).

IR absorption spectra were recorded at room temperature using a JASCO FTIR 6200 spectrometer and the standard KBr pellet disc technique. The spectra were carried out with a standard resolution of 2 cm^{-1}.

UV–Visible absorption spectra of the powdered glass samples were recorded at room temperature in the 250–600 nm range using a Perkin-Elmer Lambda 45 UV/VIS spectrometer equipped with an integrating sphere. These measurements were made on glass powder dispersed in KBr pellets. The validity of the band position is ±2 nm.

The electrochemical properties were characterized by cyclic voltammetry using a VERSASTAT3 potentiostat and the V3Studio software. Discs of glasses were used as working electrode, platinum electrode as counter, calomel as reference electrode and sulfate acid solution as liquid electrolyte. All experiments were conducted in solution of H_2SO_4 with the concentration of 5% and 38%.

ESR measurements were performed at room temperature using an ADANI PS 8400-type portable EPR spectrometer, in the X frequency band (9.5 GHz) and a field modulation of 100 kHz. The microwave power was 5 mW.

3. Results

The diffraction patterns of the $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ samples with x = 15–30 mol% V_2O_5, shown in Fig. 1, reveal only two large halos specific to the amorphous structure of the samples.

The formation of the $4PbO_2{\cdot}Pb$ glass can be described from the perspective of the $2PbO_2{\cdot}Pb_3O_4$ mixed oxides since $4PbO_2{\cdot}Pb$ can be considered a mixture of lead dioxide and "red lead" — Pb_3O_4 which are known in the literature as glass forming systems [15–17].

The FTIR spectra of $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ glasses with x = 0–30 mol% V_2O_5 are given in Fig. 2. These spectra exhibit some structural changes that occur in the vitreous matrix of the studied samples with increasing their V_2O_5 content up to 30 mol%. Lead glasses consist of a three dimensional network of [PbO_3], [PbO_4] and [PbO_6] structural units [18].

UV–VIS absorption spectra of the glasses in the $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ system where x = 0–30 mol% xV_2O_5 are shown in Fig. 3.

Fig. 4 shows plots of $(\alpha h\nu)^2$ as a function of $h\nu$ (in eV units) for the $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ glass samples where x = 5–30% V_2O_5. By extrapolating the linear portion of the curves to zero absorption, the optical band gap values, E_g, are determined. Note that the optical band gap values decrease from 3.00 eV down to 2.85 eV with increasing concentration of V_2O_5 in the lead glasses. This clear tendency of E_g to become somewhat smaller may be associated with the structural changes that are taking place caused by the addition V_2O_5 content into the lead glasses.

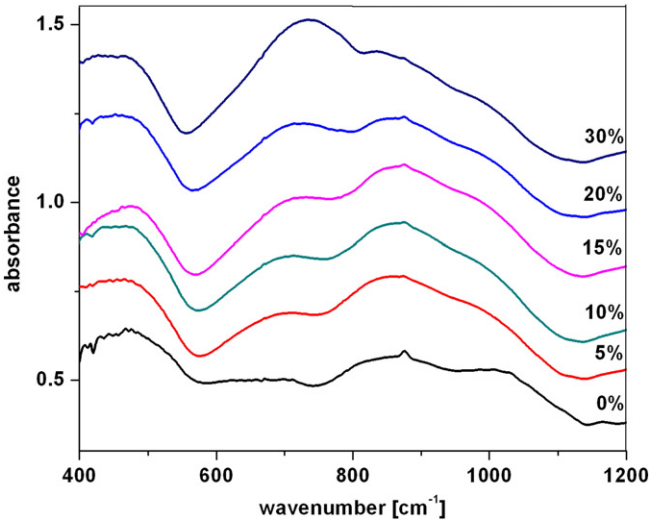

Fig. 2. FTIR spectra of $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ glasses where x = 0–30 mol% V_2O_5.

Electron Spin Resonance (ESR) spectroscopy is a powerful characterization method for tetravalent vanadium species, V^{+4}, since they give unambiguous information about the valence state, the local coordination environment and the site symmetry of paramagnetic centers.

The presence of the paramagnetic V^{+4} ions ($3d^1$ electronic configuration, $S = 1/2$ electron spin and $I = 7/2$ nuclear) in the lead-vanadate glasses gives rise to well resolved ESR spectra. These ESR spectra will give information regarding the local symmetry of the V^{+4} ions in the host network. ESR spectrum is a graph of first derivative of the absorbance depending on the magnetic field intensity (ΔA/ΔH) on the vertical axis versus magnetic field intensity, H on the horizontal axis.

The current–potential curves namely cyclic voltammograms exhibit maxima attributed to certain redox pairs. Fig. 6 exposes the cyclic voltammograms of the sample with x = 20 mol% V_2O_5 used as working electrode in an electrolyte solution of 5% and 38% H_2SO_4.

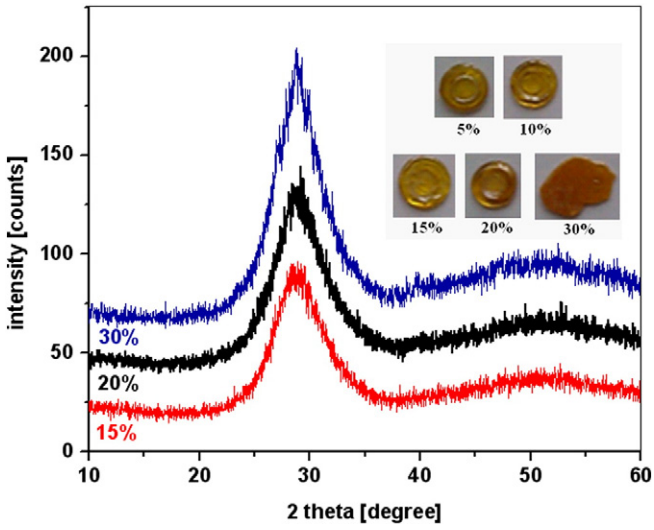

Fig. 1. XRD diffraction patterns of $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ glasses where x = 0–30 mol% V_2O_5.

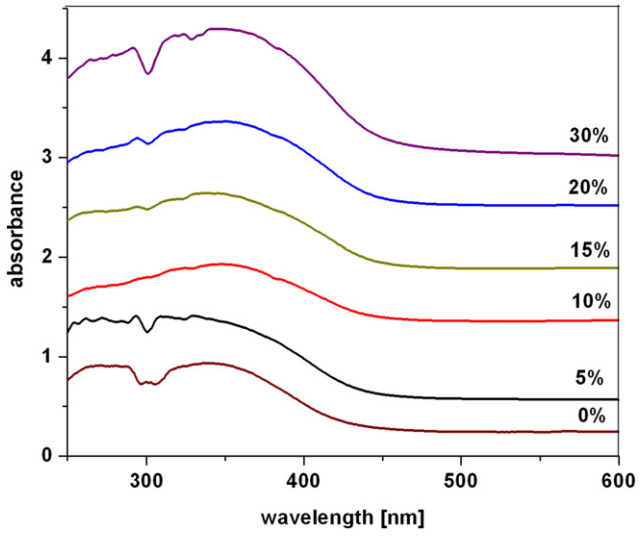

Fig. 3. UV–VIS absorption spectra of $xV_2O_5{\cdot}(100-x)[4PbO_2{\cdot}Pb]$ glasses where x = 0–30 mol% V_2O_5.