

Optical and structural investigations of zinc phosphate glasses containing vanadium ions



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ABSTRACT

Zinc phosphate glasses containing vanadium ions were studied from combined optical and infrared absorption spectral measurements. Density and molar volume calculations were obtained and interpreted in the view of non-bridging oxygen formation in glasses. Vanadium ions are assumed to exist in lower valences, mainly V^{3+} ions with sharing of V^{4+} ions. Optical band gap for the base zinc phosphate glass is estimated to be 3.75 eV. This value was observed to decrease as the vanadium oxide content increases and it was found to be 2.05 eV at the highest doping of vanadium content, 8.4 mol% V_2O_5 . The refractive indexes for the studied glasses were evaluated from the optical band gap values and their values are observed to increase with increasing the vanadium content. Electronic oxide polarizability and optical basicity were investigated for the studied glasses. Unshared V–O bonds observed from infrared absorption spectra leading to increasing non-bridging oxygen bonds in the host glass.

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1. Introduction

Phosphate glasses possess peculiar and interesting properties including high thermal expansion coefficients, lower transition temperatures with lower melting temperatures, higher electrical conductivities and marked optical properties which make them potential for various recent applications [1,2]. These include optical data transmission, sensing laser technologies, solid state batteries, sealing glasses and even extend to be host for burial of radioactive wastes [3,4].

The chemical durability of phosphate glasses can be improved by introducing multivalent oxides such as PbO and Al_2O_3 . Furthermore, phosphate glasses are known to accommodate high concentrations of transition metal ions (TM) and remain amorphous with brilliant colors.

The distribution of Q_n tetrahedral sites as n varies from zero to 3 in phosphate glasses shows the number of bridging oxygen (BO) per PO_4 tetrahedron in the phosphate network. Furthermore, the presence of modifiers like (TM) makes the depolymerization process in the structure and the formation of non-bridging oxygen atoms (NBO) which upgrade their chemical durability [5,6].

Glasses containing transition metal ions have interesting optical and electrical properties which are due to the presence of these transition metal ions in several oxidation or coordination states in the glass matrix [7,8]. Vanadium is one of the 3d transition metal ions and exhibits solely

the ability to exist in these valence states, namely trivalent, tetravalent, and pentavalent states [9–11]. Previous spectroscopic studies on vanadium containing glasses [12–16] have shown that the greenish trivalent vanadium ions exist in distorted octahedral coordination with oxygen's and exhibit two characteristic absorption bands at 350–400 nm and 580–680 nm and a third possible band in the UV region originating from the electron transfer within the vanadium ion itself. The tetravalent bluish vanadium ions are assumed to exist as vanadyl ions (VO^{2+}) and exhibit characteristic four spin-forbidden weak bands at 420 nm, 760–860 nm, and at around 1000 nm. The pentavalent colorless vanadium ions corresponding to the d^0 configuration and thus will not give rise to d–d transitions but give a characteristic UV band at 380 nm. The ratio of each valence of vanadium ions in a glass depends on the type, the composition of glass and the melting condition [10–14].

Recently, Mirzayi and Hekmatshoar [17] studied $ZnO-P_2O_5$ glass containing higher concentrations of V_2O_5 varying from 5 to 65 mol%. They observed that the molar volume data were decreased with increasing V_2O_5 content. Moreover, structural studies by Fourier transform infrared (FTIR) spectroscopy were attributed to the modification process of the phosphate network. Also, Abdelghany and Hammad [18] investigate the optical and infrared properties of $ZnO-P_2O_5$ glasses doped with WO_3 towards gamma irradiation due to the existence of heavy transition metal oxide in the glass network like WO_3 . In this study the optical and infrared absorption spectra of zinc phosphate glasses containing vanadium pentoxide were examined to justify the state of vanadium ions in the zinc phosphate glass. It is due to that

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these glasses have mixed network former as a result of the high zinc oxide ratio. Moreover, vanadium oxide have dual properties, i.e. it can act as a modifier or a former or both (modifier and former). Hence, this paper is complementary part for the previous researches concerning on the effect of transition metal oxide in the host ZnO–P₂O₅ glasses. The expected outcome of this research is vanadium ions can act as a modifier with modifying the phosphate glass as semiconducting materials due to the presence of both zinc and vanadium ions.

2. Experimental details

2.1. Glass preparation

The studied glasses were prepared from chemically pure grade ammonium dihydrogen phosphate (NH₄H₂PO₄), zinc oxide (ZnO) and vanadium pentoxide (V₂O₅). The chemical composition in mol% of the glasses is (100-x)[50ZnO-50P₂O₅]: x V₂O₅, where x is the additives vanadium pentoxide (0, 0.4, 2.2, 4.4 and 8.4% respectively). All the weighed batches were melted in porcelain crucibles at 1200 °C for 90 min. The crucibles containing the melts were rotated twice to promote acceptable homogeneity. The melts were cast into slightly reheated stainless steel molds with the required dimensions and the prepared samples were immediately transferred for annealing in a muffle furnace adjusted at 350 °C. The annealing muffle was left to cool after 1 h to room temperature at a rate of 30 °C/h.

2.2. Optical absorption spectra measurements

The UV–visible absorption spectra were measured at room temperature in the range of 200–1100 nm using a recording spectrophotometer type JASCO, V/630, Japan. Polished samples of equal thickness (2 ± 0.1 mm) were used in these measurements. Each measurement was repeated twice to confirm the positions of the absorption peaks.

2.3. Fourier transforms infrared absorption measurements

Fourier transforms infrared spectra of the glasses were measured at room temperature in the wavenumber range 4000–400 cm⁻¹ by a Fourier transform infrared spectrometer type Nicolet i 10. The KBr disk technique was adopted. The infrared measurements were carried out immediately after preparing the disks to avoid moisture attack.

3. Results and discussion

3.1. Density and molar volume

The calculated density (ρ) of the glasses [19,20] and the molar volume (V_m) was obtained from the expressions:

$$\rho = \frac{0.5(1-x)M_{ZnO}\rho_{ZnO} + 0.5(1-x)M_{P_2O_5}\rho_{P_2O_5} + xM_{V_2O_5}\rho_{V_2O_5}}{0.5(1-x)M_{ZnO} + 0.5(1-x)M_{P_2O_5} + 0.5 M_{V_2O_5}} \quad (1)$$

$$V_m = M_{wt}/\rho \quad (2)$$

where M_{ZnO} , $M_{P_2O_5}$, and $M_{V_2O_5}$ are the molecular weight of ZnO, P₂O₅, V₂O₅. ρ_{ZnO} , $\rho_{P_2O_5}$, and $\rho_{V_2O_5}$ are the densities of ZnO, P₂O₅, V₂O₅ (5.60, 2.39, and 3.35 g/cm³ respectively) and M_{wt} is defined as the total molecular weight of the studied glasses. The density and the molar volume data were recorded in Table 1 and plotted as a function of V₂O₅ dopant in Fig. 1. The calculated density of ZnO–P₂O₅ glasses is in a good agreement with that obtained from Eraiah and Bhat [21].

The density of the glasses is observed to decrease with increasing the dopant content of vanadium oxide, while the molar volume increases as V₂O₅ increased. Hence, density and molar volume is strongly dependent on the dopant content and the glass network tends to be more open structure. Open structure is the term which describes the breaking of

Table 1

The glass composition (x), density (ρ), and molar volume (V_m).

x V ₂ O ₅ mol%	The glass density (ρ) ± 0.011 [g/cm ³]	The molar volume (V_m) ± 0.780 [cm ³ /mol]
0	3.562	31.359
0.4	3.560	31.450
2.2	3.554	31.858
4.4	3.547	32.356
8.4	3.535	33.263

The density obtained from Eraiah and Bhat [20] for 0.1Sm₂O₃–0.599ZnO–40P₂O₅ is 3.485 g/cm³.

bridging oxygen bonds and the formation of non-bridging bonds will be available [22,23]. So, it can be said that the intercalation of V₂O₅ in zinc phosphate glass causes the structural change in the glass network.

3.2. Optical absorption of the base zinc phosphate glass

Fig. 2 reveals the UV–visible absorption spectrum of the base zinc phosphate glass. It shows a sharp and strong UV absorption band with a peak at 205 nm and no further UV–visible bands are identified.

Some glass scientists previously and separately identified [8,24–27] strong UV absorption in some commercial glasses. They assumed that such distinct UV absorption originated from trace impurities within the raw materials used for the preparation of these glasses and specifically they referred to iron impurities mainly Fe³⁺ ions.

3.3. Optical absorption spectra of V₂O₅ doped zinc phosphate glasses

Fig. 3 illustrates the UV–visible absorption spectra glasses containing V₂O₅. The glass containing 0.4% V₂O₅ shows a spectrum consisting of

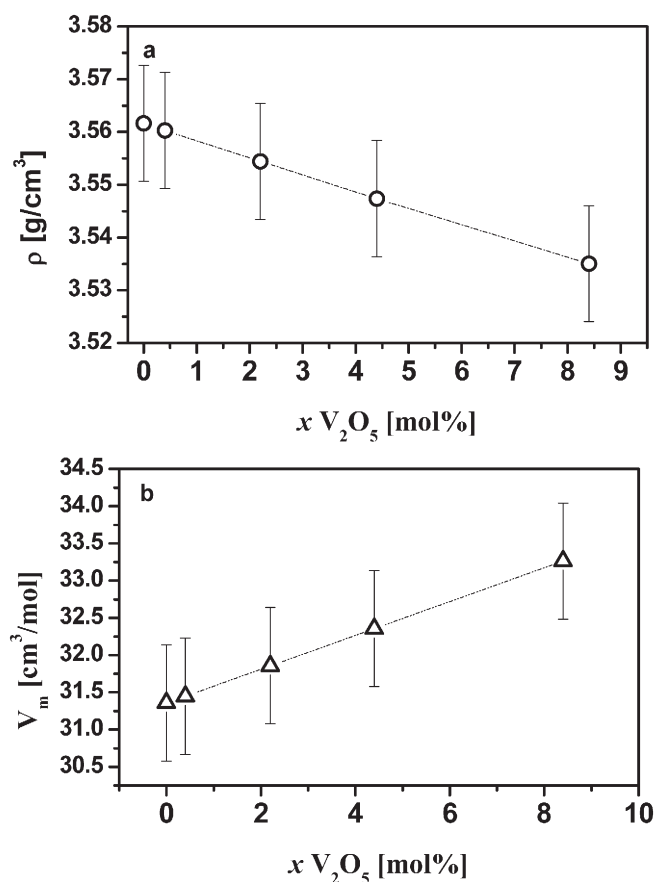


Fig. 1. Dependence of (a) glass density (ρ) and (b) molar volume (V_m) on the glass composition x .

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