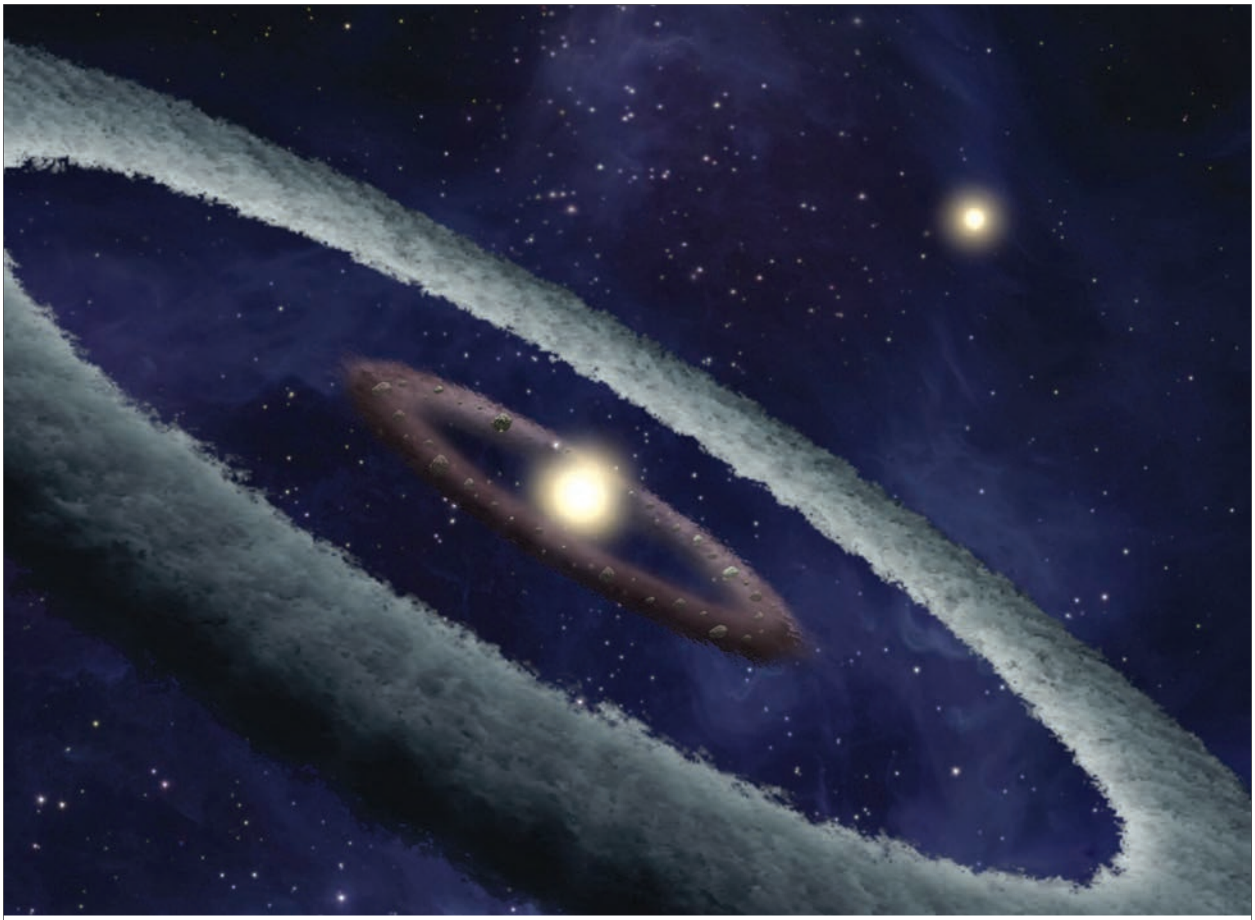

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Ultrasonic and Spectroscopic Studies on Structural Elucidation of Some Vanadium Glasses

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ABSTRACT

Semi conducting vanadium glasses with different V_2O_5 contents have been prepared by rapid quenching technique. Ultrasonic velocities measurements have been performed over a wide range of temperatures from 1020-1060 K. Elastic moduli, Debye temperature and poisson's ratio have been obtained for different V_2O_5 contents as a function of temperature. The composition dependence of velocities show a monotonic variation with the addition of V_2O_5. Ultrasonic velocity measurements (longitudinal and shear velocities) were carried by using pulse-echo technique at 5 MHz frequency showing that the ultrasonic velocity and the glass density are sensitive to the glass composition and behave identically to each other. The results indicate that the longitudinal wave velocities, shear wave velocities and elastic moduli show the same trend with composition. The X-Ray Diffraction spectral (XRD) studies have been employed to ascertain the amorphous nature of the glass specimen. To identify the functional groups present in the glass samples and to study about the morphology of the glass samples, the prepared glass samples are subjected to optical studies like FT-IR spectroscopy and Scanning Electron Microscopy (SEM), respectively. Eventually the results are discussed with a view to establish the structural characterization, compactness and mechanical properties of the glass samples.

Key words: Micro hardness, debye's temperature, FT-IR, x-ray diffraction, thermal expansion coefficient, SEM

INTRODUCTION

It is becoming increasingly important to understand the mechanical properties of glasses in addition to their other physical properties from the point of view of basic physics as well as applications. From a study of the structure property relationship of binary glasses it is found that they may be divided into two categories, as normal and anomalous, depending upon whether a particular property changes continuously with composition or suffers a discontinues change at some composition. Furthermore, one more recent investigation (Paul *et al*., 1997) of vanadium glasses indicates that they belong to the normal category. The mechanical behaviour of these two component (binary) glasses has been more or less well understood in terms of existing models. In comparison, the ternary glasses seem to have received less attention. The data on these glasses are also meager to test the existing ideas which have been found to be useful in analysing the physical process in the two component binary glasses.

In the present study, we have investigated the acoustic properties of two ternary vanadium glass systems such as (I) Na_2CO_3-V_2O_5-P_2O_5 (VSP Glass) and (II) P_2O_5 - V_2O_5-MnO_2 (VPM Glass).

Vanadium pentoxide is one of the transition metals and it exhibits semi-conducting properties and whose electrical conductivity lies between V^{5+} and V^{4+} of vandadium ions (Seshasayee and Muruganandam, 2006). Such a semi-conductivity behaviour of V_2O_5 is purely owing to its two valence V^{5+} and V^{4+} state of vanadium (Mott, 1968). This oxide metal has been categorized as a well-reformed glass former and can posses the same network either as a network former or as a network modifier owing to its concentration.

Much work has been made on glass system containing with MnO_2 and Na_2CO_3, other than vanadium glass are abundant but the above components doped with vanadium are very few. In the present work, efforts are made to study the effects of structural and physical properties of the vanadium glasses with MnO_2 and Na_2CO_3 with the exposure to ultrasonic studies, X-Ray Diffraction studies (XRD) Fourier Transformation Infrared Spectroscopy (FTIR) studies and Scanning Electron Microscopic (SEM) studies.

MATERIALS AND METHODS

Preparation of glass samples: The chemicals used in the present research work were Analytical Reagent (AR) and Spectroscopic Reagent (SR) grade with minimum assay 99% were obtained from Sd fine chemicals India and E-Merck, Germany. The composition was prepared in mole percentage (mol%) with decreasing content of P_2O_5 and MnO_2 with that of V_2O_5 in VSP and VPM glass system, respectively are depicted in Table 1. Further, all the chemicals were handled in an precautionary manner as described elsewhere.

The required amounts (approximately 20 g) in mol% (mole percentage) of required chemicals in powder form were weighed using single pan digital balance (Model SHIMADZU AX 200, Japan make) having an accuracy of 0.0001 g. The homogenization of the appropriate mixture of the component of chemicals was effected by repeating grinding using a pestle and mortar. The homogeneous mixture was put in a silica crucible and placed in an electrical furnace. Melting was carried out under controlled conditions with occasional stirring. The temperature controlled muffle furnace was gradually raised to a higher temperature at the rate of 100 K h^{-1} and a glassily

Table 1: Composition of glasses

Glass specimen	Composition mol (%)
System 1 (V_2O_5-Na_2CO_3-P_2O_5) (VSP glass)	
VSP 1	55-15-30
VSP 2	57-15-28
VSP 3	59-15-26
VSP 4	61-15-24
VSP 5	63-15-22
VSP 6	65-15-20
System 2 (V_2O_5-P_2O_5–MnO_2) (VPM glass)	
VPM 1	50-20-30
VPM 2	52-20-28
VPM 3	54-20-26
VPM 4	56-20-24
VPM 5	58-20-22
VPM 6	60-20-20

structure was noticed for VSP glass system at 1020 K and for VPM glass system 1060 K, respectively and eventually the molten glass melt was immediately poured on a heavy copper molding block having the dimension of 12 mm diameter and 6 mm length kept at room temperature. Then the glass samples were annealed at 400 K for 2 h to avoid the mechanical strains developed during the quenching process. The two opposite faces of glass ware highly polished to ensure a good parallelism. All glasses are cleaned with acetone to remove the presences of any foreign particles. The samples are prepared chemically stable and non-hygroscopic and such glass samples, are shown in Fig. 1a VSP glass samples (system 1) and 1b VPM glass samples (system 2).

Measurement of ultrasonic velocities: The ultrasonic longitudinal (U_L) and shear velocities (U_S) of the specimen were determined by using pulse-echo methods at room temperature at 5 MHz using X-cut and Y-cut transducers. These transducers act as both transmitters and receivers of the ultrasonic pulse. The transducers were brought into contact with each of the twelve samples by means of a couplant, in order to ensure that there was no air void between the transducer and the specimen. Couplant D-Gel type was used for longitudinal waves while resin was used for shear waves. By applying constant pressure on the probe the echo waveforms were obtained on the display unit and stored in the memory. Figure 2a shows one such echo waveforms obtained for longitudinal and shear waves of system 1 and Fig. 2b represents the same for system 2.

Measurement of density: The density of the glass samples was measured using relative measurement technique. Benzene was used as a buoyant liquid. The glass samples' were weighed both in air and after immersing in benzene at 303 K. The weight of the glass samples was measured in a single pan with an accuracy of 0.000 kg. The density of sample was calculated as:

$$\rho = \frac{W_1}{W_1 - W_2}\rho_B$$

where, W_1 and W_2 are the weights of the glass samples in air and in benzene and ρ_B is the density of buoyant liquid at 303 K.

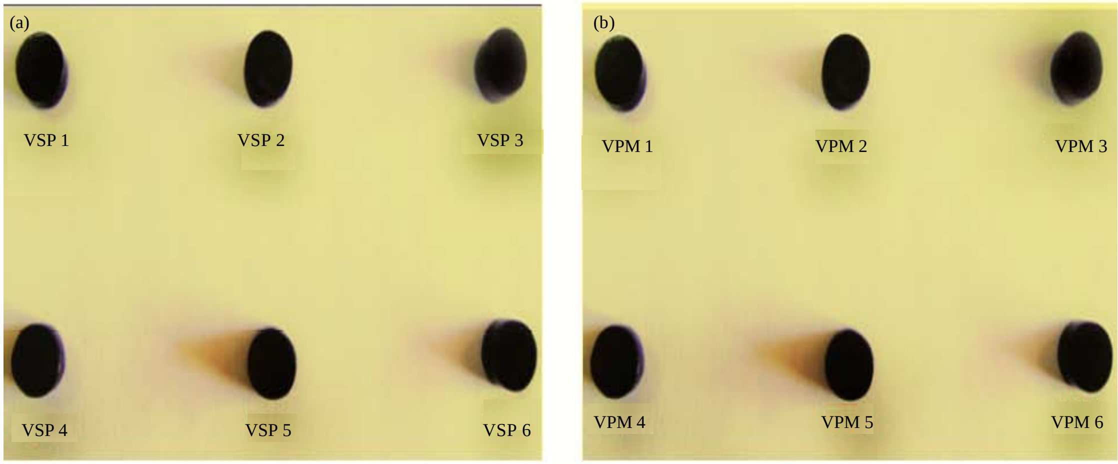


Fig. 1(a-b): (a) VSP glass samples (system 1) and (b) VPM glass samples (system 2)

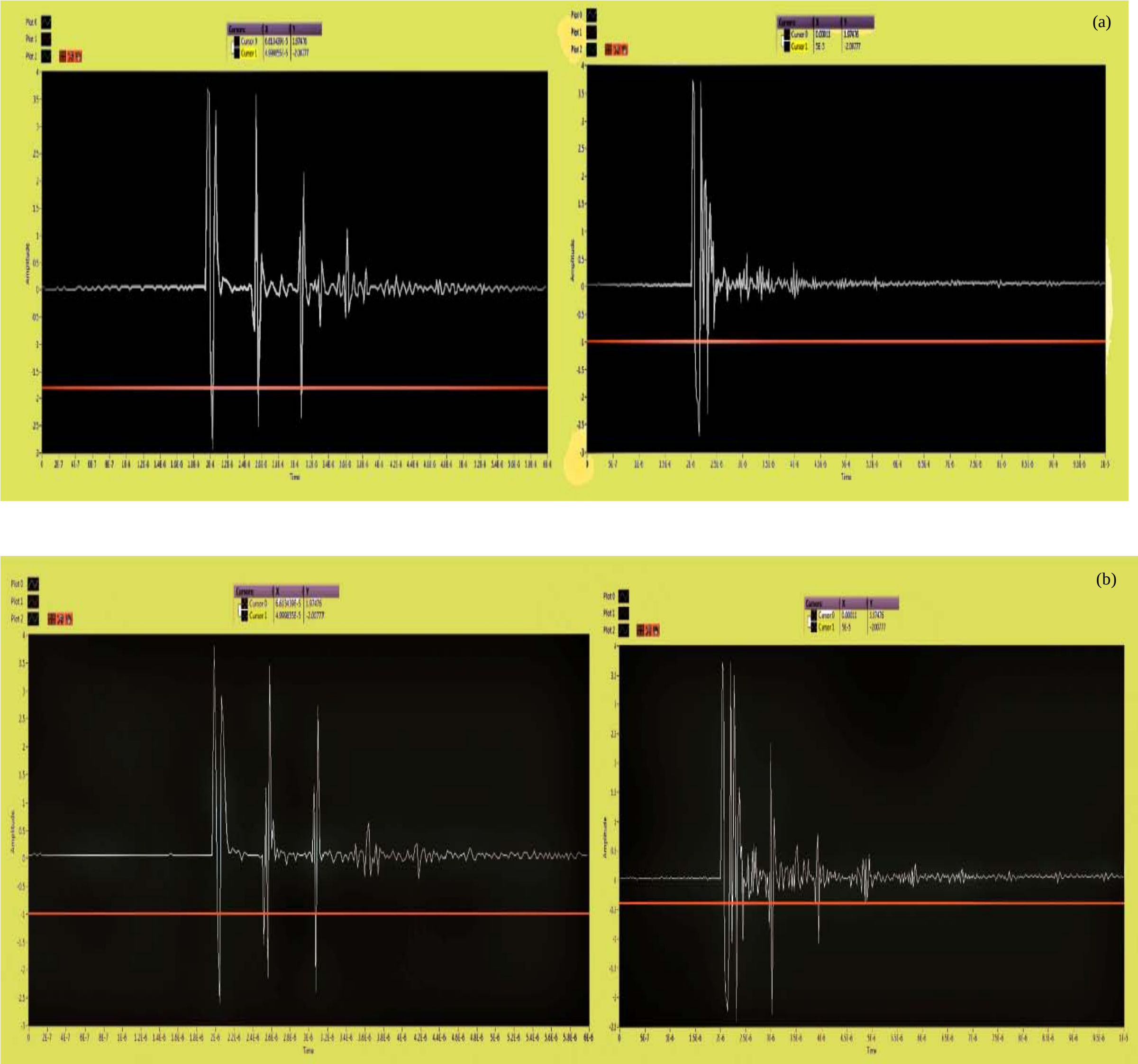


Fig. 2(a-b): (a) Longitudinal velocity (UL) and shear velocity for VSP glass system and (b) Longitudinal velocity (UL) and shear velocity (US) for VPM glass system

RESULTS

Ultrasonic study: The composition of VSP an VPM glasses in mole% are shown in Table 1. Also, it clearly predicts the content of V_2O_5 increase with decrease of mole% of phosphorous pentoxide of system 1. Similarly the content of V_2O_5 increases with decrease of mole% of MnO_2 of system 2. The experimental values of density, ultrasonic velocity (Longitudinal and Shear) of the different glass specimen with respect to change in mol% of P_2O_5 and MnO_2 are listed in Table 2a. The calculated longitudinal modulus (L), shear modulus (G), bulk modulus (K) and young's modulus (E), are reported in Table 2b. The perusal Table 3 reports the value of poisson's ratio(σ), acoustic impedance (Z), micro harness (H), Debye's temperature (θ_D) and thermal expansion co-efficient (α_p) for the two glass systems (VSP and VPM).

Table 2: Values of density (ρ), longitudinal velocity (U_l), shear velocity (U_s) and elastic moduli of VSP and VPM glass systems

		Ultrasonic velocity U(m sec^{-1})			Elastic moduli		
Name of the sample	Density ρ (kg m^{-3})	Longitudinal velocity (U_l) (m sec^{-1})	Shear velocity (U_s) m sec^{-1}	Longitudinal moduli (L)$\times10^{-9}$ Nm^{-2}	Shear moduli (G)$\times10^{-9}$ Nm^{-2}	Bulk moduli (K)$\times10^{-9}$ Nm^{-2}	Young's moduli (E)$\times10^{-9}$ Nm^{-2}
System 1 (V_2O_5-Na_2CO_3-P_2O_5)							
VSP 1	1477.65	4198.29	2464.51	26.04	8.97	14.07	22.20
VSP 2	1488.61	4385.80	2485.44	28.63	9.19	16.06	23.18
VSP 3	1503.30	4506.53	2550.47	30.53	9.77	17.49	24.66
VSP 4	1520.72	4590.66	2587.76	32.04	10.01	18.46	25.80
VSP 5	1540.76	4627.84	2501.20	34.03	10.39	20.17	26.60
VSP 6	1608.65	4699.98	2667.48	34.45	11.44	21.91	28.64
System 2 (V_2O_5–MnO_2-P_2O_5)							
VPM 1	1411.78	4336.04	2464.57	26.54	8.57	15.10	21.64
VPM 2	1414.41	4361.57	2533.62	26.90	9.07	14.80	22.25
VPM 3	1428.90	4465.61	2595.43	28.94	9.62	15.66	23.96
VPM 4	1460.37	4506.53	2618.60	29.65	10.00	16.30	24.93
VPM 5	1463.59	4676.72	2662.24	32.01	10.37	18.18	26.13
VPM 6	1479.31	4931.77	2682.64	35.98	10.64	21.78	27.44

It is interesting to note that the density of our glass systems (VSP and VPM Glass systems) exhibits continuous increases with increase in mol% V_2O_5 and the higher values of density are reported in VSP glass systems and hence the magnitudes of density values are in comparison with the order:

VSP glass system>VPM glass system

It is learnt from Table 2 that the values of longitudinal (U_1) and shear velocities (U_s) increase linearly with increase in mol% V_2O_5 in both VSP and VPM glass systems. It is seen that the rate of increase of U_1 is greater than that of U_s. In the present study of glass systems, the longitudinal ultrasonic velocity (U_1) increases from 4198.29-4699.98 m sec^{-1} for VSP glass systems and 4336.04-4931.77 m sec^{-1} for VPM glass systems. Similarly, shear velocity (U_s) increases from 2464.51-2667.48 m sec^{-1} for VSP glass and 2464.57-2682.64 m sec^{-1} for VPM glass systems on increasing the vanadium content. The increasing trend of both ultrasonic velocities may be attributed to the increase in rigidity of the glass network.

Addition of V_2O_5 with P_2O_5 an MnO_2 reply for both glass system increases the elastic moduli such as Longitudinal Modulus (L), Shear Modulus (G), Bulk Modulus (K) and Young's Modulus (E) for both glass (VSP and VPM) systems are clearly shown in Table 2. It also creates (VO_4) units and this leads to an increase in the network dimensionality and connectivity of the network.

Our observed another parameter Poisson's ratio increases from 0.237-0.291 for VSP glass systems and from 0.221-0.289 for VPM glass systems.

As seen from Table 3 the values of micro hardness increase with V_2O_5 content. The increasing of micro hardness imply that an increase in the rigidity of the glass system. The monotonous increasing trend, when V_2O_5 added with MnO_2, V_2O_5 creates our evaluated values of microhardness are found to be higher in VPM glass system comparing the VSP glass system, suggesting VPM glass system are stronger than the VSP glass system.

Table 3: Values of Poisson's ratio (σ), acousctic impedence (Z), micro hardness (H), Debye temperature (θ_D) and thermal expansion Co-efficient (K^{-1}) of VSP and VPM glass systems

Name of the sample	Poisson's ratio (σ)	Acoustic impedence $(Z)\times10^{-7}$ kg $m^{-2}S^{-1}$	Micro hardness $(H)\times10^{-9}$ Nm^{-2}	Debye temperature (θ_D) K	Thermal expansion Co-efficient ($\propto_p$) K^{-1}
System 1 (V_2O_5-Na_2CO_3-P_2O_5)					
VSP 1	0.237	0.6260	1.5665	145.42	97386.9
VSP 2	0.260	0.6528	1.4717	147.35	101737.2
VSP 3	0.262	0.6774	1.5580	151.82	104538.1
VSP 4	0.267	0.6981	1.5810	154.67	106489.9
VSP 5	0.280	0.7241	1.5240	155.66	109026.2
VSP 6	0.291	0.7444	1.9090	160.06	111352.5
System 2 (V_2O_5–MnO_3-P_2O_5)					
VPM 1	0.221	0.6129	1.3671	143.42	100582.7
VPM 2	0.240	0.6169	1.4460	149.70	101175.0
VPM 3	0.244	0.6389	1.6430	153.58	103588.8
VPM 4	0.245	0.6981	1.7230	156.70	104538.1
VPM 5	0.260	0.6845	1.8920	159.39	108486.1
VPM 6	0.289	0.7295	1.9723	161.76	114403.7

Table 3 describes the variation of Debye's temperature with V_2O_5 content. A gradual increase of Debye's temperature from 145.42-160.06 K for VSP glass systems and from to 143.42 K for 161.76 VPM glass systems are observed which indicates the increase in the rigidity of these glass systems. In our present investigation, finds that the higher values of Debye's temperature reported for VPM glass systems.

X-ray diffraction study: X-Ray diffraction investigation in a Bruker D8 advanced series (Madison-USA) powder diffractometer using Cu Kα as radiation source between 20 and 80°. The spectral representations of glass system VSP and VPM through XRD diffractogram are depicted in Fig. 3a-b. The absence of crystalline peaks in the XRD patterns of the samples confirms the amorphous glassy nature.

Spectroscopic study-FTIR interpretation: The FTIR spectra of glasses were measured at room temperature in the range 4000-400 cm^{-1} by infrared spectrophotometer type PerkinElemer Fourier transform using the KBr disc technique. The glass sample were ground to a fine powder and mixed with KBr. The mixture was then uniformly pressed with a pressure of 150 kg cm^2 to produce a transparent pellet. The infrared transmission measurement is measured immediately after preparing the pellets. The Fourier Transformation Infrared absorption spectra of VSP glass samples (system 1) and VPM glass samples (system 2) are shown in Fig. 4a-b, respectively.

The FTIR spectral studies confirm the presence of vanadate glass and formation of P-O-V bond. Table 4 and 5 predicts the FT-IR spectroscopy peak positions of VSP and VPM glass samples. Table 6 represents the FT-IR spectroscopy band assignments of both VSP and VPM glass samples.

Scanning electron microscope study (SEM) with EDS: Scanning Electron Microscope (SEM) has it ability to study the heterogeneity of glass composites to visualize various minerals components and their relation interms of overall microfabric and texture. SEM with EDS (Electron Dispersive Study) covers the observation from the fine structure of specimen surface

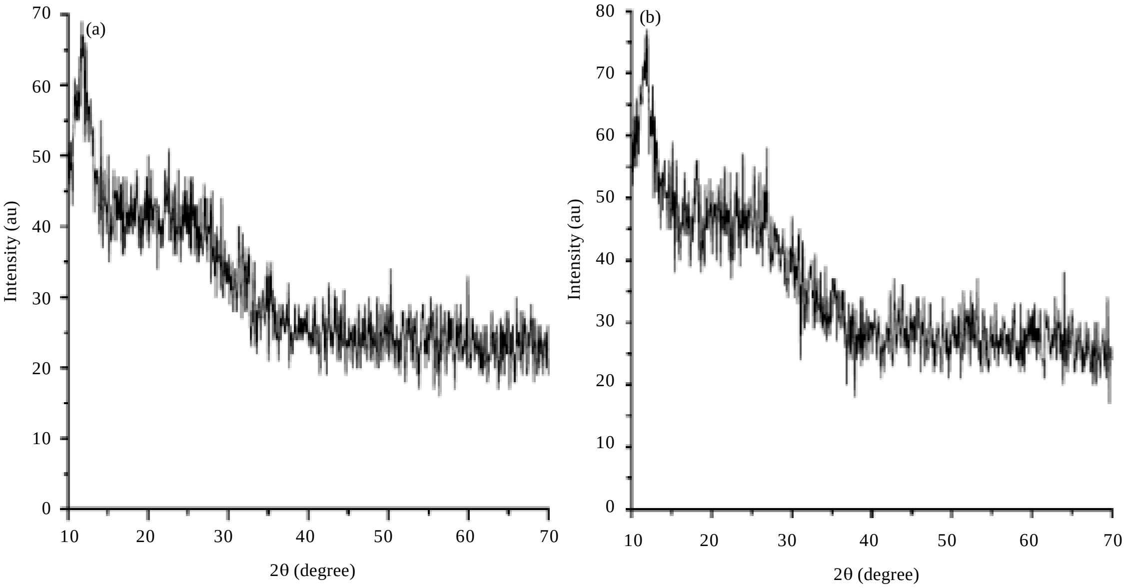


Fig. 3(a-b): (a) XRD diffraction pattern of VSP and (b) VPM glass system

Table 4: Peak position of VSP glass sample

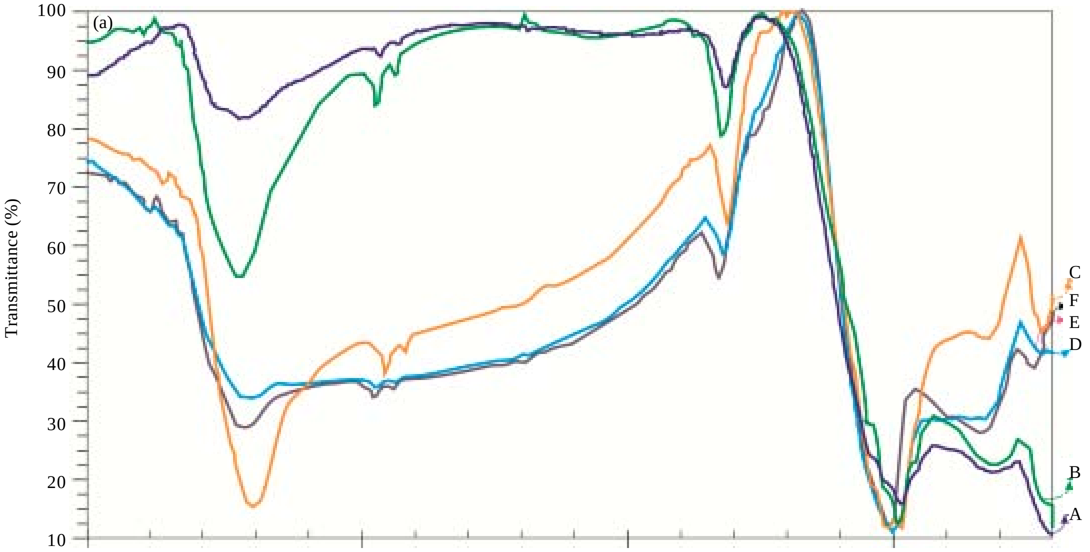
Glass No.	Peak positions (cm^{-1})						
VSP-1	-		969.00	-	2843.84	2926.03	3449.29
VSP-2	-		969.96	-	2838.36	2920.55	3433.07
VSP-3	-	611.34	969.10	1457.53	2849.32	2923.63	3438.45
VSP-4	440.90	-	976.92	1446.58	2843.84	2924.38	3430.96
VSP-5	438.36	646.58	984.66	-	2843.84	2920.55	3407.13
VSP-6	438.25	643.59	984.29	1495.89	2854.79	2926.03	3416.39

Table 5: Peak position of VPM glass sample

Glass No.	Peak positions (cm^{-1})									
VPM-1	449.32	618.73	876.71	1017.65	1463.01	1630.01	1742.47	2849.32	2923.18	3437.85
VPM-2	-	618.94	860.27	1008.22	-	1630.80	-	2854.79	2920.55	3430.63
VPM-3	-	619.31	871.23	1013.70	1468.49	1632.64	-	2854.79	2920.55	3432.46
VPM-4	449.32	667.67	878.99	1017.59	-	1644.41	1736.94	2849.32	2923.56	3439.22
VPM-5	459.13	667.91	875.41	1017.80	-	1636.13	1731.51	2849.32	2921.55	3425.59
VPM-6	-	635.62	865.75	1010.81	-	1621.92	-	-	2924.65	3441.10

to the elemental analysis on a microarea without destroying the specimen. For material characterization, the VSP and VPM semiconducting glass systems were taken and dried at hot air oven for about 1 h at 110°C. So, they are electrically conductive and the samples were powdered well over the surface of the double-sided adhesive carbon tape. These specimens are coated with the help of gold-spulter and the surface of the samples were scanned using JFS-1600 JEOL (Akishima Tokyo Japan) autofine coater model of coating time is 120 sec with 10 mA and deposited with a thin layer of gold on the sample.

A = 3449.29 2926.03 2843.84 1627.89 969.00 1090.41
B = 3038.05 2923.63 2809.32 1702.07 1632.93 969.101057.53 1030.10 1090.01 909.59 611.30
C = 3030.96 2920.38 2803.80 1633.20 1006.58 1001.101002.70 1090.01 976.921000.90
D = 3007.13 3033.07 2920.55 2838.36 1620.20 1035.62 969.96
E = 2920.55 2803.80 1630.83 980.66 803.80 606.58 838.36
F = 3416.39 2926.03 2854.79 1629.67 1495.98 984.29 643.59 438.25



A = 3437.85 2923.18 2849.32 1748.47 1630.01 1534.25 1463.01 1017.65
B = 3038.05 2923.63 2809.32 1702.07 1632.93 969.10 1057.53 1030.10 1090.01 909.59 611.30
C = 3430.63 2920.55 2854.79 1630.80 1008.22 1008.22 860.27 618.94
D = 3019.22 2923.56 2809.32 1736.99 1600.01 1017.59 878.99 667.67 809.32
E = 3425.59 2921.35 2849.32 1731.51 1636.13 1017.80 875.41 667.91 459.13
F = 3432.46 2920.55 2854.79 1632.64 1468.49 1013.70 871.23 619.31

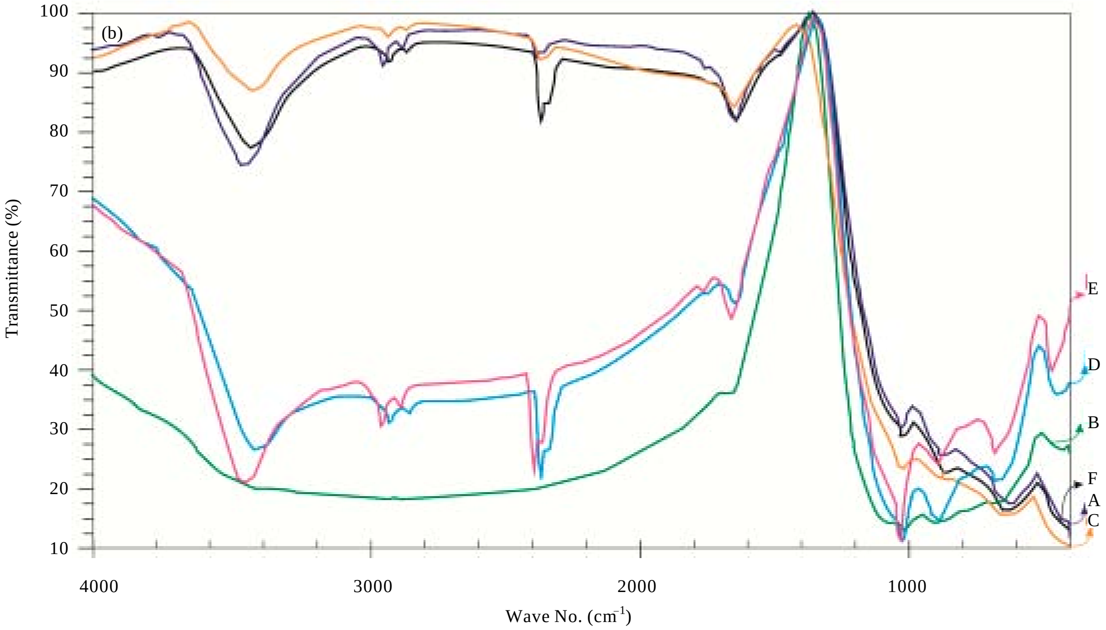


Fig. 4(a-b): FTIR spectrum for (a) VSP glass samples system 1 and (b) VPM samples system 2

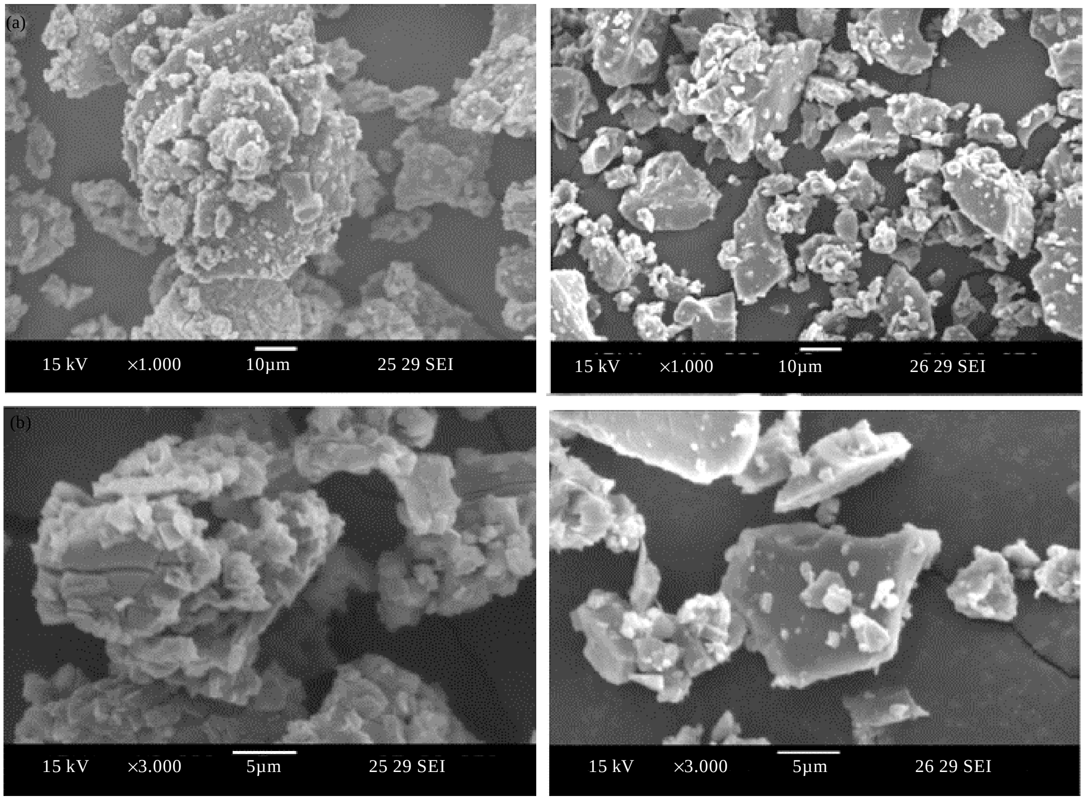


Fig. 5(a-b): (a) SEM micrographs of VSP-glass system and (b) VPM-glass system

Table 6: Band Assignments of VSP and VPM glass samples

Wave No. (cm^{-1})	Band assignment
438-440	O-P-O bending vibration
611-646	Stretching vibration of Mn-O bonds and deformation vibration of V-O-V groups
618-667	Deformation vibration of V-O-V groups
860-878	Symmetric vibration V-O-V bonds-corner sharing VO_5 polyhedra
909-984	Symmetric stretching vibration VO_2 group of the VO_4 polyhedra
1008-1017	P-O-P symmetric band stretching vibration
1446-1495	Asymmetric stretching vibration of PO_2
1621-1644	O-H bending vibration of water
2854-3441	O-H stretching vibration of water

Microstructural study using scanning electron microscope: From the Fig. 5a-b, the SEM micrographs of magnification show the softening of glass, coalescence between the particles and the morphology of amorphous nature of VSP and VPM glass systems, respectively. Table 7 reveals the Elemental Analysis of compounds present in the VSP and VPM glass system, respectively. It is observed that different sized grain particles are distributed. It consists of densely packed grains free from holes. The particles are extremely angular and spherical in nature. Some agglomerates structures were found and also spreads at the surface due to the deposition of amorphous apatite. This suggests that during formation of glass, the presence of high percentage

Table 7: Elemental analysis of compounds present in the VSP glass system and elemental analysis of compounds present in the VPM glass system

Element			
VSP glass system-V_2O_5-Na_2Co_3-P_2O_5 (system 1)		Element VPM glass system-V_2O_5-MnO_2-P_2O_5 (system 2)	
Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Na K		**P K**	
0.26	13.87	0.40	12.50
P K		**V K**	
0.59	22.94	4.58	87.19
V K		**Mn K**	
2.67	63.19	0.02	0.31
Total		**Total**	
3.53	100.00	4.99	100.00

of vanadium compounds forms cluster-like composed grain particles and aggregates. The pores and cracks at the smooth glassy surface clearly conforms the amorphous glassy nature of the samples.

DISCUSSION

Density is an effective tool to explore the degree of structural compactness, modification of the geometrical configuration of the glass network, change in co-ordination and the variation of the dimension of the interstitial holes (Rajendran, 2000). The monotonically increase of density with increase of V_2O_5 concentration can be attributed due the structural changes occurring in the co-ordination of vanadium glass network.

The V_2O_5 glasses in which V_2O_5 as the network former have the network structure mainly consisting of corner-sharing branched VO_4 tetrahedra of the same structural units as found in phosphor glasses. The network structure was reported to be made up of unaffected VO_5 groups as in vitreous V_2O_5 and affected VO_5 groups with alkaline earth ions in contrast to the vanadate glasses formed by conventional network formers in which only unaffected VO_5 groups are present (Wright *et al.*, 1985; Sen and Ghosh, 2001). These glasses are known to contain V^{4+} and V^{5+} hopping of 3 dL unpaired electron from V^{4+} to V^{5+} site which introduces a polarization of the vanadium ions around it and forms a polaron (Chung and Mackenzie, 1980; Ghosh, 1990).

Sen and Ghosh (2001) suggested that the addition of MnO_2 and P_2O_5 to V_2O_5, change the present structure to a rigid and compact structure due to change in the co-ordination number which lead to an increase in ultrasonic velocities.

The observed increase in ultrasonic velocities can also be interpreted as Higazy and Bridge (1985), where the longitudinal strain in a bond is directly dependant on the bond stretching force constant. This is inflected in our present system of glasses, where the longitudinal strain in the main chains (V-O-V linkages) is affected with the former role of V_2O_5, due to its increasing content owing to its high bond strength than that of P_2O_5 resulting in increase of overall stretching force constant (FB-O). On the other hand, the shear strain changes with the bond bending force constant (F_b). Thus, the increase of the shear wave velocity indicates that the decrease in P_2O_5 content has a pronounced bending effect on the behavior of bond bending force constant.

Glass is considered as an elastic substance and it can be characterized through a modulus of elasticity (Senin *et al.*, 1994). It is generally known that Oxide glasses doped with the transition metal oxides such as V_2O_5, MoO_3, WO_3, TiO_2, CuO, Fe_2O_3 etc., are known to exhibit semi conducting properties and hence these glasses have been extensively studied nowadays. The concentration of such transition metal oxides such as V_2O_5 in Vanadate glass plays an active role in semi-conducting glasses (Hirashima *et al.*, 1985). The elastic properties of these glasses are of considerable significance, because the studies yield information concerning the forces that are operative between the atoms comprising as the solid. Hence, the elastic properties are suitable for describing the glass structure (Saddeek, 2004). This modulus increases as the lengthening of certain applied stress diminishes. The increase in velocities too is attributed to the increasesing of rigidity in the glass (Saddeek, 2006).

The increasing trend of elastic moduli in all two glass systems indicates resistance to deformation and is most probably due to the presence of strong covalent bonds.

Poisson's ratio is an effective tool in exploring the degree of cross-link density of the glass network and its magnitude increases the cross-link density and it is the ratio of transverse and linear strains for a linear stress. According to Higazy and Bridge (1985) glass networks having a connectivity of two (zero cross-link density) have Poisson's ratio f = 0.4. Glass networks having connectivity of three (one cross- link density) having Poisson's ratio of = 0.3 while networks having a connectivity of four (two cross- link density) have Poisson's ratio of = 0.15.

Values of Poisson's ratio reported in this study from Fig. 6a-b suggest that the network of these glasses has two-dimensional structure. The increase in Poisson's ratio with increasing content of V_2O_5 is attributed to increase in the average cross-link density of the glass as proposed by Higazy and Bridge, (1985). Several Vanadium glasses show semi-conducting behavior and more precisely, vanadium ion containing glasses are identified as the n-type semiconductors for low value of the V^{4+}/V^{5+} ratio. The process of hopping of the electrons between V^{4+} and V^{5+} ions in the presence of layer concentrations of mobile captions is highly interesting (Gandhi *et al.*, 2009). The increasing trends of Poisson's ratio in this study are attached to strengthening of network linkage and attributed to hardening of the network structure.

Micro hardness expresses the stress required to eliminate the free volume (deformation of the network) of the glass. The present study of increasing value of micro hardness in all the two glass system studied as shown in Fig. 7a-b indicates an increase in rigidity of the glass. The softening point is temperature at which viscous flow changes to plastic flow. It determines the temperature stability of the glass. The higher the value of softening temperature, the greater is the stability of its elastic properties (Sidkey *et al.*, 1999). It is also interestingly to note that the continuous increase

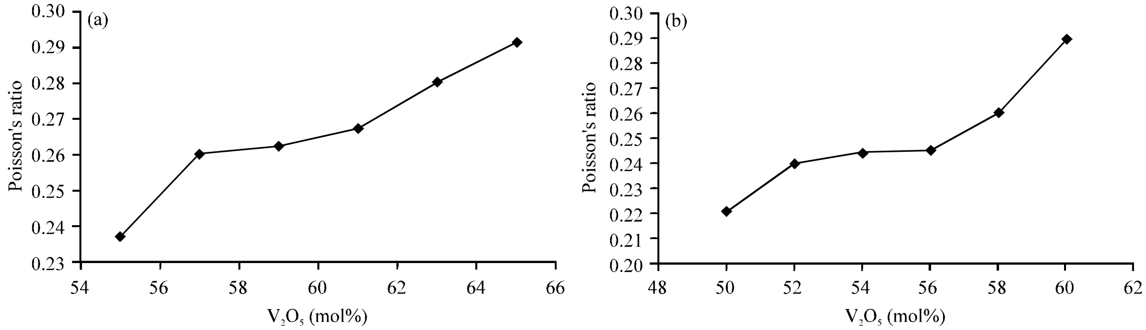


Fig. 6(a-b): (a) Variation of poisson's ratio for the VSP glasses with the composition of P_2O_5 (mol%) and (b) Variation of poisson's ratio for the VPM glasses with the composition of MnO_2 (mol%)

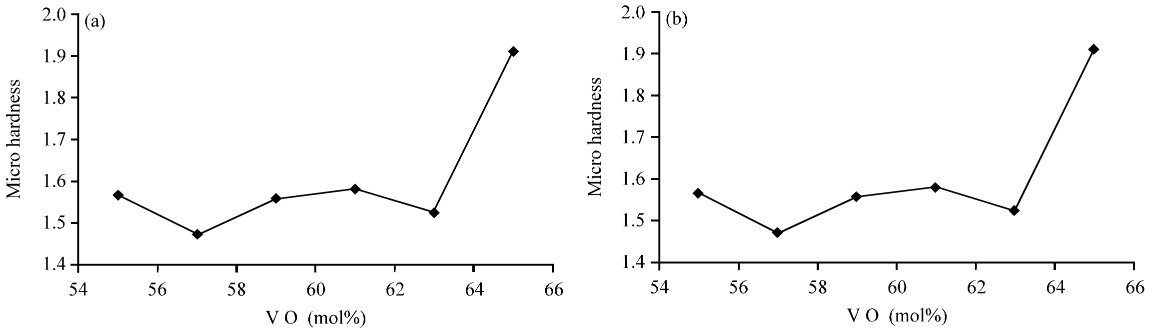


Fig. 7(a-b): (a) Variation of micro hardness for the VSP glasses with the composition of P_2O_5 (mol%) and (b) Variation of micro hardness for the VPM glasses with the composition of MnO_2 (mol%)

of Poisson's ratio (σ) as well as micro Hardness (H) in our present study reveals the absence of Non-Bridging Oxygen (NBO) and this causes the formation of glassy network. Rajendran (2000) observed that increase in elastic moduli along with σ and H with addition of glass former confirms the rigidity and hence there will be formation of stronger structural building units in this glassy network, when supports our investigation.

Debye temperature (θ_D) plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. It represents the temperature at which all the low frequency 'lattice' vibrational modes are excited. It is known that θ_D depends directly on the mean ultrasonic wave velocity (Varshneya, 1994). Such an enhancement of Debye's temperature is attributed to the increase in the number of atoms in the glass and increase in the ultrasonic velocity. One can notice that the continues increase of Debye temperature from trends of Fig. 8a-b advocates the compactness in the structure leading to increase in mean sound velocity (El-Mallawany, 2000). The increase of θ_D is further corrected to strengthening of the structural network and hardness. The perusal of Table 3 exhibits the values of acoustic impedance and thermal expansion co-efficient for the two glass system studied. The increasing trends of these values for both the glass (VSP and VPM) systems clearly confirms the strengthening of the glass network.

Our detailed rigorous study of X-ray diffractgram shows a broad hump which characteristic of the amorphous structure at around diffraction angle $2\theta = 25\text{-}27°$ to be fully amorphous indicating that these glass samples are composed of glassy phase (Khattak and Mekki, 2009) with the observation no peak corresponding to V_2O_5 indicating that V_2O_5 has completely entered the glass matrix and that the glasses formed were completely amorphous. This indicates the absence of long range of atomic arrangements and also the periodicity of the three dimensional network in the quenched materials (Greaves and Sen, 2007).

Our rigorous study from spectroscopic analysis of FTIR interpretation observes that the infrared absorption band at around the region 438-449 cm^{-1} is assigned to harmonics of bending vibration of 0 = P-0 linkage (Abid *et al.*, 2003; Khafagy, 2001). The absorption band identified at the region 611-646 cm^{-1} is assigned as deformation vibration due to V-O-V group, The stretching vibration of Mn-O bond is observed at the range 618-667.97 cm^{-1} for the VPM glass samples (Yahia *et al.*, 2009). These stretching and bending vibrations, are overlapped with each other. In VPM glass samples, when increasing the composition of V_2O_5 the vibrational wave numbers are shifted to higher. The FTIR spectra reveal that vanadium oxide acts as a former of glass network. Some of

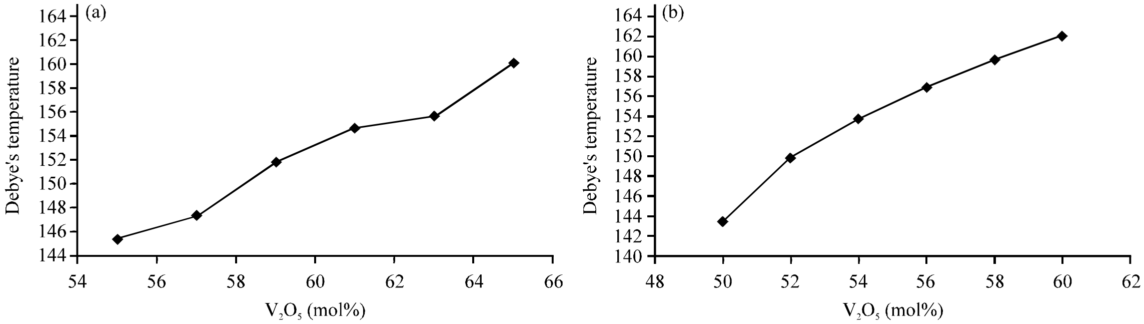


Fig. 8(a-b): (a) Variation of Deby's temperature for the VSP glasses with the composition of P_2O_5 (mol%) and (b) Variation of Deby's temperature for the VPM glasses with the composition of MnO_2 (mol%)

the infrared vibrational bands of the structural groups of V_2O_5 lie in the same region as those of P-O-P structural units and hence form the linkages of the type V-O-P. Vanadium ions take glass network forming position with VO_5 structural units may form linkages of the type V-O-P with PO_4 structural units. The band around 860-878 un^{-1} is attributed to the symmetric stretching vibration of V-O bond involved in the corner sharing of VO_5 polyhedral (Yahia *et al.*, 2009).

In VPM glass samples, the content of mole percentage of MnO_2 decreases which results that vibrational wave number shift to lower value. The absorption region consist of bands due to V = O groups in VO_5 trigonal bipyramids arising out of symmetric stretching at around the region 909.59-984.66 cm^{-1} (Sharma *et al.*, 2010). In VPM glass samples the content of P_2O_5 maintains the constant composition which shows that the frequency of symmetric stretching mode appeared constant' at the range 1008-1017.08 cm^{-1} and also it indicates that P-O-P bonds are strengthened by V_2O_5 attributes the symmetric stretching vibration of VO_2 groups of VO_4 tetrahedral in meta vanadates forming chains with V-O-V bridges (Socrates, 2004). In the present study the asymmetric stretching vibrations occurred at the region 1446-1495 cm^{-1}. An absorption band of PO_2 asymmetric stretching vibrations shifts to higher wave number because the phosphorous-oxygen bond linked to vanadium ions P-O-V (more ionic bonds) (Shaim *et al.*, 2002). The strong band at about 2350 cm^{-1} is assigned to characteristic stretching mode of the P = O bond. Several previous studies have shown that band corresponding to anti symmetric stretching vibration of doubly bonded oxygen PO_2 could be found in the range 1390-2230 cm^{-1}.

An absorption peak was observed at about 1600 cm^{-1} is due to H-O-H bending mode which reflects that samples are quite hygroscopic character of the powdered glass samples. Generally, there is no significant changes are observed beyond 1600 cm^{-1} and also spectra from 1680 cm^{-1} towards higher number have the same for all compositions (Khattak and Mekki, 2009). The bands at 1621-1644 cm^{-1} are due to O-H stretching vibration and also, the bands at 2854-3441 cm^{-1} are assigned due to O-H bending vibrations of water trapped in the glasses during the experiment. Due to the hygroscopic nature of P_2O_5 and it exist in steady percentage in VPM glass samples gives the band around 1731.51-1742.47cm^{-1} (Nakamoto, 2008). Hence the OH stretching vibrations are shifted to the higher wave number. The spectral absorption band of Na_2CO_3 of VSP glass samples arevery feeble due to conversion from Na_2CO_3 to Na_2O because of its higher glass transition temperature obtained in furnace. The observed infrared absorption peak at 2840-3460 cm^{-1} is due to strong hydrogen bonded and super position of symmetric and anti-symmetric stretching vibration of OH.

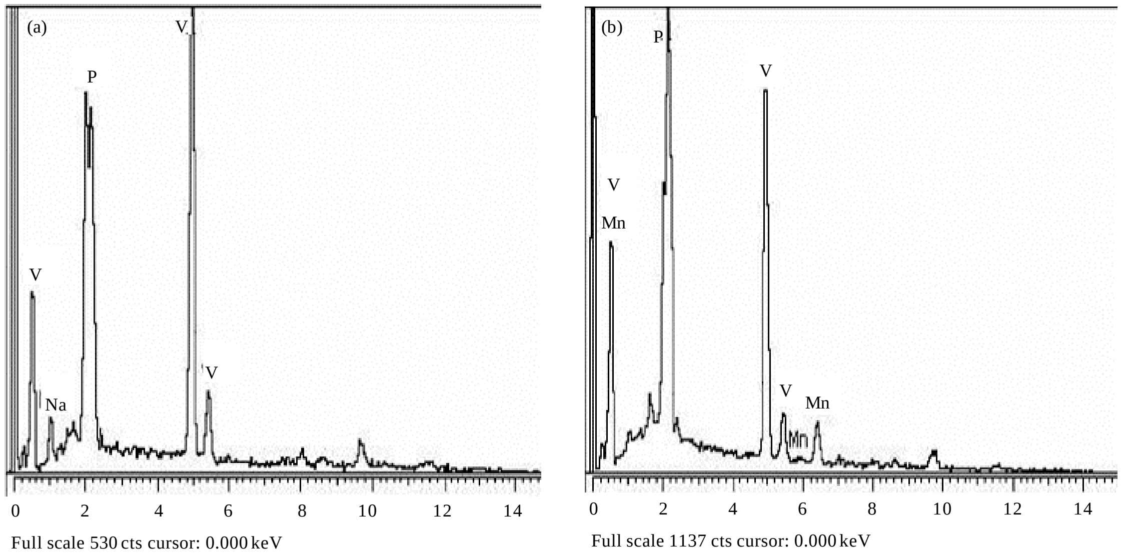


Fig. 9(a-b): EDS patterns of (a) VSP glass system and (b) VPM glass system

Elemental analysis using electron dispersive X-Ray spectroscopy: EDS spectral diagram taken for both VSP and VPM glass system as shown in the Fig. 9a-b, respectively. These spectra reveals the presence of high percentage vanadium along with sodium, phosphate and manganese depending upon their mole% used in the glass systems. Their weight% and atomic% of above elemental compounds are shown in Table 7. From the EDS spectral diagram and from the Table 7, one can observe that vanadium is more pronounced with in highest value among all the compounds in terms of weights% as well as atomic%. However, manganese shows its lowest value in terms of both weight% and atomic% depending upon their molecular weight and mole percentage taken in the glass systems.

Hence, it is obvious that SEM micrographs and EDS spectral studies are better tools for exhibiting the presence of sphere shaped large globular like orthorhombic V_2O_5 agglomerates were found spreading at the glass surface due to the deposition of amorphous nature on the average size of 5 μm.

CONCLUSION

Oxide glasses doped with the transition metal oxides such as V_2O_5 are known to exhibit semi conducting properties whose electrical conductivity is due to the electron hopping between V^{5+} and V^{4+} ions. The ultrasonic velocities (U_L and U_S) of VSP and VPM glasses varying linearly with the addition of glass former (V_2O_5) and the magnitude is in the order: VPM>VSP The evaluated acoustical, elastic and mechanical properties of VPM and VSP glasses throw light on rigidity and compactness in structural network. The observed increasing trend of micro hardness and Poisson's Ratio for both glass systems (VSP and VPM) indicate VPM glass system is stronger than VSP systems.

It is very obvious that VPM glass posses higher rigidity and compactness in structural network over the VSP glass. The functional groups present in our glass sample have been confirmed by FTIR spectral analysis. The topological aspects of the glass samples are exhaustively reported from the SEM Micrograph.

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