

appropriate amounts are mixed together and melted in silica crucible at temperature range of 1000 °C for 60 minutes until a bubble free liquid has formed. The melt is then poured in to preheated steel mould and annealed at temperature of 380 °C for 1 hour to avoid breaking of the samples by residual internal strains. The obtained samples are grinded with different grade of silica carbide and polished with cerium oxide in order to obtain maximum flatness. The nominal composition of the prepared glasses is given in the Table 1.

Table 1. Glass matrix compositions (mole %) and density of the glass samples respectively.

Glass	V ₂ O ₅ (%)	MnO ₂ (%)	PbO (%)	B ₂ O ₃ (%)	Density (D) [*] (g·cm ⁻³)
Mv1	0	20	20	60	3.52
Mv2	3	17	20	60	3.57
Mv3	6	14	20	60	3.68
Mv4	9	11	20	60	3.81
Mv5	12	08	20	60	4.04
Mv6	15	05	20	60	4.33

*The errors in the measurement of density and band gap are estimated to be 0.008 g·cm⁻³ and 0.0084 respectively.

X-ray diffraction study. The amorphous/crystalline nature of the samples is confirmed by X-ray diffraction (XRD) study using Pan Analytical X'Pert Pro X-ray diffractometer at the scanning rate of 2 degree/min and 2θ varied from 10–70 °.

Density measurements. The density of glass samples at room temperature is measured by the standard principle of Archimedes using a sensitive microbalance with pure benzene as the immersion fluid.

The density is calculated using the formula:

$$D = [W_A / (W_A - W_B)] d,$$

where W_A is a weight of sample in air, W_B is a weight of the sample in benzene and d is a density of the benzene.

FTIR measurements. The infrared transmission spectra of the glasses are measured at room temperature in the wave number range 400–4000 cm⁻¹ by a Fourier transform computerized infra-red spectrometer type (Thermo Nicolet 380 spectrometer). The prepared glasses are mixed in the form of fine powder with KBr in the ratio 1:100 mg glass powder: KBr, respectively. The weighed mixtures are then subjected to a pressure of 150 kg/cm² to produce homogeneous pellets. The infrared transmission measurements are measured immediately after preparing the pellets.

3. Results and discussion

X-ray diffraction. X-ray diffraction pattern of V₂O₅-MnO₂-PbO-B₂O₃ glass samples (Fig.1) shows no continuous or discrete sharp peaks but exhibit broad halo which reflects the characteristics of amorphous glass structure. The absence of long range atomic arrangement is

a clear indication of the glassy nature of the samples [10-13].

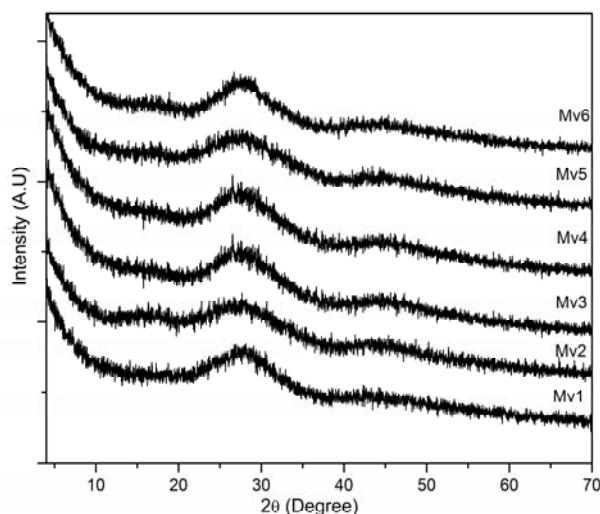


Fig. 1. X -Ray diffraction pattern of V_2O_5 - MnO_2 - PbO - B_2O_3 glasses.

Density. Density measurement is a very sensitive tool that can easily detect any structural change in the glass network. The modification in atomic geometrical configuration, co-ordination number and the dimensions of the interstitial space in the glass network decides the density and for that reason the density is a mechanism which reveals the degree of change in the structure with the glass composition. In borate glasses, density is controlled by the fraction of four-coordinated borons. It is a fact that boron has a coordination number of three or four [8, 14-15]. Consequently, boron can have its structure in triangular or tetrahedral form. The BO_4 tetrahedral are considerably denser than the symmetric BO_3 triangle [10]. Therefore tetrahedral groups are more rigid as compared to triangular groups.

The density of prepared V_2O_5 - MnO_2 - PbO - B_2O_3 glasses is given in Table 1. Proceeding with results, density of the glass system increases (from 3.52 to $4.33 \text{ g}\cdot\text{cm}^{-3}$) has been observed with the substitution of V_2O_5 contents. It has been pointed out that the presence of V_2O_5 increases the density of glass due to the availability of more oxygen from V_2O_5 which shifts the coordination of BO_3 to BO_4 . In sample Mv1 to Mv3 increase in density is due to the formation of BO_4 structural units. As the tetrahedral BO_4 groups are strongly bonded than the triangular BO_3 groups, therefore a compact structure is expected leading to a higher density [16]. Further increase in density with incorporation of V_2O_5 from sample Mv3 to Mv6 is due to the formation of VO_4 and VO_5 groups. These groups [VO_4 , VO_5] have higher value of field intensity. Hence the addition of V_2O_5 has modified the borate glass structure by creating more BO_4 , VO_4 and VO_5 groups.

The variation in density with V_2O_5 contents is shown in Fig. 2. The increase in density reveals the change in the structure of glasses with the increase of oxide contents.

FTIR. The infrared spectra for V_2O_5 - MnO_2 - PbO - B_2O_3 glasses shows large, medium, weak and broad peaks as shown in Fig. 3.

According to the literature survey, the vibrations of borate groups are mainly present in the following spectral regions:

- A. The region at 700 cm^{-1} is due to the bending of the B-O-B linkage.
- B. The region 800 - 1200 cm^{-1} is due to B-O bond stretching of various tetrahedral BO_4 units.
- C. The region 1200 - 1600 cm^{-1} is due to the stretching of various trigonal BO_3 units [17-20].

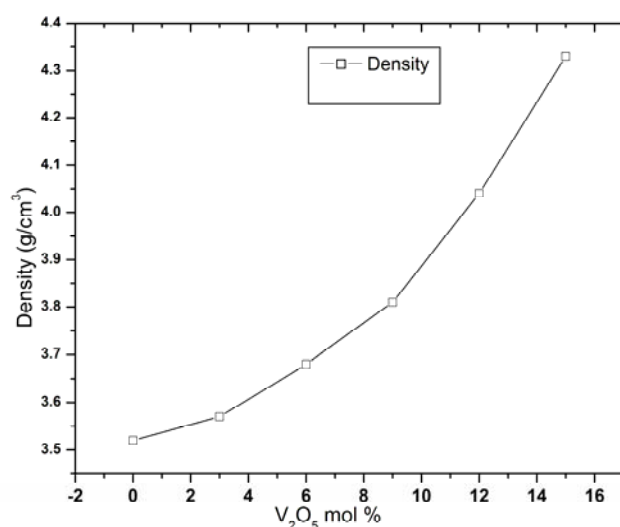


Fig. 2. Dependence of density of MnO_2 - PbO - B_2O_3 glasses on V_2O_5 content.

In the studied glasses V_2O_5 - MnO_2 - PbO - B_2O_3 , IR bands assignments has been summarized as followings.

1. Absence of band at 806 cm^{-1} shows the non existence of boroxol rings in glasses and hence consists of only BO_3 and BO_4 groups [21-22].
2. The band at 680 cm^{-1} which is present in sample Mv4, Mv5 and Mv6 is due to B-O-B bending vibrations of BO_3 groups which are not seen in other samples with lower concentration of V_2O_5 and higher concentration of MnO_2 in the glass network [11, 23].
3. The band observed at 772 cm^{-1} is due to B-O-B vibration between BO_3 and BO_4 group. Its intensity increases progressively with an increase in the contents of V_2O_5 which is due to the vibration of V-O-B bond connecting borate groups [5, 13].
4. The bands at 854 and 871 cm^{-1} are clear indicator of B-O bond stretching of BO_4 unit in tri, tetra and penta borates groups [10-11]. The band at 854 cm^{-1} starts appearing in sample Mv4 and shifts from 854 to 871 cm^{-1} with increasing contents of V_2O_5 due to V-O stretching of VO_4 group [24].
5. The weak band present at 1011 cm^{-1} is due to B-O vibration of BO_4 unit in tri, tetra and penta-borate groups. This band is increase in intensity and shifting from Mv2 to Mv6 sample due to V=O vibration of vanadium group in VO_5 bipyramidal [25]. The band at 1079 cm^{-1} is due to B-O vibration of BO_4 unit [10, 12-13].
6. The formation of band at 1179 cm^{-1} which is absent in Mv1, Mv2 and Mv3 samples has been assigned to BO_4 stretching vibration [26-27].
7. The regions between 1200 - 1600 cm^{-1} are due to B-O asymmetric stretching vibration of BO_3 units in meta-borate, pyro-borate and ortho-borate groups [26-27].
8. The regions 2400 - 3000 cm^{-1} are due to water groups [28-29].

Above discussion clearly indicates that, the formation of new band at 1011 cm^{-1} in sample Mv3 which is due to tetrahedral BO_4 group. This band is shifting towards the higher wave number (1011 to 1020 cm^{-1}) and also its intensity increases with the increase of V_2O_5 contents from Mv3 to Mv6 samples. At the same time, it is also observed that the intensity of band (at 1596 cm^{-1}) is decreased with the increase of V_2O_5 concentration in samples Mv1-Mv6. This shows an increase in BO_4 units. It is also observed that, shifting of the bands from 854 to 871 cm^{-1} with an increasing concentration of V_2O_5 reveals that it affects the local structure of borate network glasses, which has not been observed in the presence of MnO_2 in

sample Mv1. It shows that V_2O_5 has dominant effect on the structure of glass in the presence of MnO_2 . This indicates that V_2O_5 enters the glass network as network modifiers up to some mole percent, resulting the conversion of BO_3 into BO_4 group. At higher concentration, presence of VO_4 and VO_5 groups shows, (samples Mv5, Mv6) it acts as network modifier.

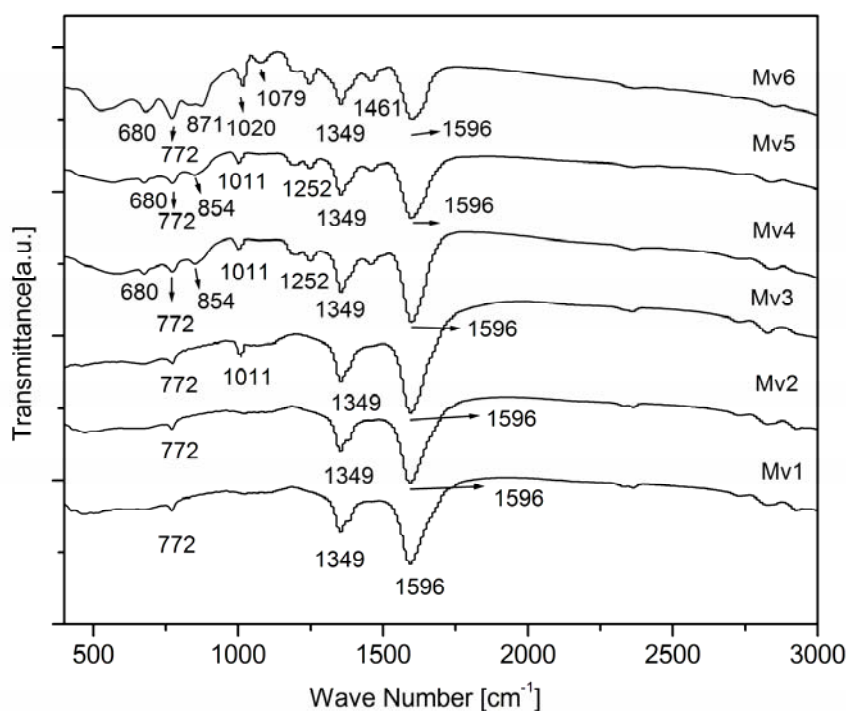


Fig. 3. FTIR spectra of V_2O_5 doped MnO_2 - PbO - B_2O_3 glasses.

4. Conclusion

In conclusion it has been found that V_2O_5 has more dominant effect than MnO_2 in the glass network. By fixing the lead and borate contents, increase in V_2O_5 concentration with the decrease in MnO_2 leads to compaction of glass network by breaking the bonds between the trigonal elements, allowing the formation of BO_4 units and in this way increases the density of the glasses. By infrared spectroscopic study it has been concluded that for V_2O_5 - MnO_2 - PbO - B_2O_3 glasses, the main structural unit comes out to be BO_3 (in pyro, meta, ortho groups) and BO_4 (in tri, tetra, and penta groups) with V-O stretching of VO_4 and $V=O$ vibration of VO_5 group. As the V_2O_5 content increases, BO_3 group starts converting in to BO_4 groups. This reveals that V_2O_5 enters the glass structure as network former as well as modifier. The presence of VO_4 and VO_5 states detected by infrared study reveals the network former behavior of vanadium at higher concentration in these glasses. Hence this work may be used for further solid state applications.

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