MICRO HARDNESS STUDIES OF BORATE GLASS SPECIMEN DOPED WITH MANGANESE AND VANADIUM IONS

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ABSTRACT

Borate based transition metal oxide ternary glass systems namely (i) V_2O_5 - B_2O_3 - Na_2CO_3 (VBS glass systems) and (ii) MnO_2 - B_2O_3 - Na_2CO_3 (MBS Glass) was prepared by conventional melt-quenching method. Glasses were prepared in six different compositions by fixing Na_2Co_3 and by varying V_2O_5, B_2O_3 and MnO_2 concentrations. Micro hardness of the glass systems are studied by Vickers's hardness tester analyzer which supports the Indention size effect. The composition dependence of the transition metal ions of vanadium and manganese has been interpreted in terms of non-bridging oxygen atoms as well as softening point of glasses. Our present study confirms that the micro hardness of our glass systems increase with increase of softening point for both glass systems.

Key Words: *Hardness, Indention size effect, softening point, melt-quenching.*

INTRODUCTION

Boron oxide is one of the best glass formers and its structure consists of a sheet-like arrangement of boron-oxygen triangles connected at all corners to form a continuous network[1]. Physical properties of borate glasses can often be altered by the addition of a commonly used network modifiers to the basic constituent. The ability of boron to exist in the three and four oxygen coordinated environment and the high strength of the (B-O) bond enables borates to form stable glasses. Boron atoms in borate crystals and glasses usually co-ordinate with either three or four oxygen atoms forming BO_3 or BO_4 structural units. These two fundamental units can arbitrarily be combined to form either 'super structural' units or different B_xO_y groups like boroxol rings, pentaborate, tetraborate, and diborate groups, etc. The function of these structural units depends on the nature and concentration of the added modifiers[2,3]. Borate glasses are very important optical materials because of their low melting point, high transparency, and high thermal stability[4]. These glasses are known to contain V^{+4} and

V^{+5} ions where the electrical conduction was attributed to the hopping of $3d^1$ unpaired electron from V^{+4} to V^{+5} site which induces a polarization of the vanadium ion around it and form a polaron[5].

In recent years, an interest in inorganic glasses containing transition metal ions has grown because these glasses have properties of technological importance in electronic, tunable solid state lasers and fiber optic communication system[6]. Most $Mn3^+$ complexes are octahedral and have a high spin arrangement with five unpaired electrons[7]. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous system[8]. By making note of the above considerations, the boric oxide, B_2O_3, acts as the one of the most important glass former, much works have been made so far on the borate glasses containing MnO_2 however the work on glasses containing MnO_2 and V_2O_5 doped together with B_2O_3 found to be rare.

EXPERIMENTAL TECHNIQUES

The chemicals used in the present research work were Analytical Reagent (AR) and Spectroscopic Reagent (SR) grade with minimum assay 99% were obtained from E-Merck, Germany. The required amounts taken in mol% of different chemicals in powder form were weighed using single pan digital balances (Model SHIMADZU AX 200) having an accuracy of 0.0001g. The homogenization of the appropriate mixture of the component of chemicals was effected by repeating grinding using a pestle and mortar. The mixture is melted in platinum crucible and the temperature controlled muffle furnace was gradually raised to a higher temperature at the rate of 100K per hour and a glassy structure was noticed for VBS and MBS glass systems at temperature range of 1100K to 1200K and eventually the molten glass melt was immediately poured on a heavy copper molding block having the dimension of 12mm diameter and 6mm length kept at room temperature are reported in Plate-1 and Plate-2.

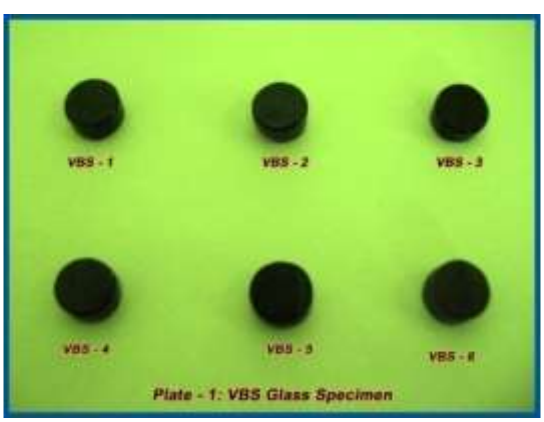


Plate-1: VBS Glass Specimen

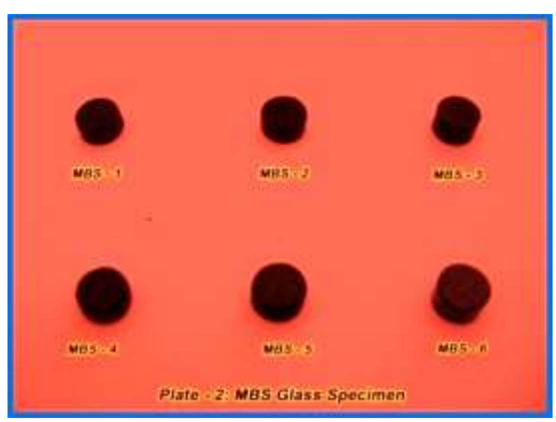


Plate-2: MBS Glass Specimen

Then the glass samples were annealed at 400K for two hours to avoid the mechanical strains developed during the quenching process. The two opposite faces of glass were highly polished to ensure a good parallelism. All glasses are cleaned with acetone to remove the presence of any foreign particles. The samples prepared are chemically stable and non-hygroscopic and such glass samples as System-I (VBS) and System-II (MBS).

The indentation was made by varying the load from 0.2 to 1 kg and the time of indention was around 15 seconds which is normally taken as a measure of the micro hardness of the material VHN is determined using the relation Yamane[9]

$$\text{VHN} = \frac{2FSin\emptyset/2}{d^2} \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (i)}$$

Where, F is the load applied θ = (136^o) is the angle of the pyramidal indentor, d is the length diagonal of the indentation. Yamane and Mackenzie[9] estimated the Vickers harness number of glass form the relation,

$$\text{VHN} = C\sqrt{\propto BG} \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (ii)}$$

Where C is a constant, $\propto$ is the bond strength factor, B is the bulk module and G is the shear modules. The decrease in VHN with a decrease in the elastic module as predicted by relation (ii) has been observed in many glasses.

Table -1 Composition of VBS and MBS glasses in mole

S.No.	Glass Specimen	Composition in mol %	Remarks
System-I-V_2O_5 - B_2O_3 - Na_2CO_3 (VBS Glass)			
1	VBS-1	03-77-20	mol % of Na_2CO_3 is constant
2	VBS-2	06-74-20	
3	VBS-3	09-71-20	
4	VBS-4	12-68-20	
5	VBS-5	15-65-20	
6	VBS-6	18-62-20	
System-II-MnO_2 - B_2O_3 - Na_2CO_3 (MBS Glass)			
1	MBS-1	03-77-20	mol % of Na_2CO_3 is constant

2	MBS-2	06-74-20	
3	MBS-3	09-71-20	
4	MBS-4	12-68-20	
5	MBS-5	15-65-20	
6	MBS-6	18-62-20	

RESULTS AND DISCUSSION

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. The boron has a coordination number three or four. The boron can have its structure in triangular or tetrahedral form. The BO_4 tetrahedral are considerably denser than the symmetric BO_3 triangle. Therefore tetrahedral groups are more rigid as compared to triangular groups[10]. The density values of the glass samples in present study exhibit an increasing trend with increasing mol.% of V_2O_5 with B_2O_3 in system-I (VBS glass system) and of MnO_2 with B_2O_3 in system-II (MBS glass system).

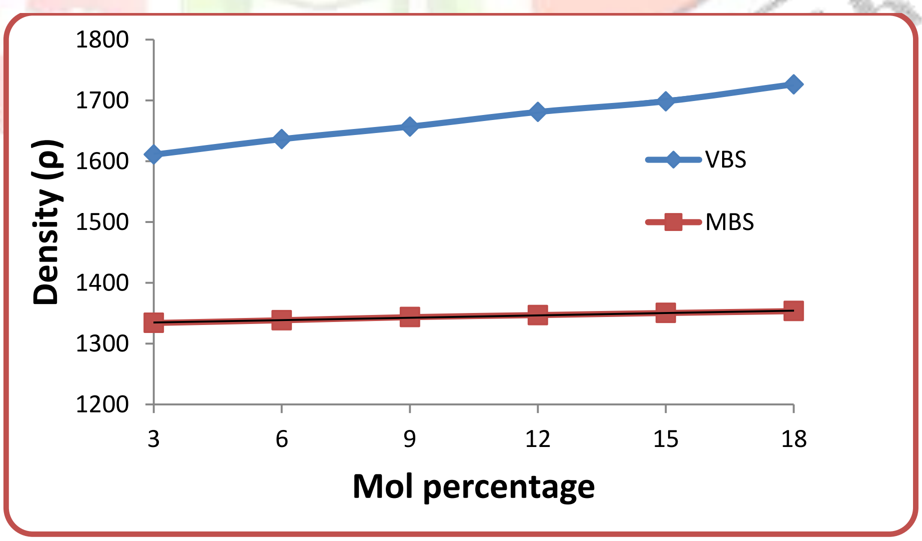
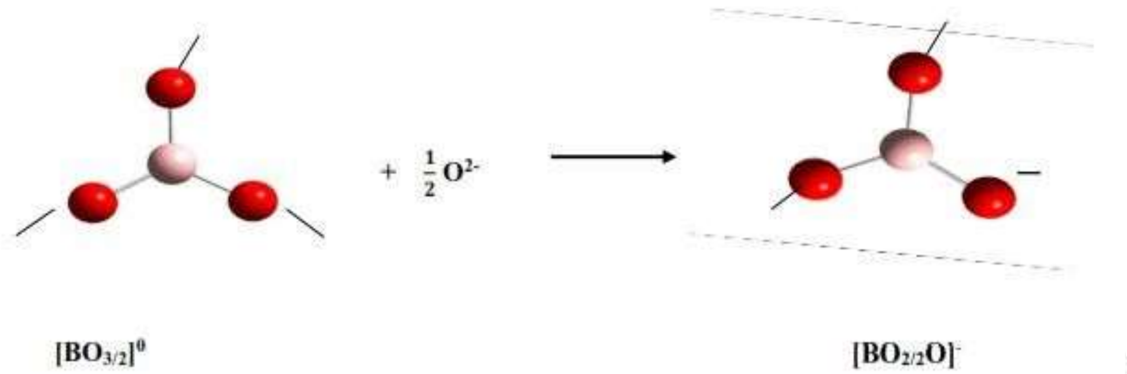
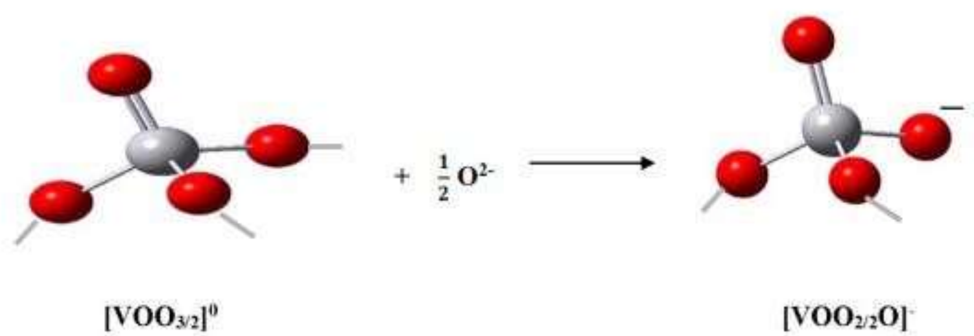


Figure 1- Variation of density for VBS & MBS glass system

The increase of density in former glass system-I (in VBS glass system) is due to the availability of more oxygen from V_2O_5 shifting the coordination of BO_3 to BO_4 and resulting in formation of non-bridging oxygen atoms (NBOs). As the tetrahedral BO_4 groups are strongly bonded than the triangular BO_3 groups, therefore a compact structure is expected to form. The increase in density with incorporation of V_2O_5 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[11]. On the other hand, the increase in density values for the second glass system (MBS-glass system) is due to availability of more oxygen from MnO_2 helping to converts BO_3 to BO_4 The resulting in formation of tetrahedral borate groups leading to compactness of the glass network[12].





The increasing mole percentage of MnO_2 can be interpreted in terms of structural changes which take place in the borate networks due to the effect of the different oxidation state of manganese ions. Further such variation with manganese content may be due to the manganese ions mostly exist in Mn^{2+} state, and occupy network forming positions with increasing MnO_2 at the expense of Na_2O as a modifier in the glass network. This will decrease the matrix occupation by Mn^{2+} ions which consolidate their structure. In these reactions, MnO_2, the manganese ions may be changed from Mn^{2+} to Mn^{3+} state occupy modifying positions, and in turn the borate ions associate with one or more non-bridging oxygen atoms, in view of the excess of modifier ions associate with borate. This leads to decrease in the polymerization of the borate network and expands (opened up) the structure of glass network resulting to an increase in density with molar volume[13].

Table -2 Value of Density and Microhardness number VHN for various glass compositions with different applied load at room temperature

Name of the glass samples	Density	VHN ($Kgmm^{-2}$)		
		Load (p kg)		
		0.2	0.5	1.0
System-I V_2O_5 - B_2O_3 - Na_2CO_3 (VBS Glass)				
VBS 1	1611.13	267	244	211
VBS 2	1636.62	289	256	232
VBS 3	1657.24	311	286	253
VBS 4	1681.19	335	308	280
VBS 5	1698.79	358	326	303
VBS 6	1726.72	391	355	327
System-II-MnO_2 - B_2O_3 - Na_2CO_3 (MBS Glass)				
MBS 1	1334.23	237	221	204
MBS 2	1338.73	264	248	233
MBS 3	1343.82	292	277	261
MBS 4	1347.23	318	301	283
MBS 5	1350.66	343	325	309
MBS 6	1353.73	367	351	335

Microhardness expresses the stress required to eliminate the free volume (deformation of the network) of the glass. The present study of this evaluated parameter notices an increasing value of micro hardness in all the two glass systems reported in Table 2, indicate an increase in rigidity of the glass. The softening point is temperature at which viscous flow changes to plastic flow, which determines the temperature stability of the glass.

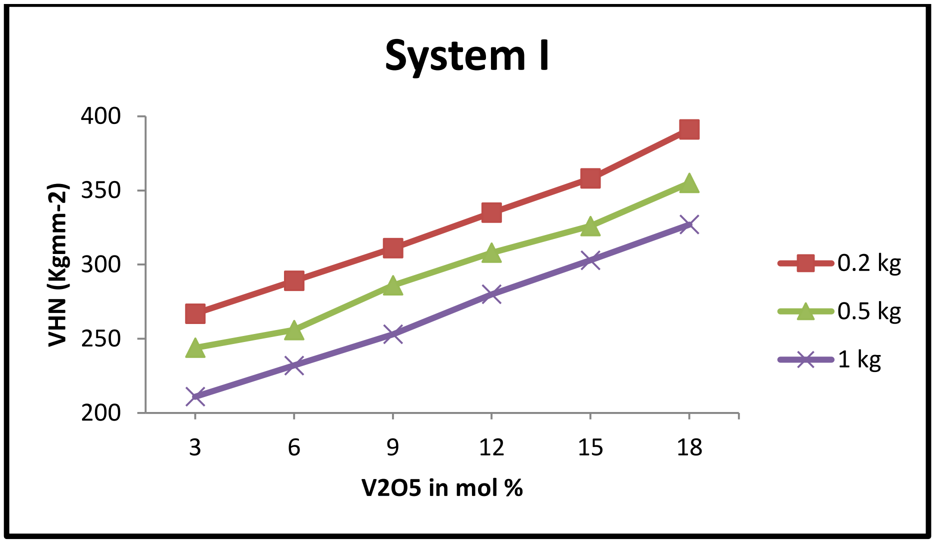


Fig -2a Variation of VHN with mole percentage of V_2O_5

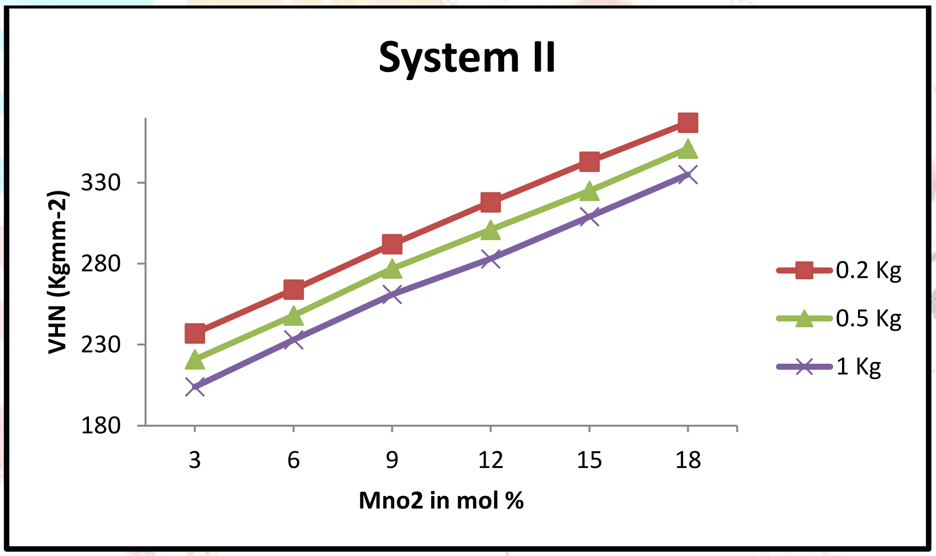


Fig -2b Variation of VHN with mole percentage of MnO_2

The Figures 2a & 2b depicts the increasing trend of micro hardness in both VBS as well as in MBS glass system. The square pyramid indentation method is the preferable for hardness measurements in glasses and other brittle materials. It is the resistance of network against elastic, plastic deformation and compression. During the process of indentation the material suffers both compression and shear resulting in the observed deformation, which consists of elastic deformation, flow and densifications[14]. The bond strength of a certain compound determines the relation of recoverable and irreversible deformation. High bond strength results in his elastic modulus, which in turn prevents bond breakage whereas, low bond strength results in bond breaking concomitant with irreversible plastic flow. The micro hardness is related to the dilatometric softening point[15]. It has been found that micro hardness of glasses systematically increase with increase in the softening temperature[16]. The values of Micro hardness Number (VHN) for different applied loads for the studied two glass systems are listed in Table 2. Similarly, the variation of VHN with mole percentage of V_2O_5 & MnO_2 for the two glass systems (VBS & MBS) has been depicted in Fig 2a and 2b respectively. The softening point is temperature at which viscous flow changes to plastic flow. It corporate the temperature stability of the glasses. The higher the value of softening temperature, the greater is the stability of its elastic properties. The increase of micro hardness in our study reveals the absence of Non-Bridging Oxygen (NBO) and this result the formation of glassy network[17]. Observed that elevation in and micro hardness with addition of glass former confirms the rigidity of the glass which results the formation of stronger structural building units in this glassy network[18]. In this two glass systems, the co-valency of the V-O bond decreases the non-bridging oxygen which leads to the connectivity of the glassy network and elastic modulus of the glass[19]. It has been confirmed that the micro hardness of glasses increases with an increase in softening point. Since the softening point follows the same behavior as the glass transition temperature. Micro hardness indentation testing measured hardness value depends of on the applied load, which is known as Indentation Size Effect (ISE)[20]. However, a Reverse Type of Indentation Size Effect (RISE), where the micro hardness increases with increasing applied load is also known[21]. From the above two indentations, our present study more pronounced for the first type of indentation (i.e.) indentation size effect (ISE). The decrease of micro hardness with increasing applied load has been reported by various researchers[22,23]. Table 2 clearly confirms the decrease of micro hardness number with respect to increase of applied level on glass specimen which indicates the indentation size effect (ISE). The increasing value of the vanadium and manganese content in mole % of two glass systems elevates the value of Vickers hardness number for both system I (VBS glass specimens) and system – II (MBS glass specimen). In VBS glass systems, manganese ions mostly exist in the Mn_{2+} state, occupy network forming positions in MnO_4 structure units and increase the rigidity of the glass network[24]. It is interesting to note that the increasing values of density support the elevation of microhardness which confirms the rigidity nature of the glass samples. The higher the value of softening temperature, the greater is the stability of its elastic properties[25]. As the microhardness values are higher in VBS glass system (system-I) comparing the MBS glass system (system-II), indicating the VBS glasses are possessing more rigidity in structural network over the MBS glasses.

CONCLUSION

- The present study critically observes that the incorporation of V_2O_5 has more influential effect comparatively with Mn_{O2} in the glassy network. The increase of v_2o_5 concentration leads to compactness of glass network by breaking the bonds between the trigonal elements, allowing the formation of BO_4 units and in this way it increases all related parameters.

- The increasing behavior of density in the glass specimens clearly attributed to its efficient packing and compactness. The observed increasing trend of micro hardness and density supports the rigidity and compactness of the both glass systems.
- The increasing trend of vickers micro hardnessnumber (VHN) with increasing load supports the identation size effect (ISE) could be attributed in terms of absence of non-bridging oxygen ions in the glasses.
- The increasing trend of density and microhardness confirms that VBS Glass system is stronger than the MBS glass system.

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