XRD and microhardness studies of Ni^{2+} and W^{6+} metal ions doped with tellurite magnesium borate glasses

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ABSTRACT

Glasses with composition 15TeO$_2$- 10MgO - (75-x) B$_2$O$_3$– xNiO and 15TeO$_2$- 10MgO - (75-x) B$_2$O$_3$- xWO$_3$ (where x = 0 to 1.0 in steps of 0.2 mol %) have been prepared by using a conventional melt-quenching method. The amorphous nature of the samples were ascertained using X-ray diffractometry. Microhardness measurements were carried out using Zwick 3212 hardness tester fitted with a Vicker's diamond pyramidal indenter. Microhardness studies revealed that the hardness of the glasses increased with an increase in applied load. Meyer's index number / work hardening exponent 'n' was calculated and found that the material belongs to hard material category.

Introduction

Oxide glasses containing transition metal oxides (TMO) are of technological interest because of the semiconducting properties that arise from the electron hopping between two transition metal ions having different valence states in the glasses [1]. B$_2$O$_3$ is one of the most important glass formers incorporated into various kinds of glass systems as a flux material, in order to attain, materials with specific physical and chemical properties suitable for high technological applications [2]. Tellurium oxide based glasses are of scientific and technical interest on account of their various unique properties, and have been considered as promising materials for optical switching devices and laser hosts. They possess high refractive index, excellent infrared transmittance, high dielectric constant, good chemical durability, and low melting temperature [3].MgO is used as an insulatorin industrial cables, asabasic refractory material for crucibles and as a principal fireproofing ingredient in construction materials. As a construction material, magnesium oxide wallboardshave several attractive characteristics: fire resistance, moisture resistance, mold and mildew resistance, and strength. It is also used as a protective coating in plasma displays and also as an oxide barrier in spin tunneling devices. Pressed MgO is used as an optical material. Crystalline pure MgOhas a small use in infrared optics.

Microhardness testing can be very useful tool for studying modern materials, but is plagued by well-known experimental difficulties. Microhardness is not only a mechanical characteristic routinely measured, but also it has been developed as a micro structural investigation method, due to the fact that microhardness is sensitive to structural parameters as well as to mechanical characterization parameters (yield stress, modulus of elasticity, some secondary relaxation transitions)[4,5]. Hardness of a material is defined as the resistance it offers to the motion of dislocations, deformation, or damage under an applied stress [6].The general definition of indentation hardness, which relates to the various forms of indenters, is the ratio of the applied load to the projected area of indentation. Generally, the apparent hardness of the materials varies with applied load. This phenomenon, known as the indentation size effect (ISE), usually involves a decrease in the microhardness with increasing applied load [7-9]. The decrease of microhardness with increasing applied load has been reported by various researchers [10, 11]. In contrast to the ISE, a reverse type of indentation size effect (reverse ISE), where the microhardness increases with increasing applied load, is also known [12-14].Thus, the present work reports result of hardness measurements aimed at improving the hardness of glasses by various dopants.

Materials and methods

The glass samples of the formula 15TeO$_2$-10MgO-(75-x) B$_2$O$_3$- xNiO (TMBN) and 15TeO$_2$-10MgO-(75-x) B$_2$O$_3$-xWO$_3$ (TMBW) (where x = 0 to 1.0 in steps of 0.2mol %) have been prepared by using the conventional melt – quenching technique. Required quantities of analytical grade of TeO$_2$, MgO, H$_3$BO$_3$, NiO and WO$_3$were obtained fromE-Merck, Germany, Hi-Media, Mumbai and Sd-Fine chemicals, India. The proper compositions were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture wasmelted in alumina crucible atabout 1213 K and the same temperature was maintained for about 45 minutes to homogenize the melt. Then the glass samples were annealed at 573 K for two hours to avoid the mechanical strains developed during the quenching process.The samples prepared were chemically stable and non-hygroscopic. The prepared glass samples were polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. Thickness of the glass samples are measured using digital vernier caliper (MITUTOYO DIGIMATIC CALIPER) with an accuracy of 0.0001 mm. The amorphous nature of glass samples were confirmed by X-ray diffraction technique using an X-ray diffractometer (Model: X' PERT POWDER XRD SYSTEM FROM PANALYTICAL).

Microhardness measurements were carried out using **Zwick 3212 hardness tester** fitted with a Vicker's diamond pyramidal indenter. All the indentation measurements were carried out on the freshly polished glass samples at room temperature. The

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indentation was made by varying the load from 0.3 to1 kg and the time of indentation was kept at 10 sec. The indented impressions were approximately square.Diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope.

Vicker'smicrohardness value (H_v)[15] has been calculatedusing

$$H_v = 1.8544 \; P/d^2 \qquad \qquad \qquad …. \qquad 1$$

wherePis the applied load, d is the mean diagonal length of the indentation impression and 1.8544 is a constant, a geometrical factor / Vicker's conversion factor for the diamond pyramid.

According to Meyer's law[16], the relation connecting the applied load is given by

$$P = ad^n \qquad \qquad \qquad …. \qquad 2$$

where n is the Meyer's index number or work hardening exponent and a is a constant for a given material. The value of work hardening exponent (n) was estimated from the plot of log P versus log d by the least square fit method. The 'n' value is useful to determine whether the material is hard or soft.

Results and discussions

X-ray diffraction pattern (Fig. 1) of the studied glass systems reveals the absence of any discrete or continuous sharp crystalline peaks, but show homogenous glassy characters.
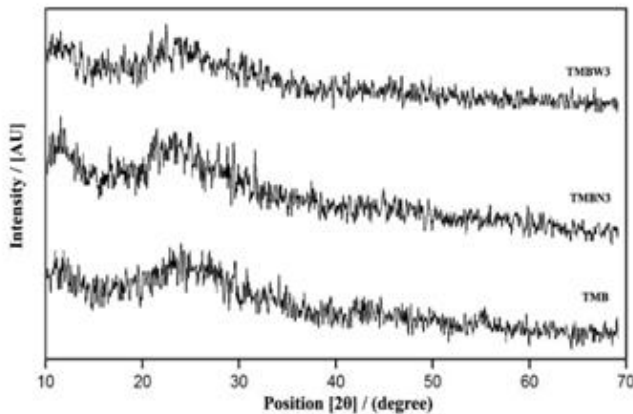

Fig. 1: The powder XRD pattern of glass samples of TMB, TMBN3, and TMBW3 at room temperature.

The experimental values of microhardness (H_v) and Meyer's index number (n) with various applied load for the TMB, TMBN and TMBW glass series at room temperature are shown in Table1. The variations of microhardness with applied load for the undopedanddoped of nickel oxide (NiO) and tungsten oxide (WO_3) in tellurite magnesium borate glasses are drawn and are illustrated in Figs.2, 3.

For all the glass systems, there is an increase in microhardness value (Figs. 2, 3) while increasing the applied load from 0.3 to 0.9 kg. When the load exceeds 0.9 kg, significant crack initiation and glass chipping occur and hardness tests could not be carried out. Further, from the Table1it was observed that the microhardness values decrease with increasing the mol % of NiO and WO_3 contents, with the entire applied load. Microhardness expresses the stress required to eliminate the free volume of the glass. The free volume in the glass is the openness of the glasses over that of the corresponding glasses [17].

From the above table, it is seen that microhardness decreases with an increase of NiO and WO_3 content for all the glasses indicating the decrease of the rigidity. The increasing value of microhardness makes the glass harder and vice versa. In all the studied glass systems the increase of the microhardness with the increasing load is in agreement with the reverse indentation size effect (reverse ISE) [5].
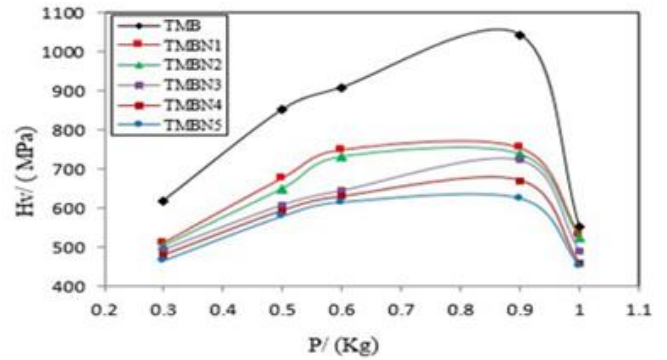

Fig.2 Variation of microhardness (H_v) versus load (P) for TMB and TMBN glasses at room temperature
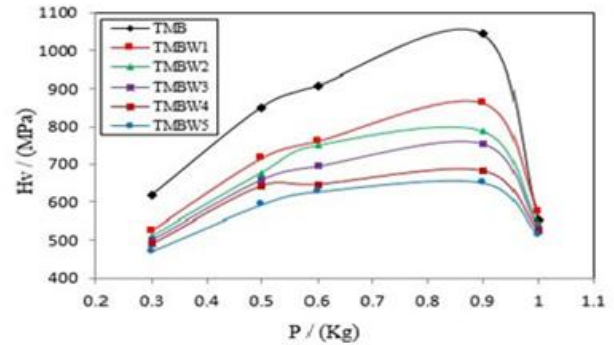

Fig.3 Variation of microhardness (H_v) versus load (P) for TMB and TMBW glasses at room temperature

Table 1. Values of microhardness (H_v) and Meyer's index number / work hardening exponent (n) for various glass compositions with different applied load at room temperature

Glass Samples Label	Microhardness H_v/(MPa)					Meyer's index number/ work hardening exponent (n)
	Load / kg					
	0.3	0.5	0.6	0.9	1.0	
$TeO_2 + MgO + B_2O_3$						
TMB	618	851	908	1043	551	1.6170
$TeO_2 + MgO + B_2O_3 + NiO$						
TMBN1	510	677	750	755	532	1.9701
TMBN2	503	650	732	739	526	1.9774
TMBN3	495	609	646	724	491	1.9733
TMBN4	481	594	630	671	460	1.9023
TMBN5	465	579	615	625	452	1.9135
$TeO_2 + MgO + B_2O_3 + WO_3$						
TMBW1	526	715	760	862	574	1.9356
TMBW2	510	677	750	788	541	1.9859
TMBW3	502	659	695	755	532	2.0350
TMBW4	490	642	646	682	524	2.0578
TMBW5	472	592	626	650	515	2.1437

According to Onitsch[18], work hardening exponent 'n' is greater than 2 when the hardness increases with the increasing load. Since the values of n (Table1) for TMBW glasses are greater than 2, the hardness of the material is found to increase with the increase of load conforming the prediction of Onitsch. From the Table1,the magnitude of H_v value is in order: TMBW> TMBN> TMB. From the magnitude of H_v, it can be concluded that TMBW glass possess higher rigidity than the other two glasses. It is well known that the magnitude of microhardness related to bond energies [19].

Conclusions

The effect of NiO and WO_3 content with doping of tellurite magnesium borate glasses have been investigated using

microhardness measurements at room temperature. Beyond the load of 0.9 Kg, significant cracking occurred, which may be due to the release of internal stresses generated locally by indentation. Each glass exhibits a significant reverse ISE with indentation load. The increasing value of microhardness makes the glass harder. Thus the microhardness studies revealed the isotropic nature of the material and it further confirms that TMBW glasses belong to hard materials in compare to TMBN and TMB glass.

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References

[1] G.D.Khattak, M.A.Salim, L.E.Wenger, A.H.Gilani,J.Non-Cryst.Solids 244 (1999) 128-136

[2] S. Mukerji, T. Kar, Metall.Mater.Trans. A 31(2000) 3087-3089.

[3] M.A. Sidkey, M.S. Gaafar, Physica B 348 (2004) 46-55.

[4]F.J.J. Balta-Celleja, Adv.Polym.Sci.66 (1985) 117.

[5] F.J.J. Balta-Celleja, L.Giri, I.M.Ward, D.L.M.Cansfield, J.Mater.Sci.30 (1995) 1139-1143.

[6] P. Hemalatha, V. Veeravazhuthi, D.Mangalaraj, J. Mater. Eng. Perform, 18 (2008) 106-108.

[7] J.Gong, X.Pan, H.Miao, Z.Zhao, Mater.Sci. Eng. A359 (2003) 391-395.

[8] K. Sangwal, Mat. Chem. Phys. 63 (2000) 145-152.

[9] S.Mukerji, T.Kar, Cryst. Res. Technol. 3 (1999) 1323-1328.

[10] S.Anbukumar, S.Vasudevan, P.Ramasamy, J.Mater.Sci. Lett. 5 (1986) 223-224.

[11]J.B. Charles, F.D.Gnanam, J. Mater. Sci. Lett. 9 (1990) 165-166.

[12]R.E.Hanneman, J.W. Westbrook Philos. Mag. 18 (1968) 73-88.

[13]P.Feltham, R.Banerjee,J.Mater.Sci.27 (1992) 1626-1632.

[14]M.Manimaran, S.N.Kalkura, P.Ramasamy, J.Mater.Sci. Lett.14 (1995) 1366-1368.

[15]S.Chenthamarai, D. Jayaraman, C. Subramanian, P. Ramasamy, Mater. Lett.47 (2001) 247 - 251.

[16]S.J. Bull, T.F. Page, E.H. Yoffe, Philos. Mag. Lett.596 (1989) 281 - 288.

[17] A.Varshneya, Fundamental of InorganicGlasses, vol.59, Academic press. New York, 1994.

[18] E.M. Onitsch, Strain rate dependence of the hardness of glass and Meyer's Law, Mickroskopie,2(1944)131 - 151.

[19]M. Yamane, J.D. Mackenzie, J. Non-Cryst. Solids, 15 (1974) 153 – 164.