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XRD and Microhardness Studies of Ni^{2+} and W^{6+} Transition Metal Ions Doped with Tellurite Barium Borate Glasses.

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Research Article

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ABSTRACT

Glasses with composition $10TeO_2.15BaO.(75\text{-}x)B_2O_3.xNiO$ and $10TeO_2.15BaO.(75\text{-}x)B_2O_3.xWO_3$ (where x= 0 to 1 mol% in steps of 0.2) have been prepared by using a conventional melt-quenching method. The amorphous nature of the samples was ascertained using X-ray diffractometry (XRD). 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

Tellurium oxide (TeO_2) based glasses are important for many applications due to nonlinear optical properties. Moreover, TeO_2 used as a host material has several advantages over other oxide glass hosts and the most important is being its low phonon frequency [1]. Glasses based on heavy metal oxide such as TeO_2 have wideapplications in the field of glass ceramics, layers for optical andelectronic devices, thermal and mechanical sensors, reflecting windows.$B_2O_3$is one of the most common glass-former. The structureof vitreous B_2O_3consists of a random network of boroxol rings and [BO_3] triangles connected by B–O–B linkages. It was reportedthataddition of a network modifier in borate glasses could producethe conversion of the triangular [BO_3] structural units to [BO_4] tetrahedral with a coordination number four[2].Barium is a good candidate for development of Ba - based radiation shielding glass owing to strong absorption of x- rays, gamma-rays and non-toxicity compared with lead[3].Compared to other tellurite glasses, WO_3containing tellurite glasses have slightly higher phonon energy and higher glass transition temperature, therefore they can be used at high optical intensities without exposure to thermal damage. Addition of $B_2O_3$to tellurite glasses provides someunique features by enhancing the thermal and chemical stability andcrystallization resistance[4]. The divalent nickel ion is an interesting paramagnetic ion to probe in the glass systems. Nickel ions are reported to occupy both tetrahedral and octahedral positions in the glass matrices[5].

Microhardness is a bond sensitive property, which provides an insight on the nature of the chemical bonding in a material[6]. When a sharp indenter such as Vickers indenter is loaded onto a glass, a residual surface impression is observed after unloading, and the material hardness is conveniently estimated from the projected area of the impression. It is known that some extent of deformation during loading is recovered duringunloading, i.e., elastic recovery.Since it is expected that the degree ofelastic recovery depends on glass systems and glasscompositions, the hardness evaluated from a residualsurface impression after unloading is insufficient for anin-depth understanding of deformation behaviors inglass. In this point of view, it is also important to evaluate the hardness during loading, i.e., the so-called'universal hardness'[7].In the past decades, there has been a considerable increase in the use of indentation techniques for determining mechanical properties of solids [8]. 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 [9,10]. 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 [11].The purpose of this work is to investigate the hardness of the glasses by various dopantssuch as NiO and WO_3. Since no such study has been conducted so far.

MATERIALS AND METHODS

The glass samples of the formula $15TeO_2$ - 10BaO - (75-x) B_2O_3 - xNiO (TBBN) and $15TeO_2$ - 10BaO - (75-x) B_2O_3 - xWO_3 (TBBW) (where x = 0 to 1.0 in steps of 0.2 mol %) have been prepared by using the conventional melt – quenching technique. Required quantities of analytical grade of TeO_2, $BaCo_3$, H_3BO_3, NiO and WO_3 were obtained from E-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 is melted in alumina crucible at about 1013 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 was 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 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's microhardness value (H_v) [12]has been calculated using

$$H_v = 1.8544\ P/d^2 \qquad (1)$$

WhereP is 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[13], the relation connecting the applied load is given by

$$P = ad^n \qquad (2)$$

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 DISCUSSION

X-ray diffraction patterns (Fig 1) of the studied glass systems reveals the absence of any discrete or continuous sharp crystalline peaks, but show homogenous glassy characters.The experimental values of microhardness (H_v) and Meyer's index number (n) with various applied load for the TBB, TBBN and TBBW glass series at room temperature are shown in Table1. The variations of microhardness with applied load for the undoped and doped of nickel oxide (NiO) and tungsten oxide (WO_3) in tellurite magnesium borate glass are drawn by using the principle of least square method and are illustrated in Figs. 2-3.

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 [14].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 Table 1 it was observed that the microhardness values decrease with increasing the mol % of NiO and WO_3 contents, with all the applied load.

The increasing value of microhardness makes the glass harder and vice versa. In all the studied glass systems the increase of the microhardness with increasing load is in agreement with the reverse indentation size effect (reverse ISE) [15].The magnitude of H_v value is in order: TBB >TBBW > TBBN. From the magnitude of H_v, with the effect of doping it can be concluded that TBBW glasses possess higher rigidity than the TBBN glasses. It is well known that the magnitude of microhardness related to bond energies [16].According to Onitsch[17], work hardening exponent 'n' is greater than 2 when the hardness increases with the increasing load. Since the values of n (Table 1) for TBBW glasses are greater than 2, the hardness of the material is found to increase with increase of load conforming the prediction of Onitsch.

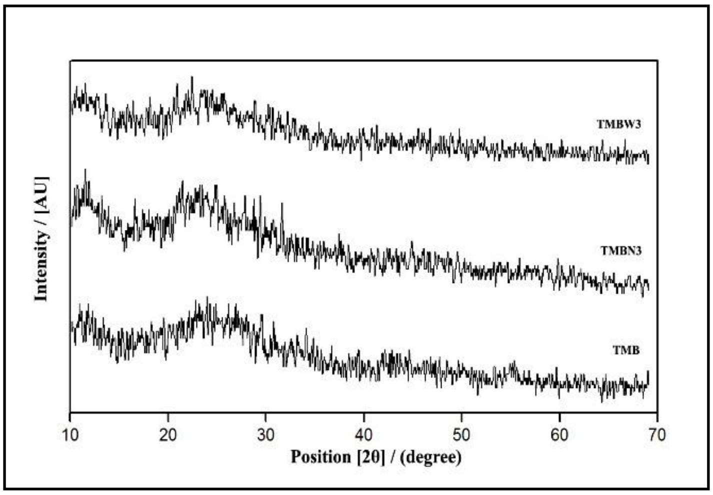

Figure 1: The powder XRD pattern of glass samples of TBB, TBBN3, and TBBW3 at room temperature.

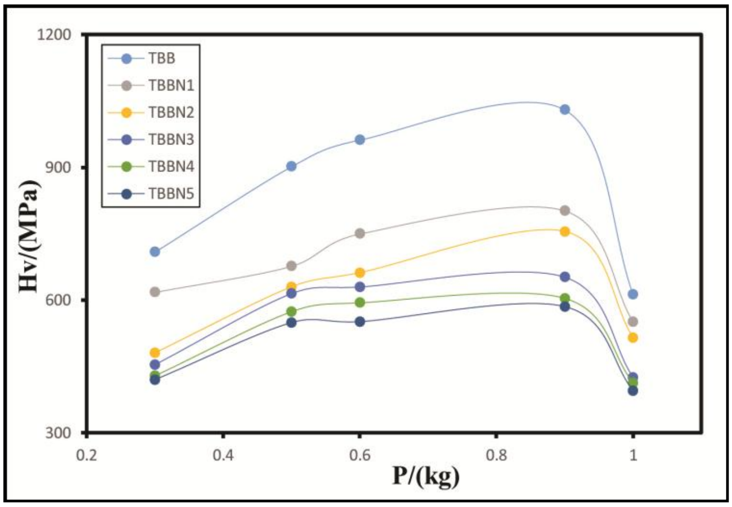

Figure 2: Variation of microhardness (H_v) versus load (P) for TBB and TBBN glasses at room temperature.

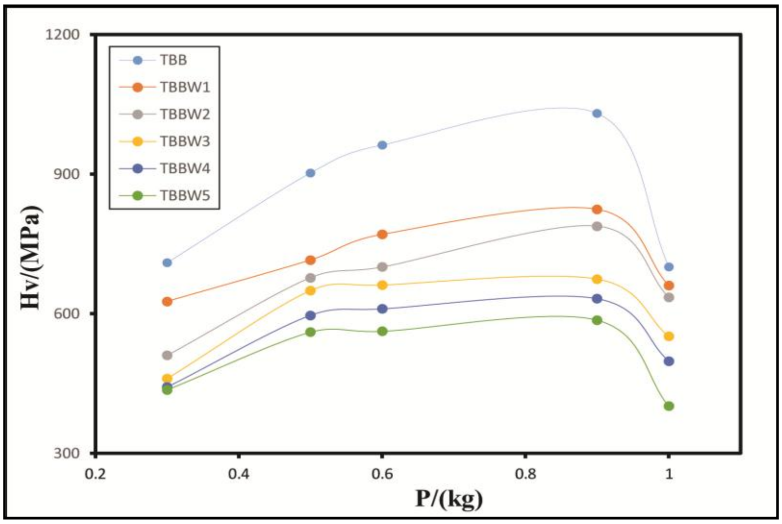

Figure 3: Variation of microhardness (H_v) versus load (P) for TBB and TBBW glasses at room temperature.

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 Hv/Mpa					Meyer's index number/ workhardening exponent (n)
	Load / (kg)					
	0.3	0.5	0.6	0.9	1.0	
	TeO_2 - BaO-B_2O_3(TBB)					
TBB	709	902	962	1030	700	1.76
	TeO_2 - BaO-B_2O_3 -NiO(TBBN)					
TBBN1	618	677	750	802	551	1.87
TBBN2	481	630	662	755	515	2.06
TBBN3	454	615	630	652	425	1.78
TBBN4	429	574	594	604	413	1.83
TBBN5	420	549	551	585	395	1.83
	TeO_2 - BaO-B_2O_3 - WO_3(TBBW)					
TBBW1	626	715	770	824	660	2.15
TBBW2	510	677	700	788	635	2.42
TBBW3	460	649	661	674	551	2.20
TBBW4	442	596	610	632	498	2.13
TBBW5	436	560	562	586	401	2.81

CONCLUSION

The effect of NiO and WO_3 content with doping of tellurite barium 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 anisotropic nature of the material and it further confirms that TBBW glasses belong to hard materials in compare to TBBN glasses.

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