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Thermal, FTIR and EPR studies of transition metal ions doped with tellurite magnesium borate glass at room temperature

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Abstract

Glasses with composition 15TeO_2-10MgO-(75-x) B_2O_3 -xNiO and 15TeO_2-10MgO-(75-x) B_2O_3 - xWO_3 (where x = 0 to 1.0 in steps of 0.2 mol %) have been prepared with a conventional melt–quenching method. The glass samples were characterized by using X-ray diffraction (XRD), Thermo Gravimetric - Differential Thermal Analysis (TG - DTA), Fourier Transform Infrared Spectroscopy (FTIR), and Electron Paramagnetic Resonance (EPR). XRD scans evidenced the amorphous state of as-quenched samples. To recognize the thermal behavior of the glasses, glass transition (Tg), crystallization peak (Tp), melting temperature (Tm) and the glass stability against crystallization (ΔT) were calculated from the thermal analyses. FTIR spectrometry in the spectral range 400 – 4000 cm^{-1} at room temperature was interpreted in terms of the structural transformations on the glass network, according to the changing B_2O_3, NiO and WO_3 content. The EPR spectra have been traced in X-band ($\upsilon \approx 9.78$GHz) at room temperature. The resonance signals at $g \approx 2.0 - 2.3$ were found for the metal ions Ni^{2+} and W^{6+} respectively. Electron paramagnetic resonance data suggest the bonding between transition metal ions and ligands as an ionic in nature.

Keywords: glasses, amorphous, structure, resonance signal and glass stability

1. Introduction

In recent years, attention has been focused more on glassy materials in view of their large optical non-linearity and high optical quality with fast response time. The development of lasers, and their use of telecommunication systems, has stimulated the research and development of new glass systems. Glasses are supercooled liquids, transparent and amorphous in nature. They are an inorganic product of fusion which has cooled to a rigid condition without any crystallization. Glasses based on tellurium oxide (TeO_2) are of scientific and technological interest because of their interesting properties: low melting temperature, high refractive indices, high third order nonlinear susceptibility, and low phonon energy. Such properties make tellurite glasses promising for use in amplifiers and nonlinear optical devices [1-3]. Tellurium oxide (TeO_2) is a conditional glass former which does not transform to the glassy state without the addition of a secondary component under conventional cooling conditions. Therefore, glass forming agents such as alkalis, heavy metal oxides or halogens are used to obtain tellurite glasses [4].

The structure of tellurite glasses is also of interest because their basic structural unit is an asymmetrical TeO_4 trigonal bipiramyds with a lone pair of electrons in an equal position, and the content of network modifier changes the coordination number of the tellurium ion with respect to oxygen ions. This change leads to a TeO_3 trigonal pyramid which is considered to restrict the glass formation. Optical properties of glasses based on TeO_2 and heavy metal oxides have stirred up significant interest in the field of new glassy materials and become promising materials for any optoelectronic applications [5].

B_2O_3 is one of the best-known glass formers and it is present in varieties of commercial glasses. The structure of amorphous B_2O_3 is made up of planar BO_3 triangles linked through B-O-B linkages. The addition of B_2O_3 to tellurite glasses provides some unique features by enhancing the thermal and chemical stability and crystallization resistance [6, 7]. Magnesium ions are usually classified as network modifiers, but there are some reports discussing the possibility of a network former role for magnesium, especially in alumino-silicate glasses. It is thus important to clarify the role of magnesium in the structure of glasses [8].

It is known that the structure and properties of oxide glasses are strongly dependent on the nature and concentration of the constituent oxides. The addition of WO_3, as a network modifier or intermediate oxide network, to tellurite glasses provides several advantageous properties, such as doping with rare-earth elements in a wide range, modifying the composting by a third, fourth, and even fifth component, enhancing the chemical stability and devitrification resistance. Furthermore, compared to other tellurite glasses, WO_3 containing 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. Although tungsten in glasses can exhibit in different oxidation states such as W^{+3}, W^{+4}, W^{+5} or W^{+6} ions or a mixture of some of them [9, 10].

Nickel oxide was early used in producing different colours to ancient glasses and glazes. The colours varied from yellow to brown and even pink or violet depending on the host glass composition [11]. Weyl [12] assumed that yellow colour in nickel glasses is due to the presence of NiO_6 complexes while the pink or violet colour is related to the presence of NiO_4 groups and that both these colours involve nickel ion in a divalent state with different numbers of surrounding oxygens. Later recent studies reach the same conclusion that nickel ions under ordinary atmospheric conditions of melting are found in alkali borate, alkali silicate as divalent ions in two different forms, octahedral (NiO_6) and tetrahedral (NiO_4) and the ratio of the two forms depends on the glass composition, the polarisability of the oxygen ligands surrounding the nickel ion, the concentration of the transition metal, and on the condition of melting the glass [13].

Although there exist numerous studies on binary and ternary tellurite glasses containing B_2O_3, MgO, NiO and WO_3, thermal and structural behaviour of tellurite based glasses need to be studied in detail to develop and use them in opto-electronic applications. Therefore, the present work has been carried out to investigate the effect of nickel and tungsten ions doped tellurite glasses with various spectroscopic techniques such as XRD, TGA-DTA, FTIR, and EPR, analysis.

2. Materials and Methods

2.1 Glass Preparation

The glass samples of the formula $15TeO_2 – 10MgO – (75-x) B_2O_3 – xNiO$ and $15TeO_2 – 10MgO – (75-x) B_2O_3 – xWO_3$ (where x = 0 to 1.0 in steps of 0.2 mol%, Table 1) have been prepared by the conventional melt- quenching method. Required quantities of analytical grade of tellurium oxide, magnesium carbonate, boric acid, nickel oxide and tungsten trioxide were obtained from E-Merck, Germany, Himedia and Sd-fine chemicals in India. The proper compositions were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture was melted in alumina crucible at about 1213K using muffle furnace (TECHINICO) for about 45 minutes to homogenize the melt. Then the glass samples were annealed at 573K for two hours to avoid the mechanical strains developed during the quenched process and then allowed to reach room temperature gradually. The prepared glasses were polished on both sides to obtain plainer surfaces before measuring their thermal and spectroscopic properties.

Table 1: Nomenclature of prepared glass samples

Nomenclature	Composition in mol %	Remarks
$TeO_2 – MgO – B_2O_3$ TMB	$TeO_2 – MgO – B_2O_3$ 15 – 10 – 75	
$TeO_2 – MgO – B_2O_3 – NiO$	$TeO_2 – MgO – B_2O_3 – NiO$	Mol % of TeO_2 and MgO is constant
TMBN 1	15 – 10 – 74.8 – 0.2	
TMBN 2	15 – 10 – 74.6 – 0.4	
TMBN 3	15 – 10 – 74.4 – 0.6	
TMBN 4	15 – 10 – 74.2 – 0.8	
TMBN 5	15 – 10 – 74.0 – 1.0	
$TeO_2 – MgO – B_2O_3 – WO_3$	$TeO_2 – MgO – B_2O_3 – WO_3$	Mol % of TeO_2 and MgO is constant
TMBW 1	15 – 10 – 74.8 – 0.2	
TMBW 2	15 – 10 – 74.6 – 0.4	
TMBW 3	15 – 10 – 74.4 – 0.6	
TMBW 4	15 – 10 – 74.2 – 0.8	
TMBW 5	15 – 10 – 74.0 – 1.0	

2. 2 X-ray Diffraction

The amorphous nature of the prepared glass samples was established through the X-ray diffraction studies using X' Pert Powder XRD System from Panalytical, German using Cu radiation.

2.3 Thermo Gravimetric Analysis - Differential Thermal Analysis

The glass transition (Tg), crystallization peak (Tp) and melting temperatures (Tm) were determined using differential thermal analysis (DTA) at a heating rate of 20 °C/min in air using the instrument SDT Q600 V8.0 Build 95. The same instrument has been used for TGA measurement.

The thermal stability of the glasses can be described by ΔT, which is defined as

$$\Delta T = Tp - Tg \text{ ---} (1)$$

Where, ΔT gives the information about the devitrification tendency of the glasses. The difference between the glass transition temperature and the onset crystallization temperature, ΔT, has been commonly used as a rough criterion of the glass thermal stability against devitrification.

2. 4 Fourier Transform Infrared

The FTIR transmission spectra of the glass samples were recorded at room temperature using a KBr pellet technique with a Spectrum RX-1 FTIR spectrometer in the spectral range 400 – 4000 cm^{-1}. This powder glass samples were thoroughly mixed with dry KBr in the ratio 1:20 by weight and the pellets were formed using a pellet press. For each spectrum 10 scans were made and the spectral resolution was 2 $cm^{-1.}$

2.5 Electron Paramagnetic Resonance

The EPR spectra of the fine powders of the samples were recorded at room temperature on Bruker EMX Plus, the USA X - band ($\upsilon \approx 9.78$ GHz) EPR spectrometer.

The EPR spectra are obtained by varying the magnetic field at constant frequency. The absorption of energy associated with the spin transition occurs in the resonant condition:

$$h\upsilon = g\beta B \text{ --} (2)$$

Where, h is Planck's constant (6.626×10^{-34} Js^{-1}), B is applied magnetic field, υ is the microwave frequency, β is a constant, the Bohr magnetron ($\beta = eh/4\pi mc = 9.723 \times 10^{-12}$ JG^{-1}).

The factor g, the gyromagnetic ratio/spectroscopic splitting factor, has a value of 2.0023 for a free electron but varies significantly for paramagnetic ions in the solid state. The value of g depends on the particular paramagnetic ion, its oxidation state and coordination number.

3. Result and Discussion

3.1 XRD Studies

X-ray diffraction patterns of the studied glass systems reveal the absence of any discrete or continuous sharp crystalline peaks, but show homogenous glassy characters. The powder X-ray diffraction spectrum of some of the glass samples of TMB, TMBN3 and TMBW3 are as shown in Fig.1.

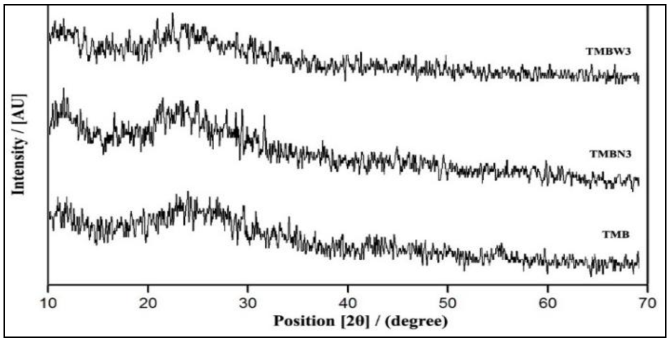

Fig 1: XRD spectrum of glass samples of TMB, TMBN3, and TMBW3 at room temperature

3.2 Thermal Analysis

Thermogravimetric analysis (TGA) and Differential Thermal analysis (DTA) are important in studying the transformation of a solid sample in a thermal process. The TGA and DTA curves for the glasses (TMB, TMBN and TMBW) prepared in this study are shown in the Figs. 2–5. The TGA curves show only considerable weight loss less than 15% in the complete range of investigation (i.e.) from 20 to 1000 °C in all the glasses studied. These TGA and DTA thermograms of the present glasses also showed the amorphous nature of the glasses like XRD. The endothermic peaks corresponding to the glass transition (T_g) and exothermic peaks due to the crystallization (T_p) are clearly observed. It is, therefore, concluded that all melt-quenched samples prepared are glass. The values of glass transition temperature (T_g), crystallization temperature (T_p), melting temperature (T_m) and thermal stability ΔT estimated from DTA curves are summarized in Table - 2.

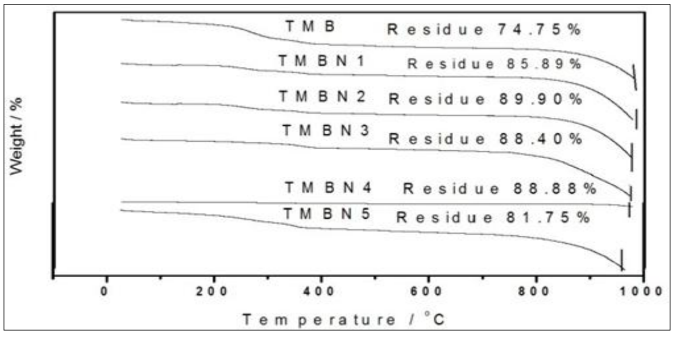

Fig 2: TGA curves of TMB and TMBN Glasses at 20^o C/min heating rate

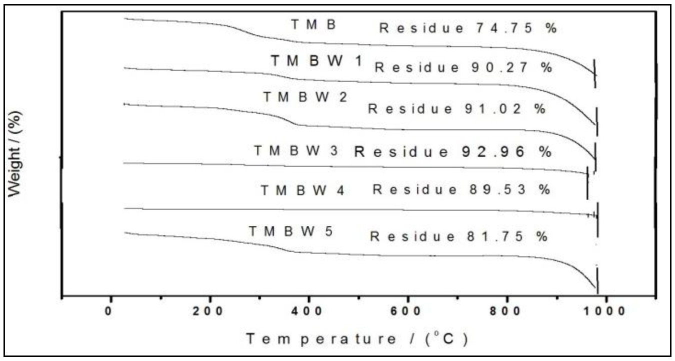

Fig 3: TGA curves of TMB and TMBW Glasses at 20^o C/min heating rate

The transition temperature (T_g) gives information on both the strength of inter atomic bonds and the glass network connectivity, in a similar way that the melting temperature does it for crystalline solids. It is seen that all the values of T_g, T_p and T_m increases with the doping of NiO and WO_3 content in tellurite magnesium borate glass system. From DTA scans, it is observed that the lack of sharp endothermic and exothermic peaks evidently specify the formation of homogenous glass. The change in the glass transition temperature T_g clearly shows that doping of NiO and WO_3 affects the glass structure. Specifically an increase in T_g with the addition of NiO and WO_3 contents indicates an increase in the rigidity of the glass network (Table - 2). This confirms that W^{6+} ions would be incorporated as network formers, either with octahedral coordination [WO_6] or tetrahedral coordination [WO_4], alternating with Te^{4+} ions and forming mixed linkages Te-O-W and W-O-W in compared to Ni^{2+} ions groups [14].

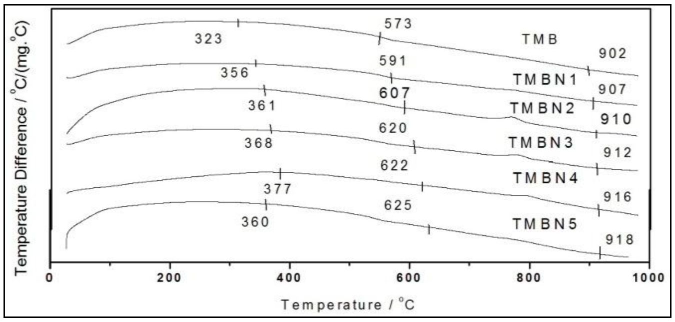

Fig 4: DTA curves of TMB and TMBN glasses at 20 °C / min heating rate

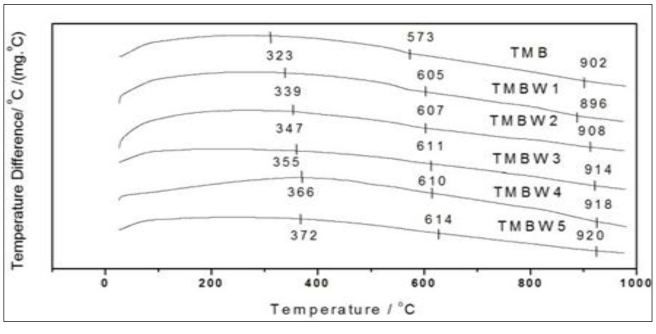

Fig 5: DTA curves of TMB and TMBW glasses at 20 °C / min heating rate

Further, the observed increase in Tg for the glasses may be due to the decreasing number of non-bridging oxygen atoms (NBO). Further, from the literature of the glasses, when a higher cross-link density of cation is replaced by a cation of lower cross-link density, the Tg of respective glasses should decrease. But in the present case this behaviour is not observed. This could be due to the difference in cross-link densities of NiO and WO_3. Therefore, the increase in Tg may be described to the different bond strength of Ni-O (≈ 382.0 KJ mol^{-1}) and W-O (≈ 672.0 KJ mol^{-1}) in comparison with the bond strength of Te-O (≈ 376.1 KJ mol^{-1}), Mg-O (≈ 363.2 KJ mol^{-1}) and B-O (≈ 808.8 KJ mol^{-1}) [15, 16]. The analysis of these results indicates the increase in Tg with the addition of NiO and WO_3 content that might be associated with the augmented, cross-link density of various micro-structural groups, the closeness of their packing and bond strength between the atoms involved [17].

Table 2: Values of glass transition temperature (T_g), crystallization peak temperature (T_p), melting temperature (T_m) and thermal stability (ΔT) of various glass samples.

Glass samples Label	Glass transition temperature T_g/°C	Crystallization Peak temperature T_p/°C	Melting temperature T_m/°C	ΔT/°C
TMB	323	573	902	250
TMB N1	356	591	907	235
TMB N2	361	607	910	246
TMB N3	377	620	912	243
TMB N4	360	622	916	262
TMB N5	368	625	918	257
TMB W1	339	605	904	266
TMB W2	347	607	908	260
TMB W3	355	611	914	256
TMB W4	366	610	918	244
TMB W5	372	614	920	242

Thermal stability ΔT is an important issue in glass science for both fundamental and technological reasons. Thermal stability (ΔT) refers to the temperature range within which the glass does not tend towards devitrification (T_p - T_g); the higher the thermal stability, the better the glass quality. The values of ΔT shows in the table are greater than 100°C with the addition of NiO and WO_3 content in the prepared glasses. The thermal stability criterion ΔT of glasses are larger than 100°C indicating that these glasses have good thermal stability and can easily be obtained in bulk forms. Thus the addition of NiO and WO_3 increases the stability of the glass and the rigidity of the network, which is an agreement with the data of the glass density [18].

3.3 FTIR Studies

Fourier transform infrared, FTIR is a useful non-destructive tool for investigation of structure and compositional differences of bulk glasses. Using this tool, essential information concerning the arrangement of the structural units of the glasses can be obtained. The FTIR transmittance spectra of TeO_2-MgO-B_2O_3 (TMB), TeO_2-MgO-B_2O_3-NiO (TMBN) and TeO_2-MgO-B_2O_3-WO_3 (TMBW) glasses are presented in the Figs. 6 & 7. For the sake of clarity the spectra are shifted upwards. The IR absorption spectra of the glasses are characterized by intense absorption bands in the frequency region over the range of 400 - 4000 cm^{-1}. The obtained transmission band and their assignments are summarized in the Table 3 & 4. According to the literature survey the vibrational modes of the borate network are mainly active in three infrared spectral regions [19, 20]. The regions are

1. The IR features located in the first region that ranges between 400 - 800 cm^{-1} is due to the various B-O-B bending modes in BO_3 and BO_4 units.
2. The second region ranges between 800 - 1200 cm^{-1} and its spectral features are due to the B-O bond stretching of $[BO_4]$ tetrahedral units.
3. The third region 1200 - 1600 cm^{-1} are due to the asymmetristretching, relaxationon of B-O⁻ bonds from the $[BO_3]$ trigonal units.

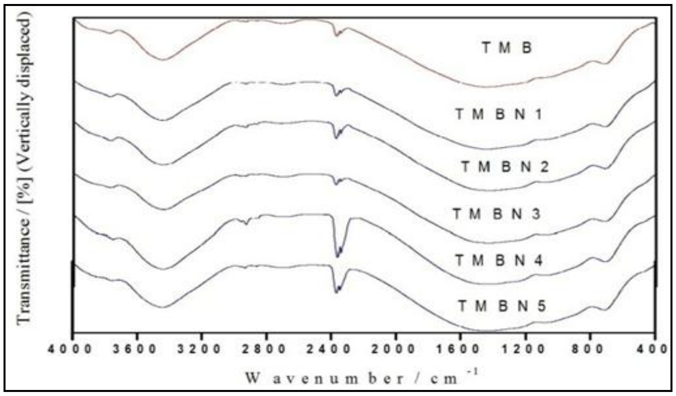

Fig 6: FTIR spectra of TMB and TMBN glasses

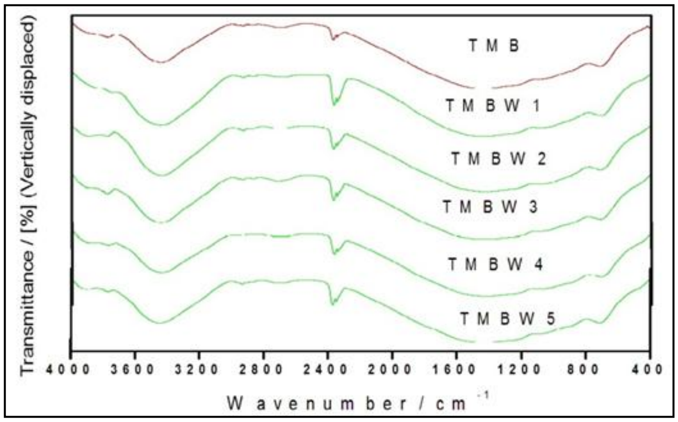

Fig 7: FTIR spectra of TMB and TMBW glasses

A fairly sharp, but low intensity peak in the region of 720 cm^{-1} was assigned to the bending vibrations of various borate segments [21]. In borate modified glasses, these three regions might be shifted to lower/higher wave numbers according to the glass composition. For amorphous materials, the position of the IR bands and resolution of the peaks is dependent on the composition. Therefore, the assignment of a certain structural IR band in a certain glass system is taken just as a guide for attribution in similar glass systems.

In the present studied glasses of TMB, TMBN and TMBW, IR band assignments have been summarized as follows:

Table 3: FTIR band assignments of Ni^{2+} doped tellurite magnesium borate glass system

Glass samples label	Wave number / (cm^{-1})	Assignments
TMB	411, 446, 714, 774 1071, 1219, 1448 2346, 2369, 2698, 2863, 2964 3448, 3771, 3802, 3905	400 - 800 cm^{-1} – Various B-O-B bending modes in [BO_3] and [BO_4] units or due to the presence of Te-O bonds. 680 - 718 cm^{-1} – Ni-O stretching vibration mode. 700 - 780 cm^{-1} – [TeO_3] trigonal pyramids. The band around 772 cm^{-1} was attributed to the stretching vibration between tellurium and NBOs of [TeO_3] trigonal pyramidal structural units. 800 - 1200 cm^{-1} – B - O bond stretching of the [BO_4] tetrahedral units. 1200-1600 cm^{-1} – Asymmetric stretching vibrations of B-O bonds from the [BO_3] trigonal units. 1252 cm^{-1} – B-O stretching vibrations in [BO_3] units from boroxol rings. ~3400 cm^{-1} – O - H group
TMBN1	462, 708, 770 1081, 1238, 1446 2346,2372,2706, 2856, 2927 3448, 3771	
TMBN2	494, 715, 772 1091, 1227, 1427 2346,2371, 2712, 2928 3448, 3770	
TMBN3	498, 718, 773 1084, 1229, 1432 2346,2372,2707, 2862, 2930 2967, 3448, 3771	
TMBN4	470, 713, 778 1094, 1243, 1428 2278,2345, 2689, 2855,2928, 3448,3752, 3803, 3822	
TMBN5	494, 712, 781 1078, 1252, 1437 2345, 2364, 2710, 2858, 2929 3448, 3752, 3822	

It is known that in vitreous B_2O_3 about 80% of boron atoms are present in boroxol rings, B_3O_6, that are interconnected independent [BO_3] groups. Borate glasses generally consist of several structural groupings like [BO_3], [BO_4], boroxol rings, triborate, and diborate units, etc. [22] in the pure B_2O_3 glass, the absorption peak at 806 cm^{-1} wave number is a characteristic band of boroxol ring. In the present glass systems the absence of this peak indicates the nonexistence of boroxol ring formation, ultimately it consists of BO_3 and BO_4 units [23]. It is well known that the borate network consists of Sp^2 planar BO_3 units and more stable SP^3 tetrahedral BO_4 units. Each BO_4 unit is linked with two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedrons. The presence of such BO_4 units is evident from the IR spectral studies. In general, NiO and WO_3 are a glass modifier and enters the glass network by breaking up the B-O-B bonds (normally the oxygen of NiO and WO_3 breaks the local symmetry while Ni^{2+} and W^{6+} ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen (NBO) ions. In this case Ni^{2+} and W^{6+} are octahedrally coordinated [24].

Table 4: FTIR band assignments of WO^{6+} doped tellurite magnesium borate glass system

Glass samples label	Wave number / (cm^{-1})	Assignments
TMB	411, 446, 714, 774 1071, 1219, 1448 2346, 2369, 2698, 2863,2964 3448, 3771, 3802, 3905	400 - 800 cm^{-1} – Various B-O-B bending modes in [BO_3] and [BO_4] units or due to the presence of Te-O bonds. 700 - 780 cm^{-1} – [TeO_3] trigonal pyramids. The band around 772 cm^{-1} was attributed to the stretching vibration between tellurium and NBOs of [TeO_3] trigonal pyramidal structural units. 800 - 1200 cm^{-1} – B - O bond stretching of the [BO_4] tetrahedral units. 852 - 864 cm^{-1} – stretching vibration of W-O-W linkages.
TMBW1	475, 710, 772 852, 1088, 1238, 1437 2278, 2345, 2365, 2691, 2926 3448, 3802, 3822	
TMBW2	480, 710, 774, 854 1085, 1235, 1426 2346, 2367, 2709, 2929 3448, 3786, 3803, 3905	
TMBW3	470, 713, 777, 858 1247, 1426	

	2346, 2367, 2719, 2858, 2932 3448, 3772, 3803, 3905	1200 - 1600 cm^{-1} – Asymmetric stretching vibrations of B-O bonds from the [BO$_3$] trigonal units. 1252 cm^{-1} – B-O stretching vibrations in [BO$_3$] units from boroxol rings. ~3400 cm^{-1} – O - H group
TMBW4	484, 719, 781, 860 1213, 1428 2346, 2367, 2711, 2935 3448, 3771	
TMBW5	494, 710, 784, 864 1039, 1264,1429 2346, 2367, 2692, 2932 3448, 3770, 3905	

The bands in the IR region 400 – 800 cm^{-1} might be mainly due to the presence of Te-O bonds. The band at 463 cm^{-1} is attributed to the stretching vibrations of Te-O-Te or O-Te-O linkages [25]. For the glasses investigated there are many bands in the region between 700 - 780 cm^{-1}. These bands are due to [TeO$_3$] trigonal pyramidal units. The band around 772 cm^{-1} was attributed to the stretching vibration between tellurium and NBOs [TeO$_3$] of trigonal pyramidal structural units [26]. Tungsten ions have an intermediate behaviour between network formers and modifiers. Thus, depending on the own nature of other glass components in the three – dimensional structure and on their percentage, they could play the role of formers or modifiers. The incorporation of WO$_3$ into tellurite glasses causes both the diminishing of trigonal bipiramyds (tbp) and the forming of non-bridging oxygens [27]. Moreover, the incorporation of WO$_3$ induces the appearing of two shoulders at 700 - 800 and 800 - 860 cm^{-1}. All the former vibrations are included in the reference spectrum of γ-WO$_3$. The structural network of this compound is formed by octahedral [WO$_6$] units, which share their vertices. The shoulder at 860 cm^{-1} is assigned to the vibration of W-O-W linkages [28].

The broad transmittance band in the region of 680 - 718 cm^{-1} is assigned to NiO stretching vibration mode. This broadness of the transmittance band indicates that the NiO powders are nano-crystals. It is generally accepted that Ni^{2+} ions are absolutely stable in oxide glasses and occurs as octahedral and/ or tetrahedral coordination, depending on the glass composition and condition of melting the glass. The observed bands at 680 – 718 cm^{-1} seem to indicate the presence of Ni^{2+} in the tellurite magnesium borate glass mostly in octahedral coordination [29].

At higher wavenumbers along the frequency region 1200 - 1600 cm^{-1} the following bands were distinguished: 1213, 1252, 1264 and 1427 - 1448 cm^{-1}. The band around 1250 cm^{-1} was assigned to B-O stretching vibrations in [BO$_3$] units from boroxol rings. This peak is evidence for the presence of boroxol rings in these glasses. The features of the band presented in the 1200 - 1600 cm^{-1} region can be attributed to the B-O stretching vibrations of [BO$_3$] structural units, which are associated with the vibrational mode inside the various borate rings and the non-bridging B-O$^-$ bonds. This band is attributed to non-bridging oxygen atoms increase in the borate units [30]. All the samples in the present systems show bands at about 3400 cm^{-1} which is attributed to the O-H groups [31].

3.4 EPR studies

Electron Paramagnetic resonance (EPR) study is important since transition metal ion impurities are one of the primary sources of absorption losses in vitreous optical materials, and information about the oxidation and the coordination states of transition metal ion extracted from EPR spectra can be used for the deliberate minimization of their absorption by a careful control of the melting process. At the same time, the EPR technique is an indirect method for the study of glass structure with transition metal ions as paramagnetic probes [32]. The EPR spectra of all the glass sample of TMB, TMBN and TMBW at room temperature have been traced out and are shown in the Figs.8 & 9 The EPR spectra of the studied TMB glass exhibit a signal at g ≈ 1.9904.

When NiO and WO$_3$ metal ions are introduced into the tellurite magnesium borate glasses, the spectra of all the investigated samples exhibit resonance lines. The TMB glass with doping of NiO shows the EPR spectra (Fig.8) which consists mainly of intense resonance lines centered at g ≈ 2.0 to 2.3 values, their relative intensity depending on the doping of ions. This g - value is in tune with the reported g – values of other systems reported with Ni^{2+} ion.

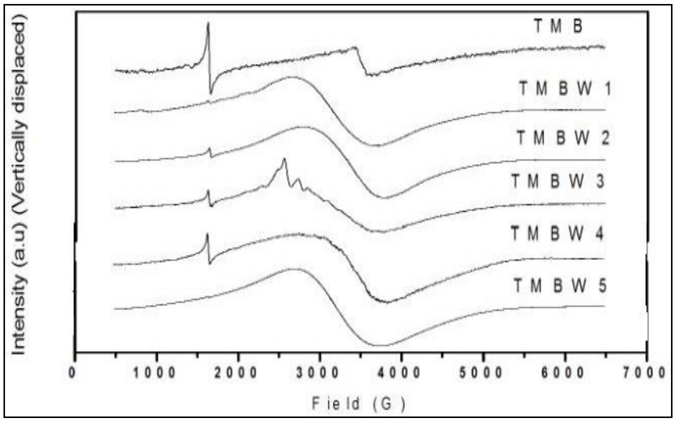

Fig 8: EPR spectra of TMB and TMBN glasses

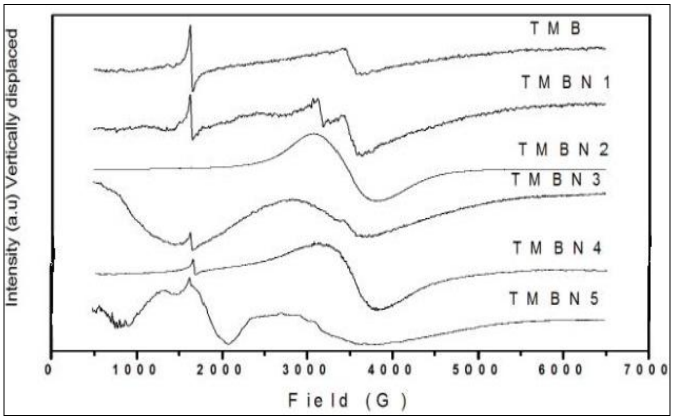

Fig 9: EPR spectra of TMB and TMBW glasses

The EPR spectra of the tungsten doped glasses exhibit a signal that is centred at g ≈ 2.27 which is due to the oxygen ion defect. It is generally accepted that tungsten ion exists in glasses in three possible valencies: $W^{6+,}$ W^{5+} and W^{4+} and the first two states are predominate and could participate in the glass network itself [33, 34]. Further, the g values of TMBN glasses (Table - 5) are increasing gradually which indicates that the Ni^{2+} ions that might be responsible for the EPR lines thinning participated in dipolar interaction. The increasing ionic bonding nature between Ni^{2+} ions and O^{2-} ions generating the octahedral symmetric ligand field were evident from the rise of the g - parameter in the content of NiO. But, however the reverse trend has been noticed in the case of WO_3 glasses. In the NiO and WO_3 doped glasses the g_{eff} values are expected to lie very near to the free ion value of 2.0023. However the g - values of TMBN and TMBW are greater than 2.0023 often occur and this larger g – values arise when certain symmetry elements are present.

Table 5: The EPR values of g and Δg of TMB, TMBN and TMBW glasses at room temperature

Glass samples	g	Δg
TMB	1.9904	0.0119
TMBN1	2.0539	-0.0516
TMBN2	2.2007	-0.1984
TMBN3	2.2063	-0.2040
TMBN4	2.2255	-0.2232
TMBN5	2.3243	-0.3220
TMBW1	2.2804	-0.2781
TMBW2	2.2763	-0.2740
TMBW3	2.2729	-0.2706
TMBW4	2.2667	-0.2645
TMBW5	2.2482	-0.2459

From the EPR spectra of TMBN and TMBW glasses it is concluded that the presence of resonance signals at g ≈ 2.0 to 2.3 which may be due to the doping of Ni^{2+} and W^{6+} ions in an environment close to the octahedral symmetry [35]. Further, from the Table - 5, the values of Δg show positive shift for TMB and negative shift for TMBN and TMBW glasses. It is also noted that the Δg value for the hyperfine splitting was indicative of the nature of bonding in the glass [36]. The negative shift of Δg values shows that the bonding is ionic in nature and conversely, if the shift is positive, then the bonding is more covalent in nature. In the present study, positive shift of Δg values in TMB glass is covalent bonding in nature, whereas a negative shift of TMBN and TMBW glasses reveals ionic in nature.

4. Conclusion

Structures, crystallization behaviour and thermal properties of a wide range of Tellurite magnesium borate doped with nickel and tungsten glasses have been studied using XRD, TGA, DTA, FTIR, and EPR techniques. The amorphous nature of the prepared glasses was confirmed by XRD. From the thermal studies, the increasing behaviour of Tg and Tp indicates the prepared glasses posses the higher cross-link density and compact structure of the glass. Further, thermal stability parameter proves the prepared glass samples having a thermally high stable glass. FTIR measurements show that, the doping of metal ions into prepared glass samples modifies or breaks Te-O bonds in the TeO_2 network, creating non-bridging oxygens (NBO) and TeO_3 molecular units. It is expected that polymerization of the glass network increases, while with the decrease in the concentration of NBO's with increasing NiO and WO_3 contents and the appearance of the bonds Te-O-B, Mg-O-B, Ni-O-B and W-O-B at higher contents. The existence of Ni^{2+} and W^{6+} in the tellurite magnesium borate glasses mostly exhibit in the octahedral coordination. The EPR spectrum of TMBN glasses shows the resonance signal at g ≈ 2.0 to 2.3 which is close to the octahedral symmetry and also TMBW glass shows the resonance signal at g ≈ 2.27 which is due to the oxygen ion defect centres. Further, the positive shift of Δg-value of TMB glass posses covalent bonding in nature, whereas the negative shift of Δg-value of TMBN and TMBW glasses posses ionic bonding in nature.

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