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Influence of Nb_2O_5 on Spectroscopic Studies of TeO_2-ZnO Glass System

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Ternary TeO_2-ZnO-Nb_2O_5 glass has been reported to have exceptional structural and elastic properties. The ternary samples of (85-x)TeO_2 - 15ZnO - (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol %) glass system are studied. The effect of Nb_2O_5 on the combination spectroscopic studies (FTIR and SEM-EDX) of the glass were investigated. XRD measurements were confirmed that all samples prepared are amorphous in nature. The FTIR observations show that TeO_3 trigonal pyramid (tp) to TeO_4 trigonal bipyramid (tbp) group conversion in the TeO_2-ZnO base glass was aided by the steadily rising Nb_2O_5 content. The SEM examination results show the flat surface without grain boundaries and dominancy of large particle grain size. The EDX mapping results confirm the increment of Nb element's weight percentage as increase in Nb_2O_5 compound. The density and oxygen packing density increases, while the molar volume of the glass samples decreases as the content of Nb_2O_5 increases. This is suggested to indicate that glass structure is compact, and the glass network become rigid. The Nb_2O_5 plays important functions in structuring and forming the glass structure, thus this study is inferred to contribute to the valuable information on the spectroscopic properties of this glass system.

Keywords: Tellurite glass; Nb_2O_5; FTIR; SEM-EDX; spectroscopic

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Glasses have special qualities that make them stand out. The study of the characteristics of glasses is one of major significance because of their potential uses in numerous engineering and technological disciplines [1]. TeO_2-based glasses have a significant optical nonlinearity as well, making them excellent candidates for a variety of photonics applications [2]. Tellurite-based glasses have attracted a lot of attention in science and technology because of their intriguing electrical, optical, and magnetic properties. Tellurite glasses are a good choice for the creation of optical devices because of these characteristics and these glasses typically function well as an insulator [3] and is a good material for optical applications like fibre optics and laser materials [4].

Several tellurite glass systems have been introduced with metal oxides such as ZnO and Nb_2O_5. The combination compound such as TeO_2-Nb_2O_5, TeO_2-ZnO, TeO_2-Nb_2O_5-ZnO, and TeO_2-TiO_2-Nb_2O_5, displays outstanding optical efficiency [5]. The addition of transition metal oxides, which have a variety of oxidation states and a high coordination number at high concentrations, such as WO_3, Nb_2O_5, MoO_3, and TiO_2, increases the mechanical and chemical stability of the glass-forming compound [6]. Moreover, Nb_2O_5 glass modifier can enhance glass stability, vitrification, and optical nonlinearity qualities [7]. Additionally, Nb_2O_5 mixed glasses are well-known as good dielectric materials and are especially effective for photocatalysts [8]. Tertiary Nb_2O_5-BaO-TeO_2 glass samples were seen to have no distinct peaks in the XRD results, confirming the materials' amorphous nature [4]. Previously, many researchers have used IR spectroscopy to examine the structural role of Nb_2O_5 in various silicate, borate, germanite, and gallate glasses. Most of them discovered NbO_6 groups in the glass network [9]. The findings demonstrated a rise in density and oxygen packing density (OPD), while molar volume decreased when Nb_2O_5 content increased. The alteration in molar volume was brought on by a change in the structure and interatomic spacing [10]. The density of any material is a crucial and useful physical characteristic for explaining structural compactness, shape and size changes, coordination numbers, and cross-link density [11]. The OPD of glass is a key factor in defining both its physical and chemical characteristics. It affects crucial elements including optical transparency, chemical resistance, mechanical strength, and thermal stability [12]. In contrast, the elastic characteristics of glasses change as compositional and structural parameters do [13], while the Scanning Electron Micro-

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scope (SEM) shall be capable of providing information on the topography, composition and other characteristics of the sample [14] and Energy Dispersive X-ray (EDX) is a method frequently used in scanning electron microscopy (SEM) to identify the elemental composition of a sample [15].

There are many reports of remarkable structural and elastic properties in ternary TeO_2-ZnO-Nb_2O_5 glass system. On the other hand, the majority of Nb^{5+} ions in quaternary tellurite glass and other glass systems, according to a fascinating spectroscopy studies function as glass formers with bridging oxygen (BO) ions at low Nb_2O_5 content. As for higher Nb_2O_5 content, the ions switch to glass modifier, due to the increasing number of non-bridging oxygen (NBO) ions in the glass network. Although there is a large number of elastic and structural investigations for ternary tellurite glasses have been reported, a combination of spectroscopic research of FTIR, SEM-EDX with density measurement on the TeO_2-ZnO-Nb_2O_5 glass system as varying the Nb_2O_5 content with TeO_2 glass host recorded less studies and the importance of related info as far as we are aware is still unclear.

In this work, we investigated the relationship of the combination of spectroscopic properties of the (85-x)TeO_2 – 15ZnO – (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol%) glass system using two different spectroscopy measurements which were Fourier Transform Infrared (FTIR) and Scanning Electron Microscope – Energy Dispersive X-Ray (SEM-EDX) with density measurement. The amorphous structure of the glass system was confirmed by employing the X-ray diffraction (XRD) pattern. In the system, TeO_2 was partially substituted with Nb_2O_5 to clarify their functions in the formation of the glass network and for spectroscopic analyses of the system.

EXPERIMENTAL

Preparation of Glasses

By combining the total amount of 5 gram from Tellurium Dioxide (TeO_2, 99.995% purity, Sigma Aldrich), Niobium Pentoxide (Nb_2O_5, 99.99% purity, Sigma Aldrich), and Zinc Oxide (ZnO, 99.99% purity, Sigma Aldrich) according to the right stoichiometry calculation, the mixed powder was grinded together for one hour in an agate mortar. The glass samples were created from starting compositions of (85-x)TeO_2 - 15ZnO - (x)Nb_2O_5 with x = 0 until 10 mol%. The powder mixture was then put into a ceramic crucible and heated for one hour at 950°C in a melting furnace. After quenching, the high viscosity melting liquid was quickly transferred to a stainless-steel mold on the other furnace for annealing purpose for four hours at 350°C.

Characterization Methods

The samples were evaluated using an X'Pert Pro Panalytical diffraction analyzer to determine the amorphousness of the glass. Because of its depth of penetration and capacity to expose the internal structural features of the material, XRD was used on thick or powdered materials [16].

Using a digital density meter which was MD-300S Densimeter and acetone as the immersion liquid, the density of the sample, ρ, was calculated at room temperature by applying the Archimedes principle using the relation [4]:

$$\rho = \left(\frac{W}{W - W_b}\right)\rho_b \qquad \text{Eq. (1)}$$

Where ρ_b is the density of acetone, 0.73, W_b is the weight of the glass sample in acetone, and W is the weight of the glass sample in air.

The density data were then used to get the molar volume (V_a) of the glass samples [10].

$$V_a = \frac{M}{\rho} \qquad \text{Eq. (2)}$$

Oxygen Packing Density (OPD) gives information on the connection and arrangement of oxygen atoms inside the glass network. The following mathematical relation was used to obtain the OPD values:

$$(OPD) = 1000 \times C\left(\frac{\rho}{M}\right) \qquad \text{Eq. (3)}$$

where ρ is density, M is molecular weight and C is the number of oxygen ions present in the formula unit.

FTIR is a helpful non-destructive method for examining changes in the composition and structure of bulk glasses [17]. Perkin Elmer model Spectrum 100 FTIR Spectrometer was implemented to measure and record the IR absorption spectra with a resolution of 16 cm^{-1} in the 400–1200 cm^{-1} range. Proper sample preparation involved grinding glass samples into fine powder.

Scanning electron microscope (SEM) is an essential method for analysing the materials' microstructure and illuminating the crystalline phases' morphology [14]. To determine the elemental makeup of the irradiated region on a perhaps submicron level, Energy Dispersive X-Ray (EDX) measures X-rays released from the sample during irradiation by an electron beam. As a result of this electron bombardment, elements release X-rays characteristic as their electrons move from electron shells with higher atomic energy levels to those with lower energy levels [15].

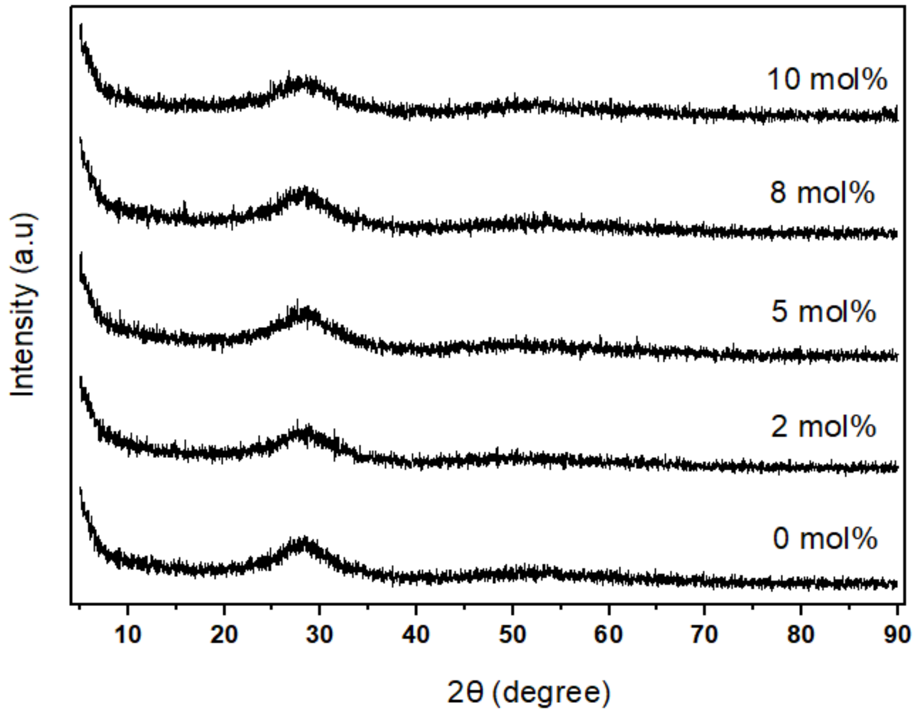

Figure 1. XRD patterns of the (85-x)TeO_2 – 15ZnO – (x)Nb_2O_5 (x=0, 2, 5, 8, 10 mol%) glasses.

RESULTS AND DISCUSSION

X-Ray Diffraction

Figure 1 displays a typical XRD pattern for all niobium pentoxide (Nb_2O_5) doped zinc tellurite (ZnO – TeO_2) glass samples. It is seen that prepared glasses have broad hump that indicate an amorphous structure [18]. No obvious distinct is found even there are varying amount of Nb_2O_5 added.

Density Measurement

Table 1 displays the values of density (ρ), molar volume (V_a) and oxygen packing density (OPD) for all samples. The addition of Nb_2O_5 in place of TeO_2 causes the density of the glass to gradually increase while the molar volume decreases. In contrast to the density which increases from 3.96 g/cm^3 for x = 0 mol% to 5.28 g/cm^3 for x = 10 mol%, molar volume, is seen to decrease from 37.34 cm^3/mol to 30.01 cm^3/mol with the increase in the Nb_2O_5 concentration. With an increase in Nb_2O_5 content, the OPD values increase. Figure 2 illustrates the changes in density and molar volume with increasing amounts of Nb_2O_5.

The increasing of the density of the glass system with the addition of $Nb_2O_5$is suggested due to an increase in molecular mass brought on by TeO_2 (159.60 g/mol) which decreasing as the heavier Nb_2O_5 (265.81 g/mol) increases. On the other hand, the decrease in molar volume is a result of different ionic sizes. [12]. The average atomic mass of the glass increases with the addition of niobium pentoxide.

Table 1. Values of density (ρ), molar volume (V_a) and oxygen packing density (OPD) of (85-x)TeO_2 - 15ZnO - (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol%) glass samples.

x (mol %)	ρ (g/cm^3)	V_a (cm^3/mol)	OPD (mol/l)
0	3.96	37.34	49.55
2	4.15	36.15	52.84
5	4.42	34.65	57.72
8	5.00	31.30	66.78
10	5.28	30.01	71.63

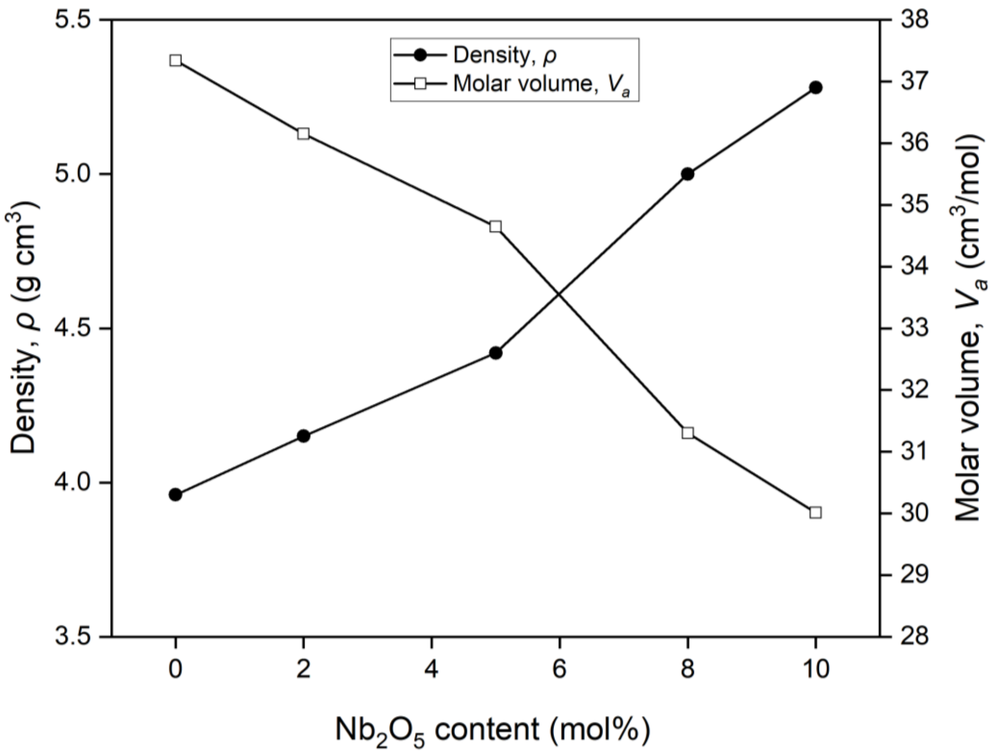

Figure 2. Density (ρ) and molar volume (V_a) of (85-x)TeO_2 – 15ZnO – (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol%) glasses.

As a result, there are more Nb-O bonds per unit of volume than Te-O bonds [6]. A higher density is produced by an increase in average atomic mass since density is defined as the mass of a substance per unit volume. Niobium atoms are added, and because of their higher mass, the glass as a whole gains mass, which raises the density of the material. The larger Nb atoms replace the smaller Te atoms in the glass structure as the amount of Nb_2O_5 increases. The change in molar volume is caused by a change in the structure causing change in interatomic spacing [10], which results in a compact structure of the glass. It may be responsible for the observed decrease in molar volume [12]. Furthermore, as the oxygen atoms in the glass network are packed closer together, the oxygen packing density of a glass rises. This indicates that glass structure is denser and smaller.

Fourier Transform Infrared (FTIR) Spectroscopy

Figure 3 shows the FTIR spectra of the (85-x)TeO_2 - 15ZnO - (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol%) glasses. Four important IR transmission bands are identified at 438–449 cm^{-1}, 661-670 cm^{-1}, 757-769 cm^{-1}, and 850–877 cm^{-1}. The 438-449 cm^{-1} IR peak is assigned to the ZnO_4 tetrahedra group in ZnO while the 661-670 cm^{-1} peak is assigned to the TeO_4 trigonal bipyramid (tbp). The frequency peaks which are assigned to the TeO_3 trigonal pyramid (tp) decrease from 769 to 757 cm^{-1} while the peaks associated with NbO_6 octahedral groups increase from 850 to 877 cm^{-1} with the addition of Nb_2O_5 content.

The presence of a network unit that contributes to the creation of bridging oxygens (BO) is indicated by the identification of the 438-449 cm^{-1} peak associated with the ZnO_4 tetrahedra group. With the addition of Nb_2O_5, red shift in wavenumber from 769 to 757 cm^{-1} indicates the decreasing of TeO_3 (tp), which shows a reduction in the formation of non-bridging oxygen (NBO). The blue shift of wavenumber in TeO_4 assigned from 661 to 670 cm^{-1} is suggested to be a sign of increasing BO. Since Nb_2O_5 is shown to increase the strength of the NbO_6 assigned peak at 850-877 cm^{-1}, this implies the presence of non-bridging oxygen (NBO) [7].

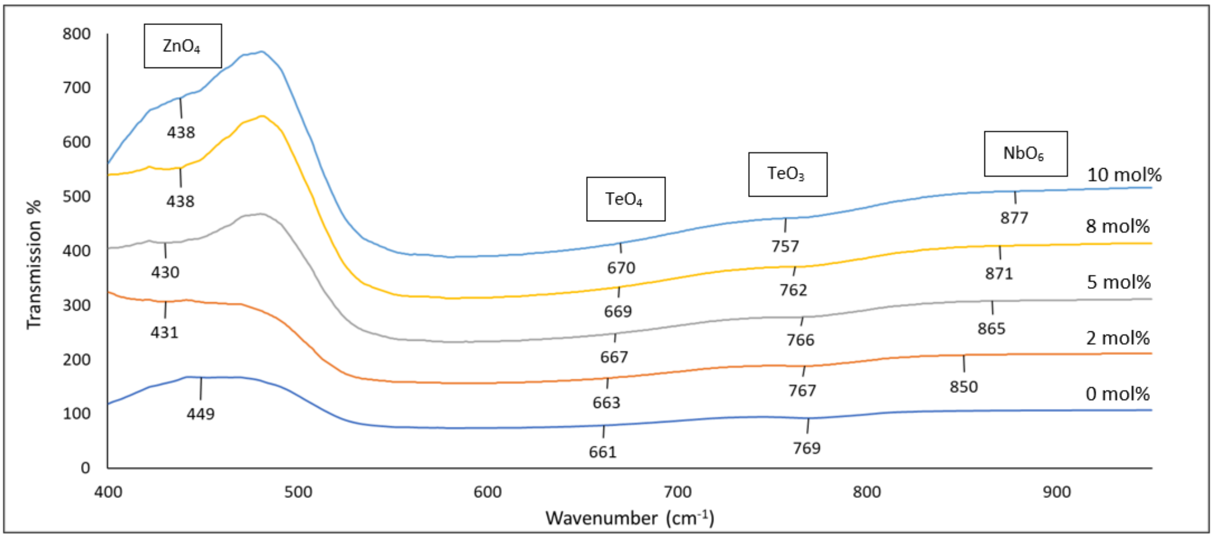

Figure 3. The IR spectra of (85-x)TeO_2 – 15ZnO – (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol%) glass samples.

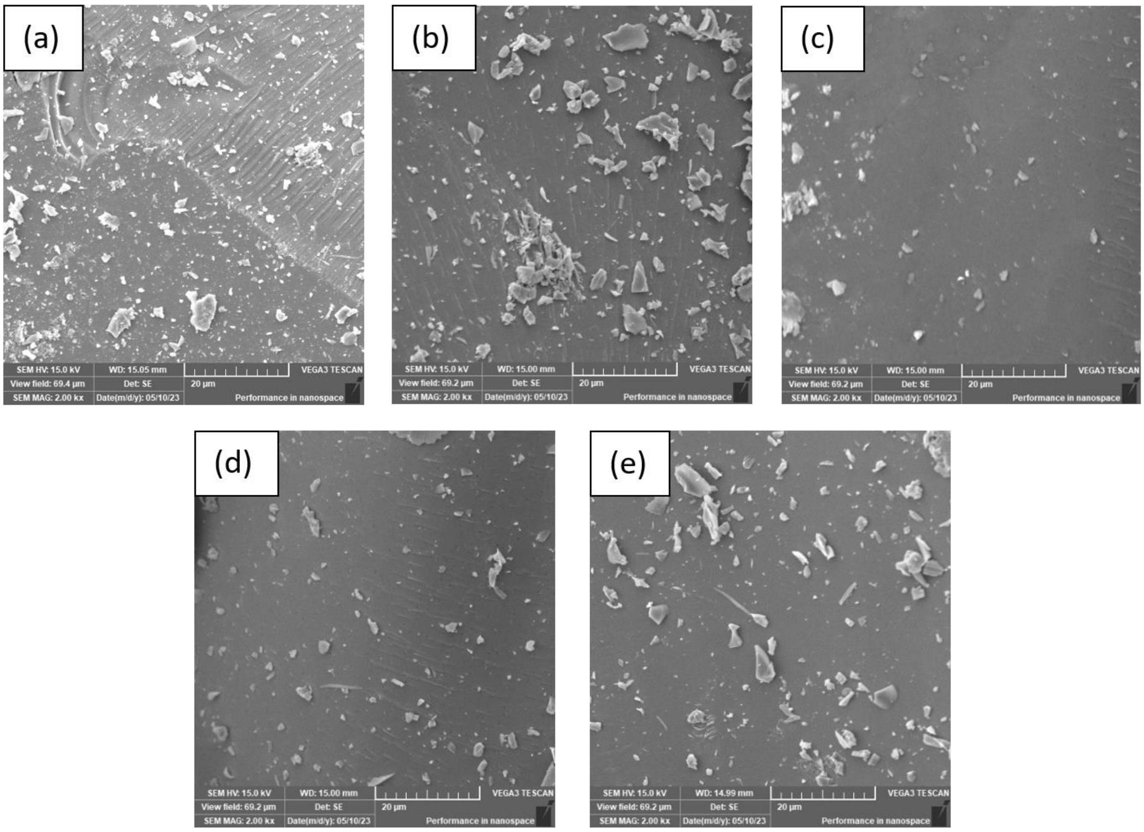

Figure 4. SEM images of the (85-x)TeO_2 – 15ZnO – (x)Nb_2O_5 x = (a) 0 mol%, (b) 2 mol%, (c) 5 mol%, (d) 8 mol% and (e) 10 mol% glasses with magnification of 2000x.

Scanning Electron Microscope - Energy Dispersive X-Ray (SEM-EDX) Spectroscopy

The sample size and morphology were investigated using SEM imaging. Elemental maps can be produced by scanning the electron beam across the sample surface and doing EDX analysis at every point on the surface [19]. These maps show how the various components of the sample are distributed dimensionally. Figure 4 represents the SEM micrographs of the (85-x)TeO_2 - 15ZnO - (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol %) glasses at magnifications of 2000x. The varying amount of Nb_2O_5 has lesser impact on the surface morphology of the glass samples. It is observed from surface morphology and microstructure that each sample does not suggest the presence of any crystal line or agglomeration. No visible crystal structures are discovered, and the overall texture of the glass is amorphous. Figure 5 shows the EDX spectra of the sample which shows the presence of O, Te, Zn and Nb element, with no additional impurities peak identified in the EDX spectra. Table 2 shows the weight percentage of the glass elements from EDX analysis. The weight percentage of O and Nb increases from 18.57% to 20.63% and 0% to 11.89%, respectively, while for Te, the weight decreases from 74.75% to 59.99%. The weight percentage of Zn varies from 6.68% to 7.49%.

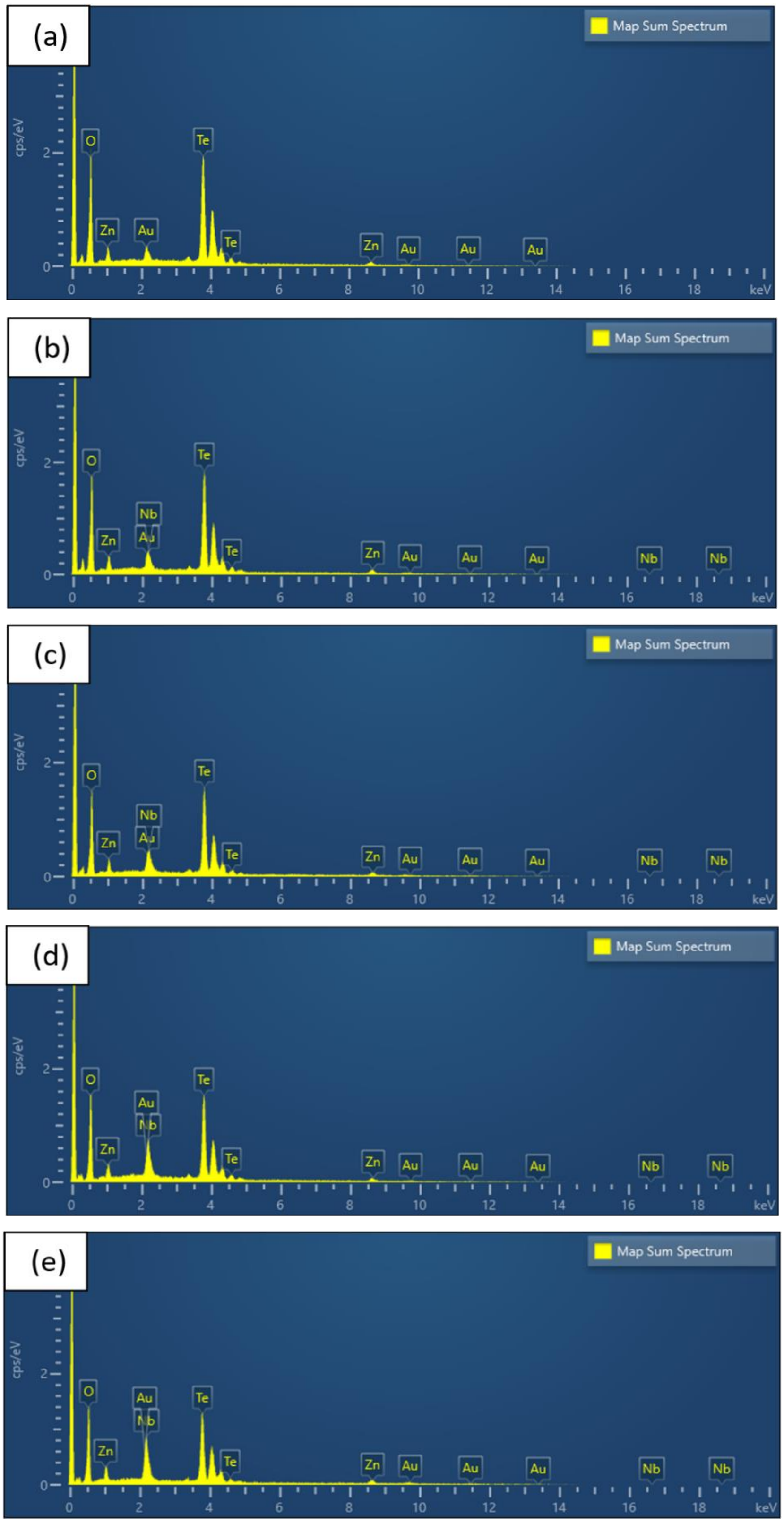

Figure 5. EDX spectra: (a) 0 mol%, (b) 2 mol%, (c) 5 mol%, (d) 8 mol% and (e) 10 mol% glasses.

Table 2. Weight percentage of elements of (85-x)TeO_2 - 15ZnO - (x)Nb_2O_5 (x = 0, 2, 5, 8, 10 mol%) glasses measured from EDX analysis.

x (mol%)	**Weight (%)**			
	O	**Te**	**Zn**	**Nb**
0	18.57	74.75	6.68	-
2	18.62	72.68	7.18	1.72
5	18.95	68.78	7.46	4.81
8	20.12	64.01	6.79	9.08
10	20.63	59.99	7.49	11.89

The surface appearance and microstructure (surface morphology) of the amorphous tellurite glass are clearly identified through SEM examination [4]. The SEM image shows that the glass has a flat surface. Amorphousness of the glass is further supported by the absence of crystalline structures, which is compatible with its non-repeating atomic arrangement [20]. The weight percentage for Nb and O increases as the mol% of Nb_2O_5 increases from 0 to 10 mol% while the weight of Te decreases as the content of TeO_2 decreases.

CONCLUSION

The successful synthesis of the ternary TeO_2-ZnO-Nb_2O_5 glass was followed by an analysis of its spectroscopic characteristics. The structural changes in the glass system demonstrated the important roles that each compound, TeO_2, Nb_2O_5, and ZnO played in the changes of the structure of the glass network. When a modifier oxide content (Nb_2O_5) was introduced, it indicated the existence and re-formation of both bridging oxygen (BO) and non-bridging oxygen (NBO) had a significant impact on the changes and modifications that happened in the glass network. The combination of spectroscopy studies which was FTIR, SEM-EDX together with density measurement were reported to complement each other. As the amount of Nb_2O_5 increases, the TeO_4 tbp increases which indicate the BO to increase. So, it thus denotes that the glass network is strong and the rigidity of the glass network is improving. Furthermore, the XRD result coincides with the SEM-EDX spectroscopy result which shows the amorphousness of the glass. As in the results, Nb_2O_5 conveys the important role as network modifier especially the spectroscopy studies of the TeO_2-ZnO glass network.

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