Modification in Structural Properties of Erbium-doped Zinc–
Sodium Tellurite Glass: Effect of Bimetallic Cu/Ti
Nanoparticles

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Abstract. The effect of bimetallic nanoparticles (NPs) on the structural and optical properties of tellurite glass doped with Cu/Ti NPs are reported. A series of glass with composition of (70–
x–y) TeO₂–20ZnO–9Na₂O–1Er₂O₃–(x)CuO–(y)TiO₂ (where x = 0.0, 0.1 and 0.04 mol%, y =
0.0, 0.1 and 0.04 mol%) are synthesized by using melt-quenching method. The structure and optical properties of tellurite glass containing Cu/Ti NPs are identified by using X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray (SEM-EDX) technique and Fourier Transform Infrared Spectroscopy (FTIR). XRD spectra show the nature of glass and the grain size. The SEM images shows the surface morphology and EDX spectra show the traces of C, O, Te, Na, Zn, Au, Er, Ti and Cu elements. FTIR spectra show the chemical bonding of constituent atom in glass matrix primarily the Zn²⁺ vibration, Cu (II)–O bonding, Te–O bending in term of TeO₃ and TeO₄ units, Cu–H stretching and O–H vibration of water group.

1. Introduction
Glasses commonly exhibit characteristic such as brittle and a transparent material. Moreover, glass is an amorphous material and has a non-periodic arrangement [1]. Tellurite glass (TeO₂) is a new type of glass host which is a non-crystalline and amorphous material. TeO₂ glass does not change into the glass state without the presence of modifier in the glass matrix [2]. The formation of the TeO₂ glasses is supported with addition of a network modifier such as metal oxide, alkali metal and alkaline earth metal [3].

Tellurite based glasses mostly investigated due to their structural and optical properties. It can be used to identify their potential application, especially in optics, photonics and optoelectronics. In the present study, our aim is to fabricate glass containing bimetallic nanoparticles (NPs) consist of copper and titanium NPs using a simple method. Further structural characterization is carried out to determine the correlation between bimetallic NPs and the constituent atoms in changing the structural properties of the glass.
2. Materials and Methods

A glass series with chemical composition of \((70-\times-\times)\text{TeO}_2 - 20\text{ZnO} - 9\text{Na}_2\text{O} - 1\text{Er}_2\text{O}_3 - (x)\text{CuO} - (y)\text{TiO}_2\), where \((x = 0.0, 0.1 \text{ and } 0.04 \text{ mol } \%; y = 0.0, 0.1 \text{ and } 0.04 \text{ mol } \%)\) are synthesized by using melt-quenching method. All materials consist of \text{TeO}_2, \text{ZnO}, \text{Na}_2\text{O}, \text{Er}_2\text{O}_3, \text{CuO} \text{ and } \text{TiO}_2 \text{ powders from Sigma Aldrich are weighed according to specific mass. Then, all powders are subjected to the milling process for 30 minutes to get the homogenous powder. A platinum crucible containing all powders is placed inside the electrical furnace at temperature of 950°C for 15 minutes. Then, the molten is poured into the brass mould and kept at room temperature for 2 days. All glass samples are cut for structural characterization. The nature of glasses is determined by using X-ray diffraction technique with model of PANalytical X’Pert 3 MRD using Cu radiations \((\lambda=1.54 \text{ Å})\) operated at 40kV and 30mA with scanning angle of 2\(\theta\) ranging from 10° - 80°. The surface morphology of glass is probed by using scanning electron microscopy-energy dispersive X-ray spectroscopy (model Hitachi–S–3400N). FTIR spectra of glass are recorded by using FTIR Spectrum 100 in range of 400 - 4000 cm\(^{-1}\).

Table 1. Glass code and glass composition of all glass samples (mol%)

| Glass Code   | \text{TeO}_2 \text{ (mol\%)} | \text{ZnO} \text{ (mol\%)} | \text{Na}_2\text{O} \text{ (mol\%)} | \text{Er}_2\text{O}_3 \text{ (mol\%)} | \text{CuO} \text{ (mol\%)} | \text{TiO}_2 \text{ (mol\%)} |
|-------------|-----------------|-----------------|-------------------------------|-----------------|-----------------|-----------------|
| TZNE        | 70              | 20              | 9                            | 1               | -               | -               |
| TZNECu0.1   | 69.9            | 20              | 9                            | 1               | 0.1             | -               |
| TZNEXTi0.1  | 69.9            | 20              | 9                            | 1               | -               | 0.1             |
| TZNECu0.04Ti0.01 | 69.86        | 20              | 9                            | 1               | 0.04            | 0.1             |
| TZNECu0.1Ti0.1 | 69.8           | 20              | 9                            | 1               | 0.1             | 0.1             |
| TZNECu0.1Ti0.04 | 68.86         | 20              | 9                            | 1               | 0.1             | 0.04            |

3. Results and Discussion

The XRD spectra for all glass samples are presents in Figure 1. TZNE glass shows a broad hump at around 30° to 40° without an appearance of sharp peak verify the amorphous nature of glass. A broad diffusion at lower scattering angle illustrates the long range of non-periodic arrangement of atoms [4]. However, the addition of metallic Cu NPs led to the appearance of a sharp peak [5]. Refer to Table 2, the peak at around 43.35°–43.39° is due to the (111) plane orientation of Cu NPs and the experimental peak value is compared with the JCPDs standard powder diffraction card for copper NPs (JCPDS no. 04 – 0836). The appearance of sharp peak in the XRD spectra reflects the FCC structure due to the contribution of Cu NPs [6]. The peak intensity of the XRD spectra depends on the size of NPs distributes in the glass matrix. [7]. The crystal size, \(D\) is determined by using the Scherrer equation:

\[
D = \frac{k\lambda}{(FWHM)\cos\theta}
\]
Table 2. Variation of FWHM and crystallize size.

| Glass Code         | 2θ  (°) | FWHM | Crystallize size, Dp (nm) | Element detected | Plane of orientation | Standard diffraction angle, JCPSD for copper: 04 - 0836 |
|--------------------|--------|------|--------------------------|------------------|---------------------|----------------------------------------------------------|
| TZNE               | -      | -    | -                        | -                | -                   | -                                                         |
| TZNECu0.1          | 43.35  | 0.14 | 62.86                    | Cu               | (111)               | 43.297                                                   |
| TZNE Ti0.1         | -      | -    | -                        | -                | -                   | -                                                         |
| TZNECu0.04Ti0.01   | 43.35  | 0.14 | 62.86                    | Cu               | (111)               | 43.297                                                   |
| TZNECu0.1Ti0.1     | 43.39  | 0.18 | 47.50                    | Cu               | (111)               | 43.297                                                   |
| TZNECu0.1Ti0.04    | 43.35  | 0.14 | 62.86                    | Cu               | (111)               | 43.297                                                   |

Figure 2 shows the SEM images illustrates the surface morphology of TZNETi0.1, TZNECu0.1Ti0.1 and TZNECu0.1Ti0.04 glass samples at a specific region. SEM images show the appearance of fractured surfaces of the glass indicates more porosity [8]. Further addition of bimetallic NPs (Cu and Ti) shows the non-spherical black spots illustrates the growth of particles on the surface of glass [9]. The corresponding EDX spectra for respective glass are displayed in Figure 3. The EDX spectra provide information about elemental traces in the glass matrix. Table 3 summarizes all the elemental trace consists of C, O, Na, Zn, Te, Au, Ti, Er and Cu. The gold (Au) peak in the EDX spectra are observed due to Au is used as the coating material. Glass sample is a non-conducting electric. Therefore, all glass samples are coated with the conducting material (Au) to give a way for the incident of electrons flow to the ground [10]. EDX spectra confirmed the contribution of bimetallic NPs in glass matrix forming bonding with other constituent atoms. The bonding formation is verified by using FTIR analysis as discussed in the next section.
Figure 2. SEM images at the specific region for (a) TZNETi0.1, (b) TZNECu0.1Ti0.1 and (c) TZNECu0.1Ti0.04 glass.
Figure 3. EDX spectra of the respective (a) TZNETi0.1, (b) TZNECu0.1Ti0.1 and (c) TZNECu0.1Ti0.04 glass.

Table 3. Tabulation of elemental traces from EDX analysis.

| Element | Series | TZNETi0.1 | TZNECu0.1Ti0.1 | TZNECu0.1Ti0.04 |
|---------|--------|-----------|----------------|-----------------|
|         |        | Weight     | Atomic         | Weight          | Atomic          | Weight         | Atomic          |
|         |        | (wt%)      | (at%)          | (wt%)           | (at%)           | (wt%)          | (at%)           |
| C       | K      | 1.58       | 9.41           | 1.50            | 6.85            | 1.21           | 5.86            |
| O       | K      | 7.94       | 35.40          | 14.33           | 49.00           | 12.41          | 45.26           |
| Te      | L      | 55.17      | 30.86          | 54.79           | 23.50           | 55.04          | 25.17           |
| Na      | K      | 2.28       | 7.08           | 3.28            | 7.80            | 3.65           | 9.27            |
| Zn      | K      | 6.96       | 7.60           | 9.16            | 7.66            | 9.72           | 8.68            |
| Au      | M      | 24.35      | 8.82           | 13.60           | 3.78            | 14.20          | 4.21            |
| Er      | L      | 1.62       | 0.69           | 2.78            | 0.91            | 3.21           | 3.37            |
| Ti      | K      | 0.09       | 0.14           | 0.06            | 0.07            | 0.03           | 0.03            |
| Cu      | K      | -          | -              | 0.50            | 0.43            | 0.38           | 0.35            |

FTIR spectra in Figure 4 provides information concerning various bonding among different ions in the glass network. Table 4 summarizes the observed peaks in the entire spectral region and their corresponding band assignments. Fundamentally, the structure of TeO$_2$ rich glasses contains three dimensional networks of TeO$_4$ tpb units with oxygen at two equatorial and axial sites in which the other equatorial site being occupied by a lone pair of electrons. The incorporation of rare earth ions in prior of erbium ions creates asymmetric TeO$_4$ polyhedron with one short, three elongated Te–O bonds and TeO$_3$ trigonal pyramids having non-bridging oxygen (NBO).

FTIR transmittance spectra shows the appearance of broad bands in range of 469 cm$^{-1}$, 514 cm$^{-1}$, 582 cm$^{-1}$, 727 - 743 cm$^{-1}$, 2004 cm$^{-1}$ and 3449 cm$^{-1}$. The band at around 469 cm$^{-1}$ region is allocated to Zn$^{2+}$ bond vibration. In addition, the band at 514 cm$^{-1}$ is assigned to the Cu (II)–O bonding [11]. The existence of two bands at around 582 cm$^{-1}$ are assigned to the Te–O stretching vibrations in TeO$_4$. The band appeared at around 724 – 743 cm$^{-1}$ assigned to the Te–O stretching vibrations in TeO$_3$ structural
units [12, 13]. The bands at around 2204 cm\(^{-1}\) is assigned to the of Cu–H stretching bonding. The band at around 3449 cm\(^{-1}\) reflects the vibration of O–H is water group. The bonding formation of Ti with other constituent atoms is not observed probably due to the lower concentration of TiO\(_2\).

**Figure 4.** FTIR spectra with varying concentration of Cu/Ti NPs.

**Table 4.** Tabulation of elemental traces from EDX analysis.

| Glass Code | Band Assignment |
|------------|-----------------|
| TZNECu0.1Ti0.1 | 469 Zn\(^{2+}\) vibration |
| TZNECu0.1Ti0.1 | 469 Cu (II)–O bonding |
| TZNECu0.04Ti0.1 | 514 Vibrations of TeO\(_4\) |
| TZNECu0.1Ti0.1 | 582 Vibrations of TeO\(_3\) |
| TZNECu0.1Ti0.04 | 743 Cu–H stretching |
| 2004 | 2004 O–H the vibration of the water group |

4. Conclusion

We demonstrated the modification in structural properties of glass containing varying the concentration of bimetallic Cu/Ti NPs by using XRD, SEM – EDX and FTIR spectra. XRD spectra show the broad hump at around 30° to 40° reflects the amorphous nature of TZNE and TZNETi0.1 glass samples. The modification in structural properties from XRD spectra shows the appearance of sharp peak at around 43.35° to 43.39° for TZNECu0.1, TZNECu0.04Ti0.01, TZNECu0.1Ti0.1 and TZNECu0.1Ti0.04 glass samples due to the contribution of Cu NPs with grain size ranging from 47.50 nm to 62.86 nm. The EDX spectra give elemental traces of C, O, Te, Na, Zn, Au, Er, Ti and Cu elements. FTIR spectra gives various bonding in glass matrix in prior to Zn\(^{2+}\) vibration, Cu(II)–O bonding, Te-O bending stretching vibrations in TeO\(_4\) units, Te-O bending vibrations in TeO\(_3\) units, Cu–H stretching and O–H vibration of water group.
5. References

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Acknowledgments

The authors are thankful to UMS and Ministry of Higher Education (MoHE) for the financial support through UMSGreat Grant (GUG0130-1/2017) and Project Research Acculturation Grant Scheme (RAG-0067-SG-2015). Khasidah wishes to thank teaching assistant scheme (SBP) for financial support.