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Research Article

MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF TeO_2-$ZnCl_2$-Nb_2O_5-TiO_2 BASED GLASS SYSTEM UNDER VARIOUS TEMPERATURES

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ABSTRACT: The objective of this study is to design a unique glass network composed of TeO_2-$ZnCl_2$-Nb_2O_5-TiO_2 to investigate the microstructural and mechanical properties. In this experiment, the proposed glass network was produced using melt quenching method. The microstructural properties and hardnesses was derived from the XRD, SEM and Vicker's Hardness measurements. Microstructures and crystalline phases was determined using the XRD diffractometry from 20 to 90 range. The estimated crystalline phases of the prepared glass samples were α-TeO_2 and γ-TiO_2. As a conclusion, tellurite-based oxide glass materials have become very much promising candidate in the areas like fiber optics, optical communication, white LED, quantum dot, quantum computing, laser technology, photonics due to their second harmonic properties.

Keywords: Tellurium oxide, optical glasses, microstructure, crystalline, hardness

1. INTRODUCTION

Recently, tellurite based optical glass materials have achieved a great trend on the field of fiber optics, fiber sensor, optical communication, laser technology, white LED, quantum dot applications [1-3]. These tellurite-based novel glass materials Total five glass samples have some special properties like high-speed transmission, higher refractive index (at around n=1.8-2.05), lower phonon energy (800eV), higher transparency etc. There are studies that show a significant increase in literature searches. In this concept, Kabalci et. al. have developed a tellurite based optical glass materials where they have found the optical bandgap (E_g) was increased up to 3.0 eV. The glass transition (T_g), bandgap (E_g), crystallization properties got extremely effected by the enhancement of boron compounds in the glass network [2]. Furthermore, Kabalci et al. have found glass tendency (K_{gl}) to be nearly 2.01 where the hardness properties get increased with respect to increase the ration Al_2O_3 [3]. Masai et al. have made experiment on Tin doped borate glass for photoluminescence where they found the quantum efficiency to be 60% [4]. Again, Kabalci et al. have analyzed a tellurite glass materials by using UV-VIS spectrophotometer where the optical direct band gap was derived up to 3 eV, and the indirect band gap also enhanced up to 2.74 eV [2]. Kumar have analyzed barium doped strontium stannate glass for Rietveld refinement of XRD and UV-VIS analysis for optical, dielectric and electrical applications, where they have found the direct bandgap up to 3.97 eV and the indirect band gap to be 3.5 eV for which is suitable for UV detector and electronic device and conduction device application, where the band gap was found the direct bandgap up to 3.97 eV and the indirect band gap to be 3.5 eV [5].

Swapna et al. have developed a vanadium oxide doped tellurite based glass materials for determination of optical, thermal and structural properties, while it observed that Nb_2O_5 components along with the increase ZnO elements dominated the optical properties of that glass network and also effected the spin Hamiltonian parameters as well. The Nb_2O_5 composition also changed the glass structure and enhanced the stability of the glass network [6].

Moreover, Swapna et. al. have proposed another tellurite based quaternary glass for optical communications, where they found that the glass transition (T_g) gets decreased with enhancing the boron oxide components. The optical band gap energy was found to be up to 1.92 eV which was extremely affected by the enhancement of boron oxide contents in the glass network [7]. Following this, again, Swapna et. al. have developed another tellurite based optical glass where they found that the optical properties got extremely effected by the boron oxide and niobium oxide contents [8]. Kostka et al. have investigated an erbium (Er^{3+}) doped borate based glass materials for photoluminescence to study the optical properties of the glass network with a focus about the PL band, and the energy states of the erbium ions, where they have found that when the glass was excited by light at 514.5 nm wavelength, narrow emission of the erbium ion (Er^{3+}) was found as the luminescence of the host glass could not be excited by this wavelength and at 1530 nm wavelength, the PL band represents a specific transition of the erbium ions [9]. Suresh et. al. have developed samarium (Sm^{3+}) and ytterbium (Yb^{3+}) doped tellurite glass and found the quantum efficiency to be 141% and the bandgap was suitable for solar cell applications [10].

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Mohamed have analyzed a lithium based barium titanate doped glass nano composite particle for Rietveld refinement crystal analysis for dielectric and electronic applications [11]. Following this, Swapna et. al. have developed an antimony trioxide doped tellurite glass materials for optical applications where they have found the bandgap energy to be 2.23 eV. The antimony trioxide had tremendously effected the optical parameters and spin Hamiltonian properties [8]. Kilic et. al had developed a tantalum pentoxide reinforced tellurite based glass for radiation shield application where they have found the photon energy to be up to 15 MeV [12]. Following that, Kabalci et al. had developed a boron based glass network for optical investigation where they have found the direct bandgap energy up to 3.6 eV [13]. Marzuki et al have developed a boro tellurite based glass network by varying bismuth oxide (Bi2O3) and lead oxide components for optical properties as well as radiation shielding applications and observed that the optical properties got highly effected by the enhancements of lead oxide component into the glass network [14].

In this study, a unique tellurite-based optical glass TeO_2-$ZnCl_2$-Nb_2O_5-TiO_2 was prepared fabricated using the conventional melt quench technique for photonics, fiber optics and optical communication applications based on preparation temperature. Following the fabrication of the glass, thermal, optical, and microstructural properties including optical bandgap energy was also determined using UV-VIS spectrophotometer within 300nm-900nm wavelength range data for Beer-Lambert Law application. The thermal characteristics of the glass materials was determined by the conventional Differential Thermal Analysis (DTA) measurement and the optical bandgap (E_g) was derived from the UV-VIS spectrophotometry experiment.

2. MATERIALS AND METHODS

The proposed glass network TeO_2-$ZnCl_2$-Nb_2O_5-TiO_2 was fabricated using the melt, and rapid cooling techniques. The required raw materials TeO_2, $ZnCl_2$, Nb_2O_5 and TiO_2 were collected commercially from sigma Aldrich chemical corporation which were 99.999% trace metal basis powders. A total of five glass samples were prepared which were labeled to be TZNT1, TZNT2, TZNT3, TZNT4 and TZNT5, respectively as shown in Table 1. The molecular formula for the glass network was $70TeO_2$-$15ZnCl_2$-$10Nb_2O_5$-$5TiO_2$. During the preparation of the glass samples, the raw materials were used to be totally 10 grams per sample. The preparation temperature of the glass samples TZNT1, TZNT2, TZNT3, TZNT4 and TZNT5 were 900°C, 1000°C, 800°C, 750°C and 950°C, respectively, as shown in Table 1.

Table 1. Glass samples as a function of the glass composites TeO_2-$ZnCl_2$-Nb_2O_5-TiO_2

Sample Code	**Glass Components (mol%)**				**Preparation Temperature(°C)**
	TeO_2	**$ZnCl_2$**	**Nb_2O_5**	**TiO_2**	
TZNT2	70	15	10	5	1000°C
TZNT5	70	15	10	5	950°C
TZNT1	70	15	10	5	900°C
TZNT3	70	15	10	5	800°C
TZNT4	70	15	10	5	750°C

While fabricating the glass samples, each inner component raw materials were mixed precisely and melted on a crucible made of platinum using an electric arc furnace model named Protherm Furnace. For the sample TZNT1, the sample was melted at 900°C where the temperature increasing rate was 10°C/min up to 900°C and waiting an additional one hour inside the furnace. Amorphous structure of the glass samples was identified by X-ray diffraction (XRD) spectroscopy. A Rigaku ULTIMA IV equipment was used (Kα of Cu, 40kV, 30mA, 2θ=10-90º). The morphology of the glass samples for the heat-treated glass samples analyzed by SEM CARL ZEISS ULTRA PLUS GEMINI. Microhardness of the prepared glass samples were determined by using Vicker's hardness techniques considering under the 02 and 01 N loading by QNESS Q250M.

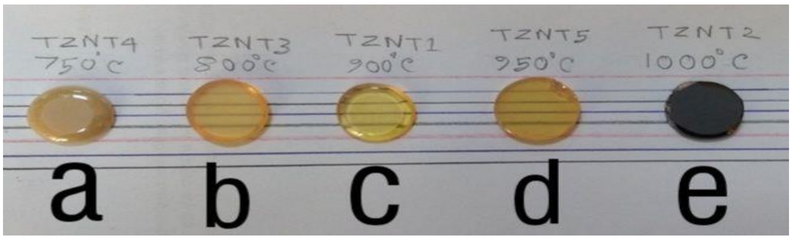

Fig 1. Prepared oxide glass samples at room temperature (a): TZNT4 at 750ºC, (b): TZNT3 at 800ºC, (c): TZNT1 at 900ºC, (d): TZNT5 at 950ºC, (e): TZNT2 at 1000ºC.

3. RESULTS AND DISCUSSIONS

3.1. Structural properties: XRD

XRD which is referred to as X-Ray Diffraction is a popular technology to study the crystalline structure of glass materials by considered powder materials. To determine the crystalline phase and the size or shape of the samples are examined through the XRD analysis at various annealing temperatures according to DTA data.

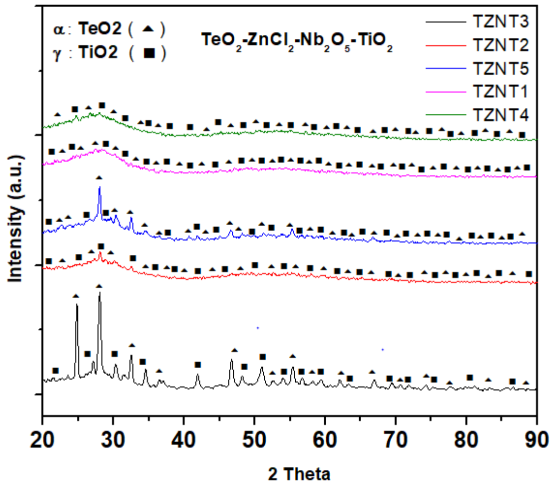

Fig 2. Plot of XRD for the samples TZNT1, TZNT2, TZNT3, TZNT4 and TZNT5

From the results obtained by the DTA study, it was suitable to melt the glass samples TZNT1, TZNT2, TZNT3, TZNT4 and TZNT5 in 500°C, 500°C, 610°C, 650°C and 500°C for the XRD analysis. From the graphical diagram, it was observed that the glasses have two crystalline phases, TeO_2 and TiO_2 as shown in Fig. 2. Here TeO_2 was marked as alpha, on the contrary, TiO_2 was marked to be gamma. According to the results, while enhancing the $ZnCl_2$ content or Nb_2O_5 contents, sharp peaks got visible which refers that the sample TZNT3 becomes more crystallined phases with α-TeO_2 and γ-TiO_2 compared to others.

3.2. Structural properties: SEM

In order to examine the surface morphology of a high temperature prepared glass sample, SEM study is a widely used experiment to determine the topographical structures. For the SEM analysis of the optical glass materials which were prepared to determine the crystalline phases, based on annealing at onset glass temperature values and then crystallization phases were performed in an acid medium with HF solution for 5 s. From the results obtained by the DTA study, the sample were annealed at the 500°C, 500°C, 610°C, 650°C and 500°C temperatures at 30 min for the samples TZNT1, TZNT2, TZNT3, TZNT4 and TZNT5, respectively for the SEM analysis.

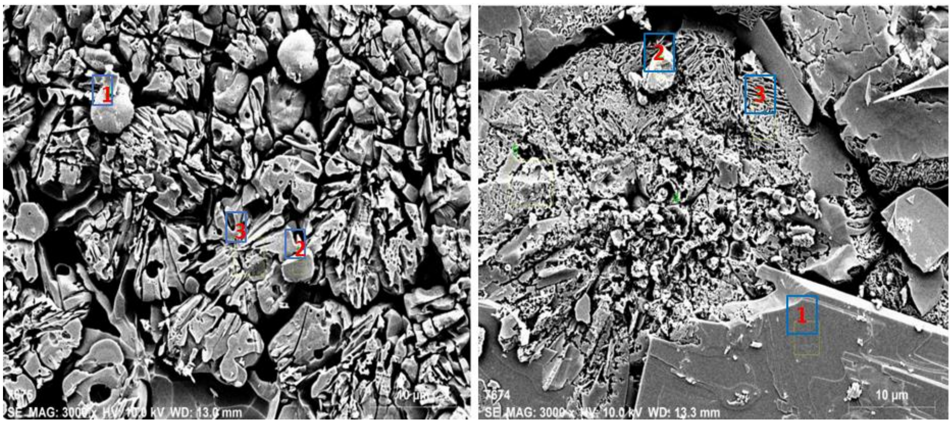

Fig 3. SEM analysis of the TZNT1, TZNT2 sample 3kx magnification

As seen in Figure 3, EDAX spectra of 3 regions selected for the surface topography of TZNT1, TZNT2 samples at 3kx magnification optical glass materials obtained at 500 degrees are also given in Table 2 and 3. Elemental spectrum convolutions of the three selected regions on the surfaces of the optical glass materials indicate that Nb, Te, O and Zn ions interact with each other to form common crystalline phases in the region. It is understood that the Cl element in the relevant regions leaves the material structure at high temperature and leaves its place to the element Ti, albeit in large quantities.

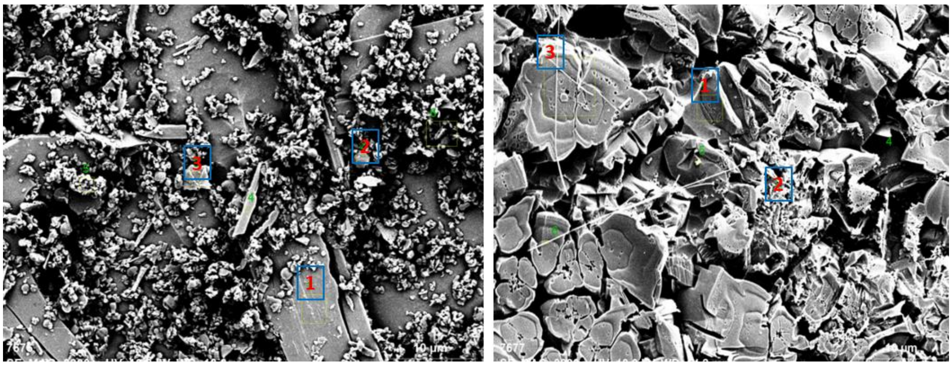

Fig 4. SEM analysis of the TZNT3, TZNT4 sample 3kx magnification

As seen in Figure 4, EDAX spectra of 3 regions selected for the surface topography of TZNT3, TZNT4 samples at 3kx magnification optical glass materials obtained at 610 and 650ºC are also given in Table 4 and 5. Elemental spectrum convolutions of the three selected regions on the surfaces of the optical glass materials indicate that Nb, O, Zn and Ti ions interact with each other to form common crystalline phases in the region. It is understood that the Cl element in the relevant regions again leaves the material structure at high temperature and leaves its place to the element Te, albeit in large quantities. Here, the structural change of the crystallization phases of the material draws attention depending on the annealing temperature in the glass network.

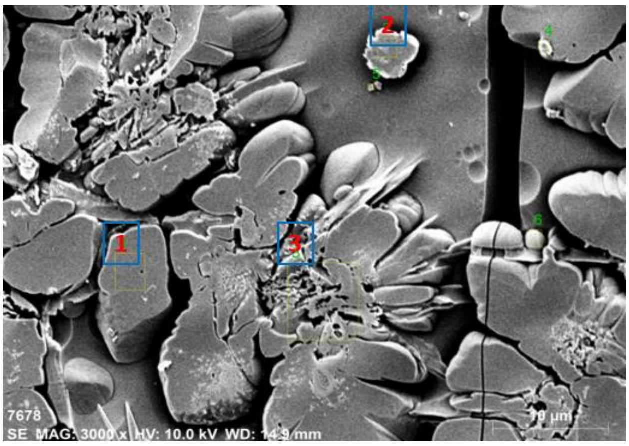

Fig 5. SEM analysis of the TZNT5 sample 3kx magnification

According to the EDAX values given in Table 6 and Fig.5, elemental spectrum distributions of the Nb, O, Te and partially Ti-based structural phase transformations show themselves as a result of elemental effect on the surface crystallization phases depending on annealing temperature values of the optical glass material for the sample TZNT5 sample 3kx magnification. As seen from the SEM-EDAX data for the all the prepared glass samples, it has been determined that the Nb element has a more effective determinant than Te element in the high temperature processes of the surface crystallization phases of the optical glass material.

Table 2. SEM-EDAX data for the samples TZNT1, Mass percent (%)

Spectrum	O	Cl	Ti	Zn	Nb	Te
1	9.86	0.00	1.22	3.23	45.96	39.74
2	6.21	0.00	1.11	2.79	53.85	36.04
3	10.04	0.00	0.79	3.68	43.06	42.44

Table 3. SEM-EDAX data for the samples TZNT2, Mass percent (%)

Spectrum	O	Cl	Ti	Zn	Nb	Te
1	4.59	0.00	0.30	0.30	67.76	27.05
2	0.09	0.00	0.48	0.15	43.00	56.28
3	12.29	0.00	2.67	0.38	44.64	40.01

Table 4. SEM-EDAX data for the samples TZNT3, Mass percent (%)

Spectrum	O	Cl	Ti	Zn	Nb	Te
1	7.63	0.00	0.00	0.68	63.90	27.80
2	20.52	0.00	22.12	4.08	52.73	0.55
3	16.37	0.00	20.01	3.17	55.43	5.03

Table 5. SEM-EDAX data for the samples TZNT4, Mass percent (%)

Spectrum	O	Cl	Ti	Zn	Nb	Te
1	10.40	0.00	1.90	5.17	48.39	34.14
2	12.59	0.00	1.65	3.77	51.16	30.84
3	12.16	0.00	1.95	3.09	48.66	34.14

Table 6. SEM-EDAX data for the samples TZNT5, Mass percent (%)

Spectrum	O	Cl	Ti	Zn	Nb	Te
1	8.54	0.00	2.03	3.06	52.58	33.80
2	9.08	0.00	0.13	8.54	58.42	23.83
3	9.08	0.00	1.88	8.06	51.54	29.45

As seen in Table 2-6, SEM-EDAX data obtained from 3 different regions of the surface after heat treatment of optical glass materials as a result of SEM analysis show the distribution of the compositions of the material at different temperature values. In these tables, the elemental distribution in the surface topography of the TZNT5-TZNT6 optical glass material briefly indicates the Nb–O–Te bond energies, while it is noteworthy that as the temperature increases, there is a transition to the states with Nb–O–Zn bond energies for the TZNT7, TZNT8, and TZNT9.

3.3. Mechanical properties: Vicker's Hardness

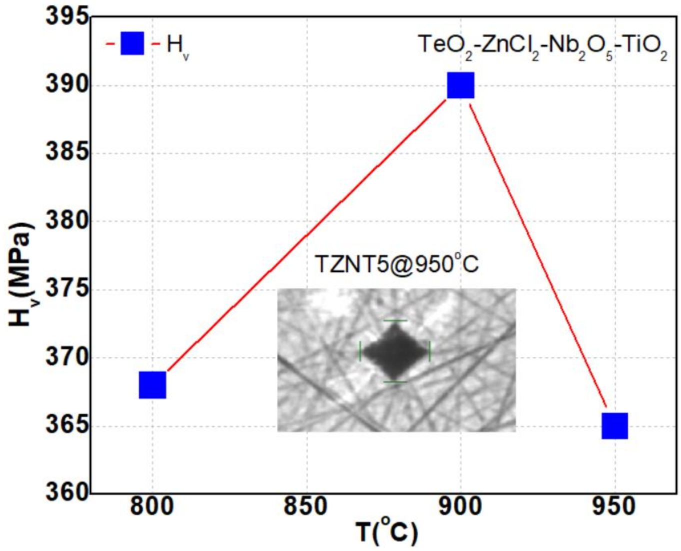

Fig 6. Vicker's hardness of the optical glass samples for TZNT3(800ºC), TZNT1(900ºC), and TZNT5(950ºC).

The surfaces of the optical glasses for which hardness measurement was carried out from surface of the well-polished samples and measurements were made from different surface points under 2 and 1 newton force. As seen in Figure 6, while the Vicker's hardness ratios for TZNT3 and TZNT5 optical glasses were similar, higher values were measured for TZNT3 glass material. For the other two glass samples, hardness measurement could not be performed due to brittleness.

4. CONCLUSION

The optical glass network TeO_2-$ZnCl_2$-Nb_2O_5-TiO_2 was fabricated using the widely used melt quenching experiments by varying the preparation temperatures. The samples labeled as TZNT1, TZNT2, TZNT3, TZNT4 and TZNT5 were prepared at various temperatures such as 900°C, 1000°C, 800°C, 750°C and 950°C on an electrical arc furnace and annealed at 300°C for six hours. The structural and mechanical properties of the glass network were extremely dominated by the enhancements of the $ZnCl_2$ and Nb_2O_5 contents. The XRD analysis revealed that the glass samples have two crystalline phases α-TeO_2 and γ-TiO_2. The Vicker's hardness values vary for applied loading for the optical glass samples.

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REFERENCES

[1] El-Mallawany R (2018) Tellurite glass smart materials: Applications in optics and beyond. Springer, Switzerland. https://doi.org/10.1007/978-3-319-76568-6

[2] Kabalci I, Körpe NÖ, Duran T, Özdemir M (2011) Optical properties and crystallization kinetics of $(TeO_2)(ZnO)(TiO_2)$ glasses. Phys. Status Solidi Curr. Top. Solid State Phys. 8:2629–2632. https://doi.org/10.1002/pssc.201084090

[3] Kabalci I, Koc E, Ozturk SS (2017) Mechanical, Structural and Thermal Properties of Transparent Bi_2O_3–Al_2O_3–ZnO–TeO_2 Glass System. J. Inorg. Organomet. Polym. Mater. 27:788–794. https://doi.org/10.1007/s10904-017-0523-y

[4] Masai H, Suzuki Y, Yangida T, Mibu K (2015) Luminescence of Sn^{2+} center in ZnO-B_2O_3 glasses melted in air and Ar conditions. Bull. Chem. Soc. Jpn. 88:1047–1053. https://doi.org/10.1246/bcsj.20150145

[5] Kumar A, Khan B, Yadav V, Dixit A, Kumar U, Singh MK (2020) Rietveld refinement, optical, dielectric and ac conductivity studies of Ba-doped $SrSnO_3$. J. Mater. Sci. Mater. Electron. 31:16838–16848. https://doi.org/10.1007/s10854-020-04240-7

[6] Swapna, Upender G, Sreenivasulu V, Prasad M (2016) Spectroscopic and optical properties of the VO^{2+} ion doped TeO_2-TiO_2-ZnO-Nb_2O_5 glass system. J. Korean Phys. Soc., 68:998–1007. https://doi.org/10.3938/jkps.68.998

[7] Swapna, Upender G, Prasad M, (2017) Raman, FTIR, thermal and optical properties of TeO_2-Nb_2O_5-B_2O_3-V_2O_5 quaternary glass system. J. Taibah Univ. Sci.. 11:583–592. https://doi.org/10.1016/j.jtusci.2016.02.008

[8] Swapna, Prasad M (2020) Influence of Sb_2O_3 on vibrational and optical properties of TeO_2-Nb_2O_5 glass system. Optik (Stuttg). 208:164108. https://doi.org/10.1016/j.ijleo.2019.164108

[9] Kostka P, Kabalci I, Tay T, Gladkov P, Zavadil J (2017) Investigation of Er doped zinc borate glasses by low-temperature photoluminescence. J. Lumin. 192:1104–1109. https://doi.org/10.1016/j.jlumin.2017.06.010

[10] Suresh K, Jaysankar CK (2018) Spectral investigations of Sm^{3+}/Yb^{3+}: TeO_2 + ZnO + Nb_2O_5 +TiO_2 glasses for the conversion of Si-based solar cell applications. J. Alloys Compd. 750:420–427. https://doi.org/10.1016/j.jallcom.2018.03.292

[11] Mohamed EA, Nabhan E, Ratep A., Hassan FM, Tahoon K (2020) Influence of $BaTiO_3$ nanoparticles/clusters on the structural and dielectric properties of glasses-nanocomposites. Phys. B Condens. Matter. 589:412220. https://doi.org/10.1016/j.physb.2020.412220

[12] Kilic G, Agawany FIE, Ilik BO, Mahmoud KA, Ilik E, Rammah YS (2021) Ta_2O_5 reinforced Bi_2O_3–TeO_2–ZnO glasses: Fabrication, physical, structural characterization, and radiation shielding efficacy. Opt. Mater. (Amst). 112:110757. https://doi.org/10.1016/j.optmat.2020.110757

[13] Kabalci I, Gökçe H, Körpe NO (2021) Potential glass network for IR applications and rare-earth ions. Acta Phys. Pol. A. 143:222–227. https://doi.org/10.12693/APhysPolA.140.222.

[14] Marzuki A, Sasmi T, Fausta DE, Harjana H, Suryanti V, Kabalci I (2023) The effect of Bi_2O_3/PbO substitution on physical, optical, structural, and gamma shielding properties of boro-tellurite glasses. Radiat. Phys. Chem. 205:110722. https://doi.org/10.1016/j.radphyschem.2022.110722

[15] Rivera VAG, Maanzani D (2017) Technological Advances in Tellurite Glasses : Properties, Processing, and Applications, 254. Springer series in Material Science, Switzerland

[16] Mamouei M, Budidha K, Baishya N, Qassem M, Kyriacou PA (2021) An empirical investigation of deviations from the Beer–Lambert law in optical estimation of lactate. Sci. Reports. 11:1–10. https://doi.org/10.1038/s41598-021-92850-4

[17] Davis EA, Mott NF (1970) Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors, The Philosophical Magazine: A Journal of Theoretical and Experimental and Applied Physics 22:179. 0903-0922. https://doi.org/10.1080/14786437008221061

[18] Jha A, Richards B, Jose G, Teddyfernandez T, Joshi P, Jiang X and Lousteau J (2012) Rare-earth ion doped TeO_2 and GeO_2 glasses as laser materials. Prog. Mater. Sci. 57:1426–1491. https://doi.org/10.1016/j.pmatsci.2012.04.003

[19] Kabalci I, Körpe NO, Duran T, and Özdemir M (2011) Optical properties and crystallization kinetics of (TeO2)(ZnO)(TiO2) glasses. Phys. Status Solidi C. 8:2629–2632

[20] Murugan GS and Ohishi Y (2005) Structural and physical properties of a novel TeO2–BaO–SrO–Ta2O5 glass system for photonic device applications. J. Non-Cryst. Solids. 351:364-371