



***STRUCTURAL, ELASTIC AND OPTICAL PROPERTIES OF ZINC  
BOROTELLURITE GLASS SYSTEMS CO-DOPED WITH  $\text{Ho}_2\text{O}_3$  AND  
 $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}$  NPs***

**USMAN ABDULLAHI**

**FS 2019 75**



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By

**USMAN ABDULLAHI**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra  
Malaysia, in Fulfillment of the Requirements for the Degree of  
Doctor of Philosophy**

**April 2019**

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## **DEDICATION**

This work is dedicated to the entire family of Alkali Usman Sita Hassan



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Abstract of a thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

**STRUCTURAL, ELASTIC AND OPTICAL PROPERTIES OF ZINC BOROTELLURITE GLASS SYSTEMS CO-DOPED WITH  $\text{Ho}_2\text{O}_3$  AND  $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}$  NPs**

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**USMAN ABDULLAHI**

**April 2019**

**Chairman : Professor Halimah Mohamed Kamari, PhD**  
**Faculty : Science**

Series of zinc borotellurite glass doped with holmium oxide ( $\text{Ho}_2\text{O}_3$ ), co-doped with holmium and silver oxide ( $\text{Ag}_2\text{O}$ ) and finally co-doped with holmium and silver oxide nanoparticles ( $\text{Ag}_2\text{O}$  NPs) were successfully synthesized using the conventional melt quenching technique. The glass series were prepared using the chemical formulas of  $\{((\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3})_{0.7} (\text{ZnO})_{0.3}\}_{1-x} (\text{Ho}_2\text{O}_3)_x$  (where  $x=0.005, 0.01, 0.02, 0.03, 0.04$  molar fraction) and  $[\{((\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3})_{0.7} (\text{ZnO})_{0.3}\}_{0.7} \{(\text{Ho}_2\text{O}_3)_{0.3}\}]_{1-y} (\text{Ag}_2\text{O}/\text{Ag}_2\text{O NPs})_y$  (where  $y=0.01, 0.02, 0.03, 0.04, 0.05$  molar fraction).

XRD results confirmed the amorphous nature of the glass samples. The infrared spectra of the glass systems indicate the presence of  $\text{TeO}_3$ ,  $\text{TeO}_4$ ,  $\text{BO}_3$  and  $\text{BO}_4$  vibrational units in the various concentration of the series. The presence of silver nanoparticles was confirmed by the TEM images. The structural, elastic and optical properties of the glass systems were studied using various characterization techniques through densimetry, Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction spectroscopy, Ultra-Violet Visible Spectroscopy (UV-Vis) and Ultrasound measurement.

For structural analysis physical parameters such as density, molar volume, oxygen molar volume, crystalline volume, excess volume, oxygen packing density (OPD) and dopant ionic concentration were studied. The density of  $\text{Ho}_2\text{O}_3$  doped series increased from  $4.5388 \text{ g/cm}^3$  at 0.005 molar fraction to  $4.9451 \text{ g/cm}^3$  at 0.04 molar fraction while molar volume decreased from  $26.1172$  to  $25.8159 \text{ cm}^3/\text{mol}$  accordingly. Similar trend of increase in density and decrease in molar volume were exhibited by the other two series. Generally, oxygen molar volume and excess volume show decreasing trend for all the three series as the concentration of the dopants were increased. While

crystalline volume, OPD, and dopant ionic concentration increase with increase in dopants concentration. This behaviour generally increase the compactness and rigidity of the synthesized glass system.

Substantial change was observed in the ultrasonic velocities (longitudinal and transverse velocities), elastic moduli (longitudinal modulus, Young modulus, bulk modulus and shear modulus), Poisson's ratio, microhardness, softening temperature and Debye temperature which ascertained the changes that exist in the structure of the glass as a result of introduction of the dopants to the host structure. In all the glass series the elastic moduli show increasing trends, so also softening and Debye temperatures while microhardness follow decreasing trend as the dopant concentration decreased. Poisson's ratio does not exceed maximum of 0.28 in its increasing trend for all the glass series. These behaviours illustrated by the generated elastic parameters are in favour of increase in the rigidity of the glass structure. The elastic moduli were also investigated theoretically using four models, Makishima- Mackenzie model, Rocherulle model, Bond compression model and Ring deformation model. It was established for this glass system that Ring deformation model gives excellent results that fit with experimental elastic moduli with more than 90% correlation coefficient in most of its values.

Being a non-crystalline material, this glass system undergoes indirect transition with indirect optical band gap decreasing ( $E_{opt}$ ) from 3.1169 eV at 0.01 molar fraction to 2.9702 eV at 0.04 molar fraction for  $\text{Ho}_2\text{O}_3$  doped series. Similarly,  $E_{opt}$  decreased from 3.1899 to 2.3242 eV and from 2.7819 to 2.2093 eV for  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  and  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  NPs co-doped series respectively. The refractive indices show increasing trend as the dopants concentration increase for all the series. It was found that doping with  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  NPs influenced the increase in refractive index most. The Urbach energy ( $\Delta E$ ) increases with increase in dopants concentration for all the three series. But the  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  NPs doped series possessed highest Urbach energy of 0.4935 eV at 0.05 molar fraction. Molar electronic polarizability ( $\alpha_m$ ) of this glass system follow increasing trend as the dopants concentration increase, with highest electronic polarizability of 11.1866 at 0.05 molar fraction realised for  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  NPs doped series. Metallization criterion of this glass series decreases with increase of dopants concentration for all the series. The  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  NPs doped series has lowest metallization criterion that falls between minimum of 0.3164 and maximum of 0.3591. The highest value of metallization criterion is 0.3865 for  $\text{Ho}_2\text{O}_3/\text{Ag}_2\text{O}$  doped series. With this range of values for metallization criterion it is alarming that the synthesized glasses can serve as non-linear optical materials. The gain bandwidth obtained theoretically using McCumber theory confirmed that the synthesized glasses are potential candidate for photonics such as fiber lasers and amplifiers. Therefore, this research contributes towards addressing the pressing challenge of developing new materials for photonics.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**SIFAT STRUKTUR, KENYAL DAN OPTIK SISTEM KACA ZINK  
BOROTELLURIT YANG DI-KO-DOP DENGAN  $\text{Ho}_2\text{O}_3$  DAN  $\text{Ag}_2\text{O}$ /  
NANOZARAH  $\text{Ag}_2\text{O}$**

Oleh

**USMAN ABDULLAHI**

**April 2019**

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**Fakulti : Sains**

Siri kaca zink borotelurit didop dengan holmium oksida ( $\text{Ho}_2\text{O}_3$ ), ko-dop dengan holmium dan argentum oksida ( $\text{Ag}_2\text{O}$ ) dan yang terakhir ko-dop dengan nanozarah holmium dan argentum oksida ( $\text{Ag}_2\text{O}$  NPs) berjaya dihasilkan menggunakan teknik konvensional sepuh lindap. Siri kaca itu dihasilkan menggunakan formula kimia  $\{((\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3})_{0.7} (\text{ZnO})_{0.3}\}_{1-x} (\text{Ho}_2\text{O}_3)_x$  (di mana  $x=0.005, 0.01, 0.02, 0.03, 0.04$  molar fraction) dan  $[\{((\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3})_{0.7} (\text{ZnO})_{0.3}\}_{0.7} \{(\text{Ho}_2\text{O}_3)_{0.3}\}_{1-y} (\text{Ag}_2\text{O}/\text{Ag}_2\text{O NPs})_y$  (di mana  $y=0.01, 0.02, 0.03, 0.04, 0.05$  molar fraction).

Keputusan XRD meyakinkan keadaan amorfus sampel-sampel kaca itu. Spektra inframerah sistem kaca itu menandakan kehadiran getaran unit  $\text{TeO}_3$ ,  $\text{TeO}_4$ ,  $\text{BO}_3$  dan  $\text{BO}_4$  di dalam berbagai kepekatan siri itu. Kehadiran nanozarah argentum dipastikan oleh imej TEM. Ciri-ciri struktur, kenyal dan optik sistem kaca itu dipelajari menggunakan berbagai teknik pencirian melalui densimetri, spektroskopi inframerah jelmaan Fourier (FTIR), spektroskopi pembelauan sinar-X, Spektroskopi UV-nampak (UV-Vis), kefotopendarcahayaan (PL) dan pengukuran ultrasonik.

Bagi analisis struktur, parameter fizikal seperti ketumpatan, isipadu molar, isipadu molar oksigen, isipadu habluran, isipadu lebihan, ketumpatan pepadatan oksigen (OPD) dan kepekatan ion dopan telah dikaji. Ketumpatan siri yang didop dengan  $\text{Ho}_2\text{O}_3$  meningkat daripada  $4.5388 \text{ g/cm}^3$  pada 0.005 molar fraction kepada  $4.9451 \text{ g/cm}^3$  pada 0.04 molar fraction manakala isipadu molar menurun daripada  $26.1172$  kepada  $25.8159 \text{ cm}^3/\text{mol}$ . corak yang sama dalam peningkatan ketumpatan dan penurunan isipadu molar juga ditunjukkan di dalam kedua-dua siri yang lain. Secara umumnya, isipadu molar oksigen dan isipadu lebihan menunjukkan corak yang menurun untuk ketiga-tiga siri apabila kepekatan dopan dinaikkan. Manakala isipadu



habluran, OPD dan kepekatan ion dopan meningkat dengan kenaikan kepekatan dopan. Kelakuan ini secara umumnya meningkatkan kepadatan dan ketegaran sistem kaca yang dihasilkan.

Perubahan yang besar dapat dilihat pada halaju ultrasonik (halaju membujur dan melintang), modulus-modulus kenyal (modulus membujur, modulus Young, modulus pukal dan modulus melintang), nisbah Poisson, kekerasan mikro, suhu pelembutan dan suhu Debye yang memastikan perubahan yang wujud di dalam struktur kaca itu adalah hasil daripada pengenalan dopan ke dalam struktur perumah tersebut. Di dalam semua siri kaca itu, modulus-modulus kenyal menunjukkan trend menaik, begitu juga dengan suhu pelembutan dan Debye manakala kekerasan mikro mengikut trend yang menurun apabila kepekatan dopan dinaikkan. Nisbah Poisson tidak melebihi nilai maksimum 0.28 di dalam trendnya yang menaik untuk kesemua siri kaca itu. Kelakuan ini ditunjukkan oleh parameter kenyal yang terhasil yang menunjukkan kepada kenaikan ketegaran struktur kaca itu. Modulus-modulus kenyal juga dipelajari secara teori menggunakan empat model, model Makishima-Mackenzie, model Rocherulle, model mampatan ikatan dan model canggaaan gegelang. Ianya telah disimpulkan bagi sistem kaca ini bahawa model mampatan ikatan memberikan keputusan yang paling baik yang bertepatan dengan modulus-modulus kenyal eksperimen dengan lebih daripada 90% pekali korelasi di dalam kebanyakan nilai-nilainya.

Sebagai bahan tidak hablur, sistem kaca ini mengalami peralihan tidak langsung dengan jurang jalur optik tidak langsung ( $E_{opt}$ ) menurun daripada 3.1169 eV pada 0.01 molar fraction kepada 2.9702 eV pada 0.04 molar fraction bagi siri didop dengan  $Ho_2O_3$ . Begitu juga  $E_{opt}$  menurun daripada 3.1899 kepada 2.3242 eV dan daripada 2.7819 kepada 2.2093 eV masing-masing bagi siri  $Ho_2O_3/Ag_2O$  and ko-didop  $Ho_2O_3/Ag_2O$  NPs. Indeks biasan menunjukkan trend yang menaik apabila kepekatan dopan ditingkatkan bagi semua siri. Pendopan dengan  $Ho_2O_3/Ag_2O$  NPs ditemui paling mempengaruhi kenaikan indeks biasan. Tenaga Urbach ( $\Delta E$ ) meningkat dengan kenaikan kepekatan dopan untuk ketiga-tiga siri tersebut. Tetapi siri yang didop dengan  $Ho_2O_3/Ag_2O$  NPs memiliki tenaga Urbach yang paling tinggi dengan 0.4935 eV pada 0.05 molar fraction. Kekutuban elektronik molar ( $\alpha_m$ ) sistem kaca ini mengikut trend yang menaik apabila kepekatan dopan ditingkatkan, dengan kekutuban elektronik yang paling tinggi adalah 11.1866 pada 0.05 molar fraction disedari pada siri yang didop dengan  $Ho_2O_3/Ag_2O$  NPs. Kriteria metalisasi siri kaca ini menurun dengan kenaikan kepekatan dopan untuk kesemua siri. Siri didop dengan  $Ho_2O_3/Ag_2O$  mempunyai kriteria penglogaman paling rendah yang jatuh di antara nilai minimum 0.3164 dan maksimum 0.3591. Nilai kriteria metalisasi yang paling tinggi adalah 0.3865 bagi siri yang didop  $Ho_2O_3/Ag_2O$ . Dengan julat nilai bagi kriteria penglogaman ini, ia menunjukkan bahawa kaca yang dihasilkan ini boleh digunakan sebagai bahan optik tidak linear. Lebar jalur gandaan yang diperolehi secara teori menggunakan teori McCumber meyakinkan bahawa kaca-kaca yang dihasilkan adalah calon yang berpotensi untuk fotonik seperti laser gentian dan penguat. Maka, penyelidikan ini menyumbang terhadap menangani cabaran kritikal dalam menghasilkan bahan baru untuk fotonik



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I lastly thanks the technical staff of the Faculty of Science as well as the staff of institute of Bioscience for their contributions towards the success of this work. Thank you all.

I certify that a Thesis Examination Committee has met on 17 April 2019 to conduct the final examination of Usman Abdullahi on his thesis entitled "Structural, Elastic and Optical Properties of Zinc Borotellurite Glass System Co-Doped with  $\text{Ho}_2\text{O}_3$  and  $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}$  NPs" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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## LIST OF ABBREVIATIONS

$\text{TeO}_2$	Tellurium oxide
$\text{B}_2\text{O}_3$	Boron oxide
$\text{ZnO}$	Zinc oxide
$\text{Ho}_2\text{O}_3$	Holmium (III) oxide
$\text{Ag}_2\text{O}$	Silver oxide
$\text{Ag}_2\text{O}$ NPs	Silver oxide nano particles
BOs	Bridging oxygens
NBOs	Non-bridging oxygens
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission electron microscopy
tbp	Trigonal bipyramids
tp	Trigonal pyramids
OPD	Oxygen packing density
$V_e$	Excess volume
$V_o$	Oxygen molar volume
$V_c$	Crystalline volume
$\rho$	Density
$R_p$	Polaron radius
$R_i$	Inter-ionic distance
$N$	Ionic concentration
$F$	Field strength

$d_{B-B}$	Boron-Boron separation
$V_m$	Molar volume
$v_L$	Longitudinal velocity
$v_s$	Shear velocity
$L$	Longitudinal modulus
$E$	Young modulus
$K$	Bulk modulus
$G$	Shear modulus
$\sigma$	Poisson's ratio
$v_m$	Mean ultrasonic velocity
$\theta_D$	Debye temperature
$T_s$	Softening temperature
$H$	Microhardness
$f_g$	Fugacity
$d$	Fractal bond connectivity
$Z$	Acoustic impedance
$K$	Extinction coefficient
$V_t$	Packing density
$G_t$	Dissociation energy
$n_b$	Number of bonds per unit volume
$\bar{n}_c$	Average cross-link density
$l$	Atomic ring size
$X_c$	Peak position
$\alpha$	Absorption coefficient

$E_{opt}$	Optical band gap energy
$\Delta E$	Urbach energy
$n$	Refractive index
$R_m$	Molar refraction
$\alpha_m$	Molar electronic polarizability
$\alpha_e$	Electronic Polarizability
$M$	Metallization criterion
$R_L$	Reflection loss
$T$	Transmission coefficient
$\epsilon$	Dielectric constant
$\alpha_{O^{2-}}$	Oxide ion polarizability
$\chi_{av}$	Average electronegativity
$\Delta\chi^*$	Optical electronegativity
$\Lambda$	Optical basicity
$\sigma_e$	Stimulated emission cross-sections
$\sigma_a$	Absorption cross-sections
$E_{ex}$	Excitation energy
FOM	Figure of merit



# CHAPTER 1

## INTRODUCTION

### 1.1 Background of the research

Tellurium oxide ( $\text{TeO}_2$ ) based glasses are currently of scientific and technological interest due to their unique properties such as low melting points, good thermal and chemical stability, slow crystallisation rates, low cut off phonon energy, high refractive indices, high dielectric constant and good infrared transmission (Azlan *et al.*, 2017).  $\text{TeO}_2$  based glasses are considered as promising materials for use in optical amplifiers on account of their large third order non-linear susceptibility (Gayathri Pavani *et al.*, 2011). As it is known that pure  $\text{TeO}_2$  cannot form glass under normal situation except under particular extreme conditions (Kundu *et al.*, 2014); additions of various oxides increase its glass forming range (Manikandan *et al.*, 2012). When tellurite combine with borates, boro-tellurite glasses are formed which are now intensively studied for their practical applications, and enhancement of the quality, transparency and refractive index of the resulted glass system (Gayathri Pavani *et al.*, 2011). Boron oxide  $\text{B}_2\text{O}_3$  is a basic glass former due to its higher bond length, lower cation size, smaller heat of fusion and tri-valence nature of boron. Basically, in  $\text{B}_2\text{O}_3$  glasses, the units are triangles, which are corner bonded in a random configuration (Kundu *et al.*, 2009). In borate glasses the main structural units are  $\text{BO}_3$  triangles forming six member (boroxol) rings connected by B-O-B linkage (Yawale *et al.*, 2000). Usually addition of metal oxides modifies the boroxol ring into complex borate groups which result in the formation of various cyclic units like diborate or tetraborate groups (Mozzi and Warren, 1970). Thus, the addition of transition metal oxide into borotellurite glasses causes changes in their structures and influences the semiconducting behaviour of the glass system when the metal oxide is acting as a modifier (Bale *et al.*, 2008a; Bale *et al.*, 2008b). Hence addition of zinc oxide ( $\text{ZnO}$ ) into boro tellurite glass network produces stability, low rates of crystallisation and enhances glass forming ability (Gayathri Pavani *et al.*, 2011).  $\text{ZnO}$  is a wide band gap semiconductor that is considered as an important multifunctional material due to its specific chemical surface and micro structural properties. It is used in various applications such as gas sensors, transparent electrodes and catalysts (Roy and Basu, 2002).  $\text{ZnO}$  can enter into the glass network either in the form of glass former, modifier or both. Nowadays doping inorganic glasses with rare-earth (RE) ions is receiving much attention from researchers. This is because rare-earth ions are extensively used to improve the physical and optical properties of host glasses due to their unique spectroscopic properties resulting from their optical transitions in the intra 4f shell (Nandi *et al.*, 2009). Moreover, it is highly pre-requisite to know the relationship between the host composition and radiative or non-radiative characters of the RE ions in order to design lasing glasses with high performance (Shen *et al.*, 2007). Among the rare-earth (RE) ions holmium ion ( $\text{Ho}^{3+}$ ) is one of the ions currently receiving attention for its spectroscopic applications. It exhibits several electronic transitions in the visible and IR regions, which have relatively long-lived  $^5\text{I}_7$  level and large peak stimulated emission cross-sections (Rao *et al.*, 2012a). In addition to that, the  $\text{Ho}^{3+}$  ion provides eye-safe potential laser emission even at room temperature with



a low threshold action that has attractive applications in atmospheric communication systems. Therefore, it is expected that glasses doped with  $\text{Ho}^{3+}$  ions are potential candidates for providing emissions which are useful for the development of visible and IR solid state lasers, respectively. Holmium doped fiber amplifier (HDFA) has many advantages as compare to other amplifiers such as EDFA and TDFA. HDFA has high efficiency as compare to EDFA. It has high gain and high power amplifier. HDFA has wide area of sensing technique where other amplifiers failed.

Pure borate glasses possess low refractive index, high melting point and high phonon energies  $\sim 1300\text{-}1500\text{cm}^{-1}$ , hence they are highly suitable for designing new optical devices when they combine with rare-earth elements due to their good RE ion solubility. On the other hand, tellurite glasses compared to other oxides glasses are useful for achieving high rate of radiative transition of RE ions due to their unique properties of high non-linear refractive index, low melting point and low phonon energy of  $\sim 700\text{-}800\text{cm}^{-1}$ . Therefore, boro-tellurite glass combines these advantageous features of borate and tellurite glasses in their interactions with RE ions, thereby producing glass system with low phonon energy, relatively high thermal stability, high chemical durability and easy fabrication (Mahraz *et al.*, 2014). For the present work undoped zinc boro-tellurite is not considered as it is found irrelevant in terms of applications. This is because the lasing and amplifier application of the synthesized glasses is due to the presence of rare earth oxide ( $\text{Ho}_2\text{O}_3$ ).

## 1.2 Problem statements

There are numerous researches on glass of various compositions in order to come out with most suitable glasses that fit into different applications. Tellurite glasses exhibit a range of unique properties which give them potential applications in pressure sensors or as new laser hosts, and these glasses are now under consideration in many other applications. Although the physical properties and structure of crystalline solids are now understood, this is not the case for amorphous materials including glass. The considerable theoretical difficulties in understanding the properties and structures of amorphous solids are amplified by the lack of precise experimental information. Research should therefore be accelerated to fill this gap. The benefits will include providing the fundamental bases of new optical glasses with many new applications, especially tellurite-glass-based optical fibers. New materials for optical switches; second-harmonic-generation, third-order-nonlinear optical materials; up-conversion glasses, and optical amplifiers need greater research attention.

In an attempt to fill some of the aforementioned research gap, researchers employed incorporation of rare earth (RE) oxides into tellurite based glasses. Rare earth doped zinc borotellurite glasses are typical examples. Doping with RE oxides enhances the optical properties of the host glass due to the existence of 4f electrons in these elements. As rare earth embedded into a solid matrix, the effect of ligand environment on the 4f shell is minimised (Reddy *et al.*, 2015). This is due to the effect of 4s and 5p which shielded the 4f shell. Hence it becomes easier for the 4f electrons to be ejected and produced the optical transitions that do not exist in the other compounds.

Several researches were conducted recently in order to explore the benefits of doping with rare earth oxides. On zinc borotellurite Ami Hazlin *et al.* (2017), Azlan *et al.* (2017), Eevon *et al.* (2016b), Faznny *et al.* (2016), Halimah *et al.* (2017) and Hazlin *et al.* (2018) all investigated the effect of different rare earth oxides on the optical properties of zinc borotellurite glass. But yet there is no research that investigated the effect of holmium trivalent ions ( $\text{Ho}^{3+}$  ions) on zinc borotellurite glass. As such this work is conducted in order to provide adequate experimental and theoretical data on structural, elastic and optical properties of zinc borotellurite glass doped with  $\text{Ho}_2\text{O}_3$  and co-doped with  $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}$  NPs.

### 1.3 Objectives of the study

The present study was conducted in order to achieve the following objectives:

1. To study the structural and elastic properties of zinc borotellurite glass doped with  $\text{Ho}_2\text{O}_3$  and co-doped with  $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}$  NPs, under the following chemical formula  $\{((\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3})_{0.7} (\text{ZnO})_{0.3}\}_{1-x} (\text{Ho}_2\text{O}_3)_x$  (where  $x=0.005, 0.01, 0.02, 0.03, 0.04$  molar fraction) and  $[\{((\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3})_{0.7} (\text{ZnO})_{0.3}\}_{0.7} \{(\text{Ho}_2\text{O}_3)_{0.3}\}]_{1-y} (\text{Ag}_2\text{O}/ \text{Ag}_2\text{O NPs})_y$  (where  $y=0.01, 0.02, 0.03, 0.04, 0.05$  molar fraction).
2. To verify the domain of validity of four theoretical elastic models on multi component zinc borotellurite glasses.
3. To investigate the effect of holmium co-doped with  $\text{Ag}_2\text{O}/\text{Ag}_2\text{O}$  NPs on the linear optical properties of zinc borotellurite glasses.
4. To determine the potential application of the synthesized glasses in Holmium Doped Fiber Amplifiers (HDFA) using McCumber theory

### 1.4 Hypotheses

Based on the objectives of the study the following hypotheses are projected:

1. It is expected that the addition of  $\text{Ho}_2\text{O}_3$ ,  $\text{Ag}_2\text{O}$  and  $\text{Ag}_2\text{O}$  NPs into the zinc borotellurite glass will influence changes in the structural properties of the host, thereby modifying other properties such as elastic and optical properties. For the enhancement of elastic properties (that is the increase in strength and rigidity of the glass), it is expected that elastic moduli, microhardness, Debye temperature and softening temperature will increase while Poisson's ratio will decrease. This is because rare earth ions promote the formation of bridging oxygens (BOs) that will increase the rigidity of the glass samples. The optical properties are expected to improve through decrease of the optical band gap and corresponding increase in refractive index, molar and electronic polarizabilities. This enhancement of optical properties is attributed to the unique 4f electrons of the rare earth ions.

2. If theoretical elastic models are valid with multi component glasses, it is expected that the experimental and the theoretical data of elastic moduli to be in a close range.
3. With introduction of the dopants it is expected that the stimulated emission cross-section obtained from the McCumber theory and the Gain band width (GBW) will be enhanced.

### **1.5 Scope and limitations of the study**

The scope of the present study is limited to the physical and structural properties, elastic properties and linear optical properties. For the measurement of physical properties density was measured using densimeter MD-300S and molar volume was calculated from the measured density. For the structural properties the glass samples were characterized using x-ray diffraction (XRD) spectroscopy, Fourier Transforms Infrared Spectroscopy (FTIR) and Transmission Electron Microscopy (TEM). For the elastic properties ultrasonic pulse-echo technique was employed, from which ultrasonic velocities were measured at frequency of 5 MHz. All other elastic parameters were calculated from the ultrasonic velocities. For the optical properties the glass samples were characterized using Ultraviolet-Visible Spectroscopy (UV-Vis) at wavelength range of 200 to 1700 nm and Photoluminescence (PL) at wavelength range of 200 to 900 nm.

### **1.6 Significance of the study**

Great expectations have been placed on the development of new glasses as indispensable materials in developing the vital industries of the near future. This can clearly be seen in such fields as optoelectronics, multimedia, and energy development. "New glasses" are those that have novel functions and properties, such as a higher light regulation, extraordinary strength, or excellent heat and chemical durability. Therefore, developing new glasses is a non-stop challenge that grows with time. Thus, the significance of the present study is to provide solution to some of the aforementioned challenges through synthesizing holmium doped zinc borotellurite glasses with enhanced mechanical and optical properties.

### **1.7 Thesis outlines**

Chapter 1 consists of the background of the study, and brief introduction of the contained oxides and their significant roles in the glass compositions. The chapter also discussed the problem statements, objective of the study, hypotheses, scope and limitations of the study and significance of the study.

Chapter 2 gives a brief review of the previous literature that are related to the present study. These literatures give reports on zinc borotellurite glasses, Rare-earth doped

zinc borotellurite glasses, Holmium doped glasses, structural and physical properties, elastic properties, optical properties and McCumber theory.

Chapter 3 discussed the existing theories, equations and models used in this study. The derivations of some theoretical equations are also shown in this chapter.

Chapter 4 describes the procedures and techniques employed by the conventional melt quenching method for the fabrication of the glass samples. The chapter also discussed the basic of the characterization techniques used in the research.

Chapter 5 discussed and analysed the results and trends of the findings in the present work. This covers the physical, structural, elastic and non-linear optical properties of the synthesized glasses.

Chapter 6 summarized the important findings of the research, with some suggestions and recommendations for future researches.

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