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# Influence of $Ho^{3+}$ ions on structural and optical properties of zinc borotellurite glass system

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ABSTRACT

A glass series of Holmium doped Zinc borotellurite glass with chemical formula $\{((TeO_2)_{0.7}\ (B_2O_3)_{0.3})_{0.7}\ (ZnO)_{0.3}\}_{1-x}\ (Ho_2O_3)_x$ where x = 0.005, 0.01, 0.02, 0.03 and 0.04 M fraction was prepared by using conventional melt-quenching method. X-ray diffraction analysis (XRD) and Fourier Transform infrared analysis (FTIR) were used to determine the structural properties of the fabricated glass. XRD results confirmed that the prepared glass is amorphous. Density and molar volume of the glass were measured and calculated. The values of the density increase with increase of dopant concentration while molar volume decreases accordingly. Ultraviolet visible spectroscopy analysis (UV–Vis) was used to determine the optical properties of the prepared glass. The refractive index, molar refraction, molar electronic polarizability, metallization criterion, indirect optical energy band gap and Urbach energy were also calculated and analysed. The refractive index was found to increase with increase of holmium ion $Ho^{3+}$ concentration, optical energy band gap decreases while electronic polarizability increases in conformity with increase of refractive index as the concentration of the dopant increases.

## 1. Inroduction

Tellurium oxide ($TeO_2$) 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 and high refractive indices [1]. $TeO_2$ based glasses are considered as promising materials for use in optical amplifiers on account of their large third order non-linear susceptibility [2]. As it is known that pure $TeO_2$ cannot form glass under normal situation except under particular extreme conditions [3]; additions of various oxides increase its glass forming range [4]. 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 [2]. Boron oxide $B_2O_3$ is a basic glass former due to its higher bond length, lower cation size, smaller heat of fusion and trivalence nature of boron. Basically in $B_2O_3$ glasses, the units are triangles, which are corner bonded in a random configuration [5]. In borate glasses the main structural units are $BO_3$ triangles forming six member (boroxol) rings connected by B-O-B linkage [6]. 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 [7]. Thus 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 [8,9]. Hence addition of Zinc oxide (ZnO) into boro tellurite glass network produces stability, low rates of crystallisation and enhances glass forming ability [2]. 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 [10]. 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 [11]. 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 [12]. Pure borate glasses possess low refractive index, high melting point and high phonon energies $\sim$1300–1500 $cm^{-1}$, hence they are highly suitable for designing new optical devices when they combine with rare-earth elements due to their good RE ion

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**Table 1**
Structural and Optical parameters of $\{((TeO_2)_{0.7}\ (B_2O_3)_{0.3})_{0.7}\ (ZnO)_{0.3}\}_{1-x}\ (Ho_2O_3)_x$. Glass system for different values of x.

| Parameters | x = 0.005 | x = 0.01 | x = 0.02 | x = 0.03 | x = 0.04 |
|---|---|---|---|---|---|
| ρ (gm/cm$^3$) ± 0.0728 | 4.5388 | 4.6136 | 4.6831 | 4.8192 | 4.9451 |
| $V_m$ (cm$^3$/mol) ± 0.0791 | 26.1172 | 25.9762 | 26.1472 | 25.7496 | 25.8159 |
| $V_o$ (cm$^3$/mol) ± 0.0715 | 13.6350 | 13.5229 | 13.5351 | 13.5375 | 13.2145 |
| $V_c$ (cm$^3$/mol) ± 0.1334 | 24.1916 | 24.2958 | 24.5042 | 24.7126 | 24.9210 |
| $V_{excess}$ (cm$^3$/mol) ± 0.1826 | 1.9256 | 1.6804 | 1.6430 | 1.2369 | 0.8949 |
| OPD (gm-atm/l) ± 0.3982 | 73.3407 | 73.9485 | 73.8818 | 73.8645 | 75.6742 |
| $E_{opt}$ (eV) ± 0.0855 | 2.4636 | 2.9336 | 2.9193 | 2.7263 | 2.7132 |
| ΔE (eV) ± 0.0248 | 0.4427 | 0.3163 | 0.3701 | 0.3896 | 0.4512 |
| Ref. index n ± 0.0261 | 2.5589 | 2.4152 | 2.4192 | 2.4750 | 2.4789 |
| Molar ref. $R_m$ ± 0.1586 | 16.9508 | 16.0276 | 16.1576 | 16.3688 | 16.3073 |
| Polarizability $\alpha_m$ ± 0.0629 | 6.7265 | 6.3602 | 6.4118 | 6.4956 | 6.4712 |
| Met. Criterion M ± 0.0058 | 0.3510 | 0.3830 | 0.3821 | 0.3692 | 0.3683 |

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 ~700–800 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 [13].

The objective of the present work is to study the effect of Holmium ion $Ho^{3+}$ on the structural and linear optical properties of Zinc boro-tellurite glass system. To the best of our knowledge this paper is one of the pioneer report of the effect of $Ho^{3+}$ ions on the properties of Zinc boro-tellurite glass. The network structure of the glass system formed was studied using Fourier transform infrared spectroscopy (FTIR) analysis. The influence of Holmium ions on the density, molar volume, Urbach energy and indirect optical energy band gaps were analysed.

## 2. Experimental methods

Holmium doped Zinc borotellurite glass system with chemical composition.

$\{((TeO_2)_{0.7}\ (B_2O_3)_{0.3})_{0.7}\ (ZnO)_{0.3}\}_{1-x}\ (Ho_2O_3)_x$ where x = 0.005, 0.01, 0.02, 0.03 and 0.04 M fraction was synthesized by using conventional melt-quenching method. The chemical powder of Tellurium (IV) oxide, $TeO_2$ (99.99%, Alfa Aesar), Boron oxide, $B_2O_3$ (98.50%, Alfa Aesar), Zinc oxide, ZnO (99.99%, Alfa Aesar) and Holmium (III) oxide, $Ho_2O_3$ (99.50%, Alfa Aesar) were weighted in accordance with calculated compositions using digital weighing machine with an accuracy of ± 0.001 g.

The weighted chemicals powder were put in an alumina crucible and stirred with glass rod for 45 min in order to obtain homogeneous mixture. The alumina crucible and its content was then transferred to an electric furnace for the pre-heating process at 400 °C for a period of 1 h to ensure water content or moisture is removed from the mixture.

The alumina crucible was then transferred to another electric furnace at 950 °C for 2 h melting process. At the same time, polished stainless steel mould was put at the first electric furnace for the free heating process at 400 °C.

After the 2 h melting process, the molten chemical powder was cast into the pre-heated mould and taken back as soon as possible to the first furnace for 1 h annealing process at 400 °C. The electric furnace was then switched off and the prepared sample was allowed to cool to room temperature. The sample was then polished using silicon carbide paper to 2 mm thickness in order to obtain flat, parallel and shiny surfaces for optical measurements.

For optical measurement the sample was taken to Ultra-violet visible (UV–Vis) spectroscopy for characterization using UV-1650PC UV–Vis spectrometer (Shimadzu) with the wavelength range from 220 to 1700 nm to obtain the optical absorption.

Some portion of the sample was crushed using a plunger and grinded using pestle and mortar. The acquired fine powder was sent to X-ray diffraction (XRD) and Fourier Transform Infra-Red (FTIR) spectroscopies for structural analysis.

The density of the samples was measured at room temperature using Archimedes' principle with distilled water as the immersion liquid. The weights of the samples in the air and the distilled water were measured by a digital densimeter with weighing accuracy of ± 0.001 g. The volume and specific gravity of the samples were also measured by the densimeter.

## 3. Results

### 3.1. Density and molar volume

Density is an effective tool used to explore the degree of structural compactness of the geometrical configurations of the glass network [14]. For this work the densities of our glass samples were measured by electronic densimeter MD-300S using Archimedes principle with distilled water as immersed liquid. Mathematically the density of a given sample can be calculated using the following relation:

$$\rho_s = \frac{M_a}{V} \tag{1}$$

where $\rho_s$ is the density of the sample in g/cm$^3$, $M_a$is the mass of the sample in air and $V$ is the volume of the sample measured in g and cm$^3$ respectively.

The molar volume $V_m$ of the samples was calculated using the following equation:

$$V_m = \sum \frac{X_i M_i}{\rho} \tag{2}$$

where $X_i$ is the molar fraction, $M_i$ is the molecular weight of the ith component and ρ is the density of the sample. The values of $V_m$ and ρ are presented in Table 1 while their inverse behaviors are illustrated in Fig. 1.

Oxygen molar volume and crystalline volume were also calculated and presented in Table 1.

Oxygen molar volume ($V_o$), Crystalline volume ($V_c$) and Excess volume ($V_{excess}$) were calculated using the following Equations [3]:

$$V_o = \frac{V_m}{\sum X_i n_i} \tag{3}$$

where $n_i$ is the number of oxygen of ith component

$$V_c = \sum X_i V_i \tag{4}$$

$V_i$ is the molar volume of ith component in crystalline phase (i.e. $V_i$ = 28.1479, 28.3001, 14.5061 and 44.9297 cm$^3$/mol for α-$TeO_2$, $B_2O_3$, ZnO and $Ho_2O_3$ respectively using their corresponding crystalline densities of 5.67, 2.46, 5.61 and 8.41 g/cm$^3$).