OPTICAL PROPERTIES OF NEODYMIUM AND ERBIUM DOPED TELLURITE GLASS COATED WITH GRAPHENE OXIDE

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UNIVERSITI PENDIDIKAN SULTAN IDRIS

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ABSTRACT

This study aimed to enhance the optical properties on neodymium oxide (Nd_2O_3) and erbium oxide (Er_2O_3) doped tellurite-based glass coated with graphene oxide (GO). The two series of tellurite glasses with chemical composition of $\{[(TeO_2)_{0.7} (B_2O_3)_{0.3}]_{0.7} (ZnO)_{0.3}\}_{1-y} (Nd_2O_3)_y$ and $\{[(TeO_2)_{0.7} (B_2O_3)_{0.3}]_{0.7} (ZnO)_{0.3}\}_{1-y} (Er_2O_3)_y$ with varying concentrations of Nd^{3+} and Er^{3+} ions from y=0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 mol% were prepared and coated with GO using melt-quenching and spray coating methods. The physical, structural and optical properties of prepared glasses were characterized using densimeter, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Ellipsometer, and ultraviolet- visible (UV-Vis) spectrophotometer. The structural analysis determined by XRD pattern proved an amorphous structure for the glass samples. The obtained results through FT-IR analysis showed the formation of non-bridging oxygens (NBOs) in the glass network system. The SEM images revealed the surface morphology of GO on the glass surface. The values of the refractive index were escalated with the increasing concentration of neodymium from 2.301 to 2.332, and erbium from 2.275 to 2.299 with the existence of GO. This was due to the presence of a high degree number of oxygen atoms consisted in GO structure. The values of optical bandgap energy were enhanced with the increasing concentrations of neodymium from 3.315 to 3.381 eV while for erbium from 3.392 to 3.495 eV. The increment of optical bandgap energy was due to the high in GO optical absorptions. The electronic polarizability values of glass samples were enhanced for neodymium from 8.815 to 8.887 $Å^3$ while for erbium from 8.815 to 8.894 $Å^3$ due to high surface area and low particle density in GO. In conclusion, the synthesized GO is a good candidate for use as a coating material on tellurite-based glass surfaces. This study may contribute to the potential uses for high optical performance of fiber optics applications.

SIFAT OPTIK BAGI NEODIMIUM DAN ERBIUM TERDOP KACA TELLURIT DISALUT DENGAN GRAFIN OKSIDA

ABSTRAK

Kajian ini bertujuan untuk meningkatkan sifat optic pada neodimium oksida (Nd_2O_3) dan erbium oksida (Er_2O_3) terdop kaca berasaskan tellurit disalut dengan grafin oksida (GO). Dua siri kaca tellurit dengan komposisi kimia $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Nd_2O_3)_y$ dan $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Er_2O_3)_y$ dengan kepekatan yang berbeza oleh neodimium dan erbium ion daripada y=0.005, 0.01, 0.02, 0.03, 0.04, dan 0.05 mol% telah disediakan dan disalut dengan GO menggunakan kaedah lebur lindap dan salutan semburan. Sifat fizikal, struktur, dan optik bagi kaca yang disediakan telah dicirikan menggunakan densimeter, mikroskop pengimbasan elektron (SEM), pembelauan sinar-X (XRD), inframerah transformasi Fourier (FT-IR), elipsometer, dan cahaya nampak ultralembayung (UV-Vis). Analisis struktur telah ditentukan oleh XRD telah membuktikan struktur amorfus bagi sampel kaca. Hasil yang diperolehi melalui analisis FT-IR menunjukkan pembentukan oksigen bukan penyambungan (NBO) dalam sistem rangkaian kaca. Imej SEM mendedahkan morfologi permukaan GO pada permukaan kaca. Nilai indeks biasan didapati bertambah dengan peningkatan kepekatan neodimium dari 2.301 hingga 2.332 dan erbium dari 2.275 hingga 2.299 dengan kewujudan GO. Ini disebabkan oleh kehadiran bilangan atom oksigen yang tinggi terdiri daripada struktur GO. Nilai tenaga jurang jalur optik didapati meningkat selari dengan peningkatan kepekatan neodimium dari 3.315 hingga 3.381 eV manakala bagi erbium dari 3.392 hingga 3.495 eV. Peningkatan tenaga jurang jalur optik adalah disebabkan oleh penyerapan optik yang tinggi dalam GO. Kebolehkutuban elektronik oleh sampel kaca telah meningkat untuk neodimium dari 8.815 hingga 8.887 $Å^3$ manakala untuk erbium dari 8.815 hingga 8.894 $Å^3$ disebabkan oleh kawasan permukaan yang tinggi dan ketumpatan zarah yang rendah dalam GO. Kesimpulannya, GO yang telah disintesis merupakan bahan yang sesuai untuk kegunaan sebagai bahan salutan pada permukaan kaca berasaskan tellurit. Kajian ini boleh menyumbang kepada penggunaan yang berpotensi untuk prestasi aplikasi gentian optik.

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A	Area	m^2
d	Thickness	m
E_{opt}	Optical Bandgap Energy	Joule (J)/eV
ω	Radian Frequency	Fm^{-1}
ħω	Photon Energy	Joule (J)/eV
ΔE	Urbach Energy	Joule (J)/eV
ρ	Density	kg/m^3
V_m	Molar Volume	m^3/mol
λ	Wavelength	m
ɳ	Refractive Index	-
α_e	Electronic Polarizability	$Å^3$
$\alpha_0{}^{2-}$	Oxide Ion Polarizability	$Å^3$
ʌ	Optical Basicity	-
BO	Bridging Oxygen	-
Er	Erbium	-
FT-IR	Fourier Transform Infrared	-
GO	Graphene Oxide	-
NBO	Non-bridging Oxygen	-
Nd	Neodymium	-

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rGO	Reduced Graphene Oxide	-
SEM	Scanning Electron Microscopy	-
tbp	Trigonal Bypiramidal	-
T_g	Glass Transition Temperature	-
T_m	Melting Temperature	-
XRD	X-ray Diffraction	-

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter introduces with the background of research and illustrates the evolution of glass technology to be considered as the important part in this thesis. This is followed by the research objectives, research problems, scope and limitations of the study, and the significance in this work. Then, this chapter summarizes with the outline of the thesis.

1.2 Research Background

Glasses are one of the interesting material as they have been extensively received the high demanding due to their common in daily practical, technology and ornamental usage routine. For instance, the latest development towards the glass science and technology are involved in making of window panes, optoelectronics, optical lenses, and optical fibers. Glasses also acquire the several unique properties, including high transparency, excellent strength, good hardness, corrosion resistance, and may fabricate in any sizes and shapes effortlessly.

Tellurite glasses offer the scientific and technological interest due to their physical properties such as low melting point, high refractive index, high dielectric constant, and excellent infrared transmission compared to other network oxide glass (Kalampounias, Nasikas, & Papatheodorou, 2011; Yu et al., 2017). Furthermore, tellurite glasses possess good chemical durability, excellent mechanical strength, and allow the wide spectral in the range of 3-18 µm which attribute to the high possibility in fabricating the stable glass (Gomes et al., 2017; Selvaraju & Marimuthu, 2012).

Tellurium oxide, TeO_2 and zinc oxide, ZnO are the good combination which acquire the great ability to form the stable glasses; thus, these glasses have been widely investigated especially in optical fiber applications. The inclusion of ZnO may provide superior mechanical properties in the rigidity of tellurite glasses and contributes broad in the glass making, low ability to crystallize as well as low optical bandgap energy and also give the higher refractive index.

Hence, it is predicted that the tellurite system with the addition of borate oxide, B_2O_3 enhances the glass transparency and its refractive index which is useful in optical applications. Despite that, glasses incorporated with borate offered the outstanding properties including, low melting point, high thermal stability, as to dissolve in high concentration of rare-earth ions, which means these glasses are more convenient for the optical devices usage.

The ZnO-B_2O_3-TeO_2 glass system is attractive to be doped with the trivalent lanthanides ions of rare-earth material for future applications in optical devices such as laser glasses, optical sensors, and fiber-optic communications. Tellurite glasses also gained the wide significance due to their prospective as hosts of rare-earth oxides for the development of fibers and lasers technology. Therefore, the introduction of neodymium and erbium in the present study may lead to the improvement of glass formation, structure, and optical properties in the tellurite glass network system.

Thus, the aim of this research is; to investigate the effect of graphene oxide (GO) for optical efficiency on rare-earth oxides doped tellurite glasses. The rare-earth oxides are supposed to give an excellent optical efficiency and contribute to the enhancement of emitted light as well. Besides, the rare-earth ions are able to offer excellent optical properties such as emission of wide spectral range in order to recognize the laser properties of the material. Additionally, the structural characterizations had been done to support and prove the results in optical properties of the glass samples. The determination of optical parameters including, optical bandgap energy, Urbach energy, refractive index, electronic polarizability, oxide ion polarizability, and optical basicity had been identified for optical properties in this work.

1.3 Research Problems

The technological interest on the glass materials focused on their potential applications in the field of optoelectronics such as fiber optics and also laser technology has gained much attention since the history of glassmaking are exceeded more than 5000 years ago, and making the glass as one of the most crucial and impressive materials. Indeed, the glass materials have established as a key technology that impacts on our daily lives as this research field may contribute to the significant advances mainly in optical fiber, which enable to the Internet revolution.

The commercial on fiber optics technology used the silicate glasses since many years ago however, the problem encountered with silicate glasses which is, they produced the high loss and also possessed the high melting temperature about 1700 °C (Onodera et al., 2019). Therefore, those limitations need to be overcome in order to reduce the high loss and melting temperature and also, the most important part is, to increase the optical efficiency in the glass system for advanced fiber optics technology.

Thus, the tellurite glasses had been introduced due to their advantages over the silicate glasses, which give the potential applications as a tellurite-based glass of optical fibers. By comparing the silicate and also tellurite glasses, the development of “new tellurite glasses” itself have the novel properties and acts as the fascinating glass materials which significantly more promising in fiber optics technology. Moreover, tellurite glasses are known as the stable glass formers and have the potential advantages compared to other glasses, including phosphate, germanate, silicate, and borate due to their outstanding properties as main materials, far beyond the other oxide glasses. The tellurite glasses give the good solubility when doped with rare-earth oxides as compared to silicate glasses, which can enhance the performance characteristics resulting in a wide scale of optical glass fiber.

Rare-earth (RE) oxides doped glass has been investigated as good candidates since each of them have the advantages towards commercial applications. For instance, erbium-doped in fiber amplifiers which performing at the 1.5 µm wavelength regions is the most crucial in the perspective of long-range optical fiber communication while neodymium oxide in glass emitting the emission bands near 1.3 µm, respectively. Thus, rare-earth ions including neodymium and erbium have attracted the attention which may exhibit the good potential to be implied in enhancing on optical characteristics.

Regarding on the tellurite glasses which exhibit a range of many properties especially, these glasses are considered in many future applications including, the optics telecommunications and fiber laser glass. However, there are still lacking in achieving the good refractive index value that needed in optical fiber applications. Due to this, a new investigation on the effect of graphene especially on the tellurite glasses surface had been explored in this work. As far as can be concerned, the technology of graphene is more high demand and becomes an interesting topic due to many advantages on graphene, itself. Based from the previous study, the graphene actually may improve the properties on the semiconductor materials and also can be applied in many kinds of applications mainly for optoelectronics devices (Prasad et al., 2020).

Furthermore, the glass materials coated with graphene oxide (GO) had been captured a great deal of significance due to its ability to enhance the performance and quality in the field of optical fibers. Even though, there are extensive research on the tellurite-based glass has been studied, yet the investigation on the optical performance of tellurite glasses coated with GO has not been reported in previous research. In spite of few studies on graphene-based material for sensing application has been done (Hernaez et al., 2017), the clear explanation and recent research on GO are still lacking on the glass application. Furthermore, the investigation of graphene oxide-coated tellurite glass focused on the active rare-earth to be doped into tellurite-based glass has been revealed in this study. Hence, the outcome of this research is the first step to develop novel materials for fiber optics technology applications.

1.4 Objectives of Research

This research primarily aimed to fabricate the tellurite glass doped with neodymium and erbium ions by utilizing melt-quenching technique. The aim was targeted to achieve by dividing the research work into some points that stated in the main objectives, which can be summarized as follows:

i. To characterize the physical and structural properties of neodymium and erbium doped tellurite glass coated with graphene oxide (GO).

ii. To determine the refractive index, optical bandgap energy and Urbach energy of neodymium and erbium doped tellurite glass coated with graphene oxide (GO).

iii. To analyze the electronic polarizability, oxide ion polarizability and optical basicity of neodymium and erbium doped tellurite glass coated with graphene oxide (GO).

1.5 Scope and Limitations of Study

This research is focused on the structural and optical properties of neodymium and erbium doped tellurite glass coated with graphene oxide (GO). The two series of tellurite glasses with compositions of $\{[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Nd_2O_3)_y$ and $\{[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{0.7}\ (ZnO)_{0.3}\}_{1-y}\ (Er_2O_3)_y$ were prepared using melt-quenching technique. Then, two series of neodymium and erbium doped tellurite glasses were coated with graphene oxide (GO) on the tellurite glass samples surface using spray coating method.

The physical properties including, density and molar volume of coated-tellurite glasses were identified by Archimedes Principle. Then, several analysis methods were used for glass characterizations such as Fourier Transform Infrared Spectrometer (FT-IR), X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM) to investigate the structural properties of tellurite glasses coated with GO. The X-ray diffraction (XRD) had been analyzed in order to prove the amorphous nature on tellurite glasses. Meanwhile, the FESEM had been carried out to confirm the existence of GO structures on the glass samples surface and FT-IR in order to analyze the structural bonding of TeO_2 and BO_3 and also the presence of non-bridging oxygen (NBO) existing in the glass network system. The optical properties of tellurite-based glass were identified by using Ultra-violet visible (UV-vis) to determine the optical absorption, optical bandgap energy, Urbach energy, refractive index, electronic polarizability, oxide ion polarizability, and also optical basicity.

The previous studies proposed that the coating of glass fibers through the dip coating technique had been developed to prepare the highly-conductive glass fibers (Fang, Xiong, Hao, Zhang, & Wang, 2019). Since the lack of studies about graphene-based materials on the glass materials thus, it was noted that such investigation has not been revealed yet for the new fiber optics technology applications. As the novelty for this work, graphene, known as a “wonder material” compliments the superior advantages due to its stronger, high transparency, thereby making it very promising to be considered as a coating material. Moreover, owing to its significant properties, graphene oxide (GO) coating can contribute for optical properties on tellurite glasses mainly for advanced fiber optics technology applications.

1.6 Significance of Research

Regarding this research, the characterization of sample glasses consists of the physical, structural, and optical properties of tellurite-based glasses, which extremely important for the applications of optical fiber technology. Accordingly, the main purpose of research is to enhance the optical efficiency by introducing graphene oxide (GO) coated on the tellurite glasses surface. Hence, the fabrication and spectroscopic studies of sample glasses form this experimental which were attributed as the better approaches to enhance the optical efficiency of tellurite-based glass for fiber optics technology applications.

By taking the advantages on graphene oxide-coated to the glass materials, it has been examined that GO is one of an ideal material in considering as a protective coating due to it can achieve a compromise which making the suitable candidate especially for the commercial applications. Additionally, through science and technology development of the fiber optics, it can be referred as the medium or advanced technology which was associated with the transmission or propagating the information by the light signals over the long distances through a very thin and transparent fiber, respectively. In this work, a new technological development of fiber optics can be significantly enhanced by introducing GO as the multi-functional in obtaining the high performance for optical efficiency commonly used in the fiber optics telecommunication services.

In addition, this research leads to the better improvements for future fiber optics by replacing the current fiber optics with the miracle materials called graphene oxide (GO). It has been known that the optical fiber broadband transmit the data by using infra-red light wave spectrum at “speed of light” about 3.0×10^8 m/s which essentially become the potential pathway in transmitting the information to all over the world. Thus, upgrading the current fiber optics with “graphene fiber optics” in networking ultimately can allow or interpret the information to pass through faster from one destination to another than current fiber optics.

1.7 Thesis Outline

This thesis work consists of five chapters that describe the glass preparation and characterization of neodymium and erbium-doped tellurite glasses coated with graphene oxide (GO). The thesis outline in this study is described as follows:

Chapter 1 introduces the research purpose including the background of research, research problems, research objectives, the scope and limitations of research, and the significance of the research. Chapter 2 describes the fundamental theory applied in this glass work, including the glass structure, the glass network system, physical, structural, and optical properties. The theoretical reviews of graphene (which have been used in the experiment) are also presented in this chapter.

In Chapter 3, the fabrication of glass, which is the methodology and experimental techniques involved in this research work, are presented comprehensively. Chapter 4 elaborates the results of experimental details conducted on the physical, structural, and optical properties on the tellurite-based glass coated with GO. Finally, chapter 5 summarizes the conclusion obtained regarding this research and future outlook towards the application for the new development of fiber optics.