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



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UNIVERSITI PENDIDIKAN SULTAN IDRIS

2020



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

**AZLINA BINTI YAHYA**

**THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE  
DEGREE OF MASTER OF SCIENCE  
(MASTER BY RESEARCH)**

**FACULTY OF SCIENCE AND MATHEMATICS  
UNIVERSITI PENDIDIKAN SULTAN IDRIS**

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## ACKNOWLEDGEMENT

First and foremost, I would like to extend my thankfulness and greatest glory to the Almighty, for giving me the strength and good health to pursue and complete my master's study successfully.

I would like to express my genuine appreciation to my supervisor, Dr. Muhammad Noorazlan Abd Azis for his invaluable help and tremendous encouragement throughout this study. I am most grateful for his teaching and advice, and my research work would not have been accomplished without all the support that I have always received from him. Also, my precious thanks to my co-supervisor, Professor Dr. Suriani Abu Bakar for her kindness and support to complete this master's journey. Her success had inspired me and becomes a great motivation for me to the road of success. May Allah always grant both of you with the good health and happiness.

Then, I would like to expand my deepest gratitude to the Nanotechnology Research lab members, Dr. Muqoyyanah, Dr. Khayri, Dr. Ali, Rosmanisah, Nur Jannah, and Hafizah Rajaa for guiding me and giving the continuing support to complete this research work. Besides, thanks a million to UiTM's members for sharing the good ideas and knowledge during this study period. I also would like to thank to lab assistance at Chemistry Department, Faculty of Science and Mathematics, UPSI and Faculty of Bioengineering and Technology, Jeli Campus, UMK for helping me in completion this research. May Allah reward all of you with the goodness and success.

A special credit and appreciation to my beloved parents, Yahya Abdullah and Tengku Zainab Tengku Ain and also family members, for their love, prayers, sacrifices and caring for me throughout this research period. Lastly, I offer my regards and blessings to all of those who had supported me in any aspects to complete this thesis successfully.





## ABSTRACT

This study aimed to enhance the optical properties on neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) and erbium oxide ( $\text{Er}_2\text{O}_3$ ) doped tellurite-based glass coated with graphene oxide (GO). The two series of tellurite glasses with chemical composition of  $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$  and  $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Er}_2\text{O}_3)_y$  with varying concentrations of  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  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  $8.887 \text{ \AA}^3$  while for erbium from  $8.815$  to  $8.894 \text{ \AA}^3$  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 ( $\text{Nd}_2\text{O}_3$ ) dan erbium oksida ( $\text{Er}_2\text{O}_3$ ) terdop kaca berasaskan tellurit disalut dengan grafin oksida (GO). Dua siri kaca tellurit dengan komposisi kimia  $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Nd}_2\text{O}_3)_y$  dan  $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$  dengan kepekatan yang berbeza oleh neodimium dan erbium ion daripada  $y=0.005, 0.01, 0.02, 0.03, 0.04$ , dan  $0.05 \text{ mol\%}$  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  $\text{\AA}^3$  manakala untuk erbium dari 8.815 hingga 8.894  $\text{\AA}^3$  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.



**TABLE OF CONTENTS**

	<b>Page</b>
<b>DECLARATION OF ORIGINAL WORK</b>	ii
<b>DECLARATION OF THESIS</b>	iii
<b>ACKNOWLEDGEMENTS</b>	iv
<b>ABSTRACT</b>	v
<b>ABSTRAK</b>	vi
<b>TABLE OF CONTENTS</b>	vii
<b>LIST OF TABLES</b>	xiii
<b>LIST OF FIGURES</b>	xv
<b>LIST OF ABBREVIATIONS</b>	xx
<b>LIST OF APPENDICES</b>	
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Introduction	1
1.2 Research Background	2
1.3 Research Problems	4
1.4 Objectives of Research	7
1.5 Scope and Limitations	7
1.6 Significance of Research	9
1.7 Thesis Outline	11







## CHAPTER 2 LITERATURE REVIEW

2.1	Introduction	12
2.2	Tellurite Glass Structure	13
2.3	Trivalent Rare-Earth Ions Doped Tellurite Glass	
2.3.1	Neodymium Ions, $\text{Nd}^{3+}$	22
2.3.2	Erbium Ions, $\text{Er}^{3+}$	28
2.4	Graphene Oxide	
2.4.1	Atomic Structures and Properties	33
2.4.2	Graphene Oxide Synthesis Method	39
2.5	Physical Properties	
2.5.1	Density and Molar Volume	44
2.6	Structural Properties	
2.6.1	Microscopic Morphology	57
2.6.3	Structural Arrangement and Network Formation	58
2.7	Optical Properties	
2.7.1	Optical Absorption Spectra	63
2.7.2	Optical bandgap energy	90
2.7.3	Urbach energy	105





2.7.4	Refractive Index	108
2.7.5	Electronic Polarizability	114
2.7.6	Oxide Ion Polarizability	117
2.7.7	Optical Basicity	119
2.8	Summary	122

## CHAPTER 3 RESEARCH METHODOLOGY

3.1	Introduction	123
3.2	Glass Preparation Technique	
3.2.1	Melt-quenching Method	124
3.2.2	Synthesis of Graphene Oxide	
3.2.2.1	Electrochemical Exfoliation Method	127
3.2.3	Spray Coating Method	129
3.3	Physical Properties Characterization	
3.3.1	Density and Molar Volume Measurement	131
3.4	Structural Properties Characterization	
3.4.1	Field Emission Scanning Electron Microscopy Analysis	131
3.4.2	X-ray Diffraction Technique	133





3.4.3	Fourier Transform Infrared Analysis	134
3.5	Optical Properties Characterization	
3.5.1	Ultraviolet-Visible Spectroscopy	135
3.5.2	Refractive Index	136
3.6	Research Methodology	137
3.7	Summary	138

## CHAPTER 4 RESULTS AND DISCUSSION

4.1	Introduction	139
-----	--------------	-----



4.2	Neodymium Doped Tellurite Glass Coated with Graphene Oxide	
-----	------------------------------------------------------------	--

### 4.2.1 Physical Properties Characterization

4.2.1.1	Density and Molar Volume	140
---------	--------------------------	-----

### 4.2.2 Structural Properties Characterization

4.2.2.1	Field Emission Scanning Electron Microscopy Analysis	142
---------	---------------------------------------------------------	-----

4.2.2.2	X-ray Diffraction Analysis	144
---------	----------------------------	-----

4.2.2.3	Fourier Transform Infrared Analysis	145
---------	-------------------------------------	-----



### 4.2.3 Optical Properties Characterization

4.2.3.1 Optical Absorption Spectra	149
4.2.3.2 Optical Bandgap Energy	150
4.2.3.3 Urbach Energy	153
4.2.3.4 Refractive Index	156
4.2.3.5 Electronic Polarizability	159
4.2.3.6 Oxide Ion Polarizability	161
4.2.3.7 Optical Basicity	163

## 4.3 Erbium Doped Tellurite Glass Coated with Graphene Oxide

### 4.3.1 Physical Properties Characterization

4.3.1.1 Density and Molar Volume	166
----------------------------------	-----

### 4.3.2 Structural Properties Characterization

4.3.2.1 Field Emission Scanning Electron Microscopy Analysis	168
4.3.2.2 X-ray Diffraction Analysis	170
4.3.2.3 Fourier Transform Infrared Analysis	171

### 4.3.3 Optical Properties Characterization

4.3.3.1 Optical Absorption Spectra	174
4.3.3.2 Optical Bandgap Energy	175
4.3.3.3 Urbach Energy	178
4.3.3.4 Refractive Index	181
4.3.3.5 Electronic Polarizability	184
4.3.3.6 Oxide Ion Polarizability	187
4.3.3.7 Optical Basicity	189

### 4.4 Summary

## CHAPTER 5 CONCLUSION AND FUTURE WORKS

5.1 Introduction	193
5.2 Conclusion	194
5.2 Suggestions for Future Outlooks	196

REFERENCES	197
------------	-----

APPENDICES	xxii
------------	------



## LIST OF TABLES

Table No.		Page
2.1	The Comparison between Crystalline and Amorphous Glass Structure	15
4.1	Density and Molar Volume of Neodymium-doped Tellurite Glass Coated with GO	141
4.2	Assignments of FT-IR Spectra of Neodymium-doped Tellurite Glass Coated with GO	148
4.3	Optical Bandgap ( $E_{opt}$ ) and Urbach Energy ( $\Delta E$ ) for Uncoated and Coated Glass with GO of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(B_2O_3)_{0.3}\}_{0.7}(ZnO)_{0.3}\}_{1-y}(Nd_2O_3)_y$ Glass System	155
4.4	Refractive Index for Uncoated and Coated Glass with GO of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Nd_2O_3)_y$ Glass System	158
4.5	Electronic Polarizability for Uncoated and Coated Glass with GO of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Nd_2O_3)_y$ Glass System	160
4.6	Oxide ion Polarizability for Uncoated and Coated Glass with GO of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Nd_2O_3)_y$ Glass System	162
4.7	Optical Basicity for Uncoated and Coated Glass with GO of $\{[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}\}_{1-y}(Nd_2O_3)_y$ Glass System	165
4.8	Density and Molar Volume of Erbium-doped Tellurite Glass System Coated with GO	168





4.9	Assignments of FT-IR Spectra of Erbium-doped Tellurite Glass Coated with GO	173
4.10	Optical Bandgap ( $E_{\text{opt}}$ ) and Urbach Energy ( $\Delta E$ ) for Uncoated and Coated Glass with GO of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	180
4.11	Refractive Index Values for $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	183
4.12	Electronic Polarizability Values for $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glasses Coated with GO	186
4.13	Oxide ion Polarizability Values for $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glasses Coated with GO	188
4.14	Optical Basicity for Uncoated and Coated Glass with GO of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	191





## LIST OF FIGURES

Figure No.		Page
2.1	Schematic Illustration of Glass Transition Which Indicated the Volume Versus Temperature for a Glass-forming System Representing in the Liquid Phase (Red Line), Crystalline Solid Phase (Green Line), and Supercooled Liquid (Blue Line) (Napotalino, Glynos, & Toto, 2017)	14
2.2	Tellurite Glass Structure in the Glass System Network (McLaughlin, Tagg, Zwanziger, & Hae, 2000)	17
2.3	Ball and Stick Representation of the Structural Units Present in Tellurite Glass. (a) Trigonal Bipyramidal, $\text{TeO}_4$ (b) Distorted Trigonal Bipyramidal, $\text{TeO}_{3+1}$ (c) Trigonal Pyramid, $\text{TeO}_3$ (Manning, Ebendorff-heidepriem, & Monro, 2012)	20
2.4	Graphitic Forms of Carbon Family Materials (a) 0-D Buckyballs of Fullerene (b) 1-D Roll of Carbon Nanotube (c) 3-D Stack of Graphite (Geim & Novoselov, 2007)	33
2.5	The Electronic Bands of $\pi$ and $\pi^*$ with Respect to the Valence and Conduction Bands at the Six Corners in the Dirac Cones which meet at the Dirac Points and Indicate that Zero-bandgap of Graphene (Dubois, Zanolli, Declerck, & Charlier, 2009)	34
2.6	The Lattice Structure and Corresponding Band Diagrams of (a) Graphene (b) Graphene Oxide (Abid, Sehwat, Islam, Mishra, & Ahmad, 2018)	36







2.7	Schematic Representation of Different Graphene-based Nanomaterials include (a) Few-layered Graphene (FLG), (b) Graphene Oxide (GO), (c) Graphene Nanosheets, and (d) Reduced Graphene Oxide (rGO) which belong to the Graphene Derivatives Group (Jastrzębska, Kurtycz, & Olszyna, 2012)	38
2.8	Flow Chart and Schematic Illustration of Graphene Synthesis by Different Approaches (Edwards, Coleman, 2013; Lee et al., 2018)	40
2.9	Schematic Representation of the most Common Methods for GO Synthesis (Marcano et al., 2010)	42
2.10	The Development Timeline of Graphene History (Dreyer, Ruoff, & Bielawski, 2010)	43
2.11	Schematic Illustration of an Atomic Structure of the Amorphous Silica Which Viewing a Random Arrangement of Silica tetrahedral (Lunt, Chater, & Korsunsky, 2018)	59
2.12	Schematic Illustration in States of Conduction and Valence Bands (Morigaki & Ogihara, 2006)	64
2.13	The Photon Emission Process Occurred for (a) Direct and, (b) Indirect Bandgap Semiconductors (Sun, 2010)	91
3.1	Flow Diagram of Glass Fabrication Process for all Glass Samples Coated with GO	126
3.2	Experimental Set Up to Synthesize GO through Electrochemical Exfoliation Method	127
3.3	Schematic Illustrations of (a) Synthesis GO through Electrochemical Exfoliation Method and, (b) Intercalation of SDS into GO layers	128





3.4	The Experimental Procedure of GO-coated Glass through Spray Coating Method	129
3.5	Schematic Diagram of GO-coated Glass through Spray Coating Method	130
3.6	The Experimental Set Up to Anneal the Glass Samples After Coated with GO through 2-Zone Tube Furnace	130
3.7	FESEM (Hitachi SU 8020) used to Investigate the Surface Morphology of Tellurite Glass Samples Coated with GO	132
3.8	XRD Measurement (Bruker, D2 Phaser) used to Investigate the Amorphous Nature for the Tellurite Glass Samples Coated with GO	134
3.9	UV-Vis Spectrophotometer (Agilent Technologies Cary 60) used to Identify the Optical Absorption Spectra	135
3.10	Flow Chart of Research Methodology for this Study	137
4.1	Density and Molar Volume versus Neodymium Concentration for Tellurite Glass Coated with GO	141
4.2	FESEM Micrographs (a)-(c) Large Agglomerate, (b) Large Crumple Structure, and (d) Thick Multilayers of GO Deposited onto Neodymium-doped Tellurite Glass Surface (Li et al., 2017)	143
4.3	XRD Diffraction Pattern Obtained for Neodymium-doped Tellurite Glass Coated with GO	145
4.4	FT-IR Spectra Obtained for Neodymium-doped Tellurite Glass Coated with GO	147
4.5	Optical Absorption Spectra for $\{[\text{TeO}_2]_{0.7} (\text{B}_2\text{O}_3)_{0.3}\}_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Coated with GO	150



4.6	Plot of Optical Bandgap Energy, $(\alpha\hbar\omega)^{1/2}$ against Photon Energy, $\hbar\omega$ of $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Coated with GO	152
4.7	Variation of Optical Bandgap Values for Uncoated and Coated Glass with GO	152
4.8	Urbach Energy for $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Glass System	153
4.9	Variation of Urbach Energy for Uncoated and Coated Glass with GO for $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Glass System	154
4.10	Refractive Index for Uncoated and Coated with GO of $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Glass System	157
4.11	Electronic Polarizability for Uncoated and Coated with GO of $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Glass System	159
4.12	Oxide Ion Polarizability for Uncoated and Coated with GO $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Glass System	161
4.13	Optical Basicity for Uncoated and Coated of $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$ Glass System	164
4.14	Density and Molar Volume versus Erbium Concentration for Tellurite Glass Coated with GO	167
4.15	FESEM Micrographs of GO Deposited onto Tellurite Glass Surface (a)-(c) Agglomerate GO (b)-(d) Thick Layers GO (Han & Kim, 2013)	169



4.16	XRD Diffraction Pattern of Erbium-doped Tellurite Glass Coated with GO	170
4.17	FT-IR Spectra of Erbium-doped Tellurite Glass Coated with GO	172
4.18	Optical Absorption Spectra of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Coated with GO	175
4.19	Plot of Optical Bandgap Energy, $(\alpha\hbar\omega)^{1/2}$ against Photon Energy, $\hbar\omega$ of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Coated with GO	177
4.20	Variation of Optical Bandgap Values for Uncoated and Coated Glass with GO	177
4.21	Urbach Energy for $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	178
4.22	Variation of Urbach Energy for Uncoated and Coated Glass with GO of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	179
4.23	Refractive Index for Uncoated and Coated Glass with GO of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	182
4.24	Electronic Polarizability for Uncoated and Coated Glass with GO for $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	185
4.25	Oxide Ion Polarizability for Uncoated and Coated Glass with GO for $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	187
4.26	Optical Basicity for Uncoated and Coated of $\{[(\text{TeO}_2)_{0.7}(\text{B}_2\text{O}_3)_{0.3}]_{0.7}(\text{ZnO})_{0.3}\}_{1-y}(\text{Er}_2\text{O}_3)_y$ Glass System	190



## LIST OF ABBREVIATIONS

A	Area	$\text{m}^2$
d	Thickness	m
$E_{\text{opt}}$	Optical Bandgap Energy	Joule (J)/eV
$\omega$	Radian Frequency	$\text{Fm}^{-1}$
$\hbar\omega$	Photon Energy	Joule (J)/eV
$\Delta E$	Urbach Energy	Joule (J)/eV
$\rho$	Density	$\text{kg/m}^3$
$V_m$	Molar Volume	$\text{m}^3/\text{mol}$
$\lambda$	Wavelength	m
$\eta$	Refractive Index	-
$\alpha_e$	Electronic Polarizability	$\text{\AA}^3$
$\alpha_0^{2-}$	Oxide Ion Polarizability	$\text{\AA}^3$
$\Lambda$	Optical Basicity	-
BO	Bridging Oxygen	-
Er	Erbium	-
FT-IR	Fourier Transform Infrared	-
GO	Graphene Oxide	-
NBO	Non-bridging Oxygen	-
Nd	Neodymium	-

rGO	Reduced Graphene Oxide	-
SEM	Scanning Electron Microscopy	-
tbp	Trigonal Bypiramidal	-
T <sub>g</sub>	Glass Transition Temperature	-
T <sub>m</sub>	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  $\mu\text{m}$  which attribute to the high possibility in fabricating the stable glass (Gomes et al., 2017; Selvaraju & Marimuthu, 2012).

Tellurium oxide,  $\text{TeO}_2$  and zinc oxide,  $\text{ZnO}$  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  $\text{ZnO}$  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  $\mu\text{m}$  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  $\mu\text{m}$ , 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 (Hernaiz 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  $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Nd}_2\text{O}_3)_y$  and  $\{[(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}]_{0.7} (\text{ZnO})_{0.3}\}_{1-y} (\text{Er}_2\text{O}_3)_y$  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  $\text{TeO}_2$  and  $\text{BO}_3$  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  $3.0 \times 10^8$  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.

