

OPTICAL PROPERTIES OF ERBIUM DOPED TELLURITE GLASS WITH
DIFFERENT NaCl COMPOSITION

IZZAH AFIFAH BINTI ISMAIL

A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Science (Physics)

Faculty of Science
Universiti Teknologi Malaysia

JUNE 2014

To my late father
beloved family and friends
future husband

ACKNOWLEDGEMENT

Alhamdulillah praise to Allah SWT, the Almighty, for giving me strength, courage and patience to complete this study.

First and foremost, I would like to thank my supervisor Dr Ramli Arifin for his advice, guidance and encouragement throughout completing this project.

Thank you to all the lecturers who have share their knowledge and experience during my dissertation. I also would like to thank Material Analysis Laboratory's staff, Mr Mohd Jaafar and Mrs Nur Anis for their help and support during my experimental work.

Last but not least to my fellow friends who have been helping and guiding me throughout completing this dissertation project. Not forgetting to my family members for their love and support.

ABSTRACT

A series of glasses based on $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ (where $x = 0.0, 2.5, 5.0, 7.5$ and 10.0 mol %) are successfully prepared by melt quenching technique. The amorphous nature of the glass have been characterized using X-ray Diffraction technique and the optical properties are characterized by means of UV-Vis-NIR and photoluminescence spectroscopy. The value of the optical band gap and the Urbach energy are calculated from the absorption edge data. The value of optical band gap lies between 2.99 eV and 3.13 eV for the indirect transition whereas the value of Urbach energy varies from 0.17 eV to 0.27 eV. From the luminescence spectrum, it is found that the luminescence emission spectra centered at 435 nm, 475 nm and 563 nm which assigned to the transition of $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ to $^4\text{I}_{15/2}$ respectively under 375 nm of excitation wavelength. Most properties observed to be dependent in a systematic manner on the NaCl content.

ABSTRAK

Satu siri kaca pada komposisi $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ (dengan $x = 0.0, 2.5, 5.0, 7.5$ and 10.0 mol%) telah berjaya dihasilkan dengan menggunakan teknik pelindapan leburan. Sifat amorfus kaca tersebut telah ditentukan dengan kaedah pembelauan sinar-X dan sifat sifat optic kaca tersebut ditentukan dengan menggunakan spektroskopi ultra ungu dan cahaya nampak dan spektroskopi fotoluminesen. Nilai jurang tenaga optik dan tenaga Urbach diperolehi daripada kiraan data serapan pinggir. Jurang tenaga E_g berada pada julat 2.99 eV sehingga 3.8 eV untuk peralihan tidak langsung manakala nilai tenaga Urbach pula berada pada julat 0.17 eV sehingg 0.27 eV. Daripada spectrum luminesen, dapat diperhatikan bahawa spektra rencatan luminesen berpusat pada 435 nm, 475 nm dan 563 nm, masing-masing dikaitkan dengan transisi ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ to ${}^4\text{I}_{15/2}$ dengan pengujaan gelombang pada 375 nm. Kebanyakan ciri yang diperoleh bergantung pada kandungan sistematik NaCl.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SYSMBOLS	xiii
	LIST OF APPENDICES	xiv
1	INTRODUCTION	1
	1.0 Introduction	1
	1.1 Background of Study	1
	1.2 Problem Statement	2
	1.3 Objectives of the Study	3
	1.4 Scope of Study	4
2	LITERATURE REVIEW	5
	2.0 Introduction	5
	2.1 Basic Structure of Glass	5

2.2	The Glass Formation	7
2.3	Tellurite Glass	9
2.4	Oxyhalide Tellurite Glass	10
2.5	The Lanthanides	11
2.6	X-ray Diffraction (XRD)	12
2.7	UV-Vis-NIR Spectroscopy	14
2.8	Photoluminescence	18
3	METHODOLOGY	20
3.0	Introduction	20
3.1	Sample Preparation	20
3.2	X-Ray Diffraction	22
3.3	UV-Vis Spectroscopy	23
3.4	Photoluminescence Spectroscopy	24
4	RESULTS AND DISCUSSION	25
4.0	Introduction	25
4.1	Glass Formation	25
4.2	X-ray Diffraction Analysis	26
4.3	UV-Vis-NIR Spectroscopy	27
4.3.1	Absorption Spectra	27
4.3.2	Optical band gap energy (E_{opt}) and Urbach energy (ΔE)	29
4.4	Photoluminescence Spectroscopy	34
5	CONCLUSION AND RECOMMENDATIONS	36
5.0	Introduction	36
5.1	Conclusion	36
5.2	Recommendation	37
	REFERENCES	39
	Appendices A-B	45-48

LIST OF TABLES

TABLE NO.	TITLE	PAGE
3.1	The nominal composition of the ternary TeO ₂ -Na ₂ O-NaCl-Er ₂ O ₃ glass system	21
4.1	The appearance and nominal composition for (79.5-x)TeO ₂ -20Na ₂ O-xNaCl-0.5Er ₂ O ₃ glass system	26
4.2	The absorption peaks of the (79.5-x)TeO ₂ -20Na ₂ O-xNaCl-0.5Er ₂ O ₃ glass system	29
4.3	Optical band gap (E _{opt}) of (79.5-x)TeO ₂ -20Na ₂ O-xNaCl-0.5Er ₂ O ₃ glass system	30
4.4	Urbach Energy, ΔE of (79.5-x)TeO ₂ -20Na ₂ O-xNaCl-0.5Er ₂ O ₃ glass system	32
4.5	The excitation wavelength (λ _{exc}) and their emission transition of Erbium doped glass by various authors	35

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Difference in the structure of glass and crystalline	6
2.2	The change of specific volume against temperature	8
2.3	Schematic diagram of α -TeO ₂ structure	10
2.4	Schematic of Bragg Law	13
2.5	X-ray diffraction patterns for (a) amorphous phase and (b) for crystalline phase	14
2.6	Partial energy diagram for a photoluminescence system	19
3.1	Flow chart of sample preparation	22
3.2	Shimadzu 3101PC UV-VIS-NIR Scanning Spectrophotometer	23
3.3	Perkin Elmer Instruments LS 55 Luminescence Spectrometer	24

4.1	X-ray diffraction pattern for sample 3 of $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ glass system	27
4.2	The UV-Vis-NIR absorption spectra of the $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ glass system	28
4.3	UV-Vis-NIR 1435 nm to 1610 nm absorption spectra of $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ glass system	28
4.4	A typical $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ for $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ for S1	30
4.5	Variation of E_{opt} (eV) against concentration of NaCl (mol %) for S1	31
4.6	A typical $\ln(\alpha)$ vs photon energy, $\hbar\omega$ for $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-x\text{NaCl}-0.5\text{Er}_2\text{O}_3$ glass system	32
4.7	Variation of Urbach energy, ΔE against concentration of NaCl	33
4.8	Photoluminescence spectrum for $\text{TeO}_2-\text{Na}_2\text{O}-\text{NaCl}-\text{Er}_2\text{O}_3$ glass system	34

LIST OF SYMBOLS

α	-	Absorption coefficient
C	-	Constant
d	-	Sample thickness
ΔE	-	Width of the band tail
E_g	-	Band gap energy
E_{opt}	-	Optical energy gap
\hbar	-	Planck constant
λ	-	Wavelength
ω	-	Angular frequency
T_m	-	Glass melting temperature
T_g	-	Glass transition temperature
T_c	-	Crystallization temperature
θ		Diffracted angle

LIST OF APPENDICES

APPENDIX.	TITLE	PAGE
A	Calculation of glass composition	43
B	Optical Absorption in UV and Visible Region	45

CHAPTER 1

INTRODUCTION

1.0 Introduction

In this chapter, the general information about this study will be described in details. This study is about modifier variation assisted optical response in erbium tellurite glass. The background of study, objectives of the study, statement of problem and scope of the study will be explained in this chapter.

1.1 Background of Study

In general, glass is a transparent, hard and brittle material. Glass is very unique material and has many special properties compared with other material such as plastic or metal. All glass is an amorphous solid but not all amorphous solid is a glass. The amorphous (non-crystalline) term can be understood as the arrangement of atoms in the materials. The arrangement of atoms in amorphous materials is short range order which is the arrangement are not in periodic manner. In contrast with

amorphous structure, a crystal structure has a long range order and periodic arrangement of atoms. Glass usually formed by solidification of melt without occur any crystallization. In other words, it is formed by cooling from the molten state of higher temperature to stable state of low temperature. The cooling should be fast enough so that the melt of right viscosity does not form into crystal.

Tellurite glasses are known to be very suitable hosts for doping with rare-earth element. They show good properties in chemical durability, mechanical stability and also superior transparency in a wide spectral range of 3-18 μm . These properties make the tellurite glasses a better candidate for practical laser application (Weber *et.al.*, 1981; Nii *et.al.*, 1998). Researcher has interest in tellurite glass because of their low transition temperature and also their excellent infrared transmission. Thus this glass is a potential for various longer-wavelength applications (Sahar and Noordin., 1995).

The erbium-doped tellurite glasses also have shown chemical and optical properties that suitable for optical application such as laser light modulator (Uhlmann and Kreidl., 1983) and thermally stable for fiber drawing (Neindre *et.al.*, 1999). The determination of the optical parameters such as refractive index, extinction coefficient, band gap energy, material dispersion of glass, and their nonlinear aspects is fundamental topic and important in a sector of technology (Jlassi *et.al.*, 2011).

1.2 Problem Statement

Research shows that, tellurite glass have been studied almost decade, with highlight generally on their synthesis and properties (El-Mallawany, 2002). The application of the tellurite glass is important especially in the industrial application in laser glass technology. Er^{3+} doped tellurite glass is one of the excellent candidates for optical communication materials due to their high refractive index, high solubility of

rare earth, large resistance against corrosion and good transparency in the region from visible to infrared (0.35-6 μ m) (Chen et.al., 2003; Lin et.al., 2003). Tellurite glasses modified by halides and oxide-halides of the non transition metal ions have already been investigated by previous researchers. Most of these researchers focused on the glass formation range of the oxyhalide tellurite glass. Moreover, the modifier used are mostly PbCl₂ or ZnCl (Wang et.al, 1988; Kostka et.al, 2003; Fortes et.al, 2003; Sahar et.al, 2012) but few have used the NaCl (Ivanova, 1990). However, there are no systematic study has been made so far on the glass system of (79.5-x)TeO₂-20Na₂O-(x)NaCl-0.5Er₂O₃. Therefore, an investigation of the optical properties of erbium doped tellurite glass with NaCl variation was carried out and the results of this study are presented in this thesis.

1.3 Objectives of the Study

In order to achieve more information on the glass properties, the objectives of this study as follow:

- a) To prepare (79.5-x)TeO₂-20Na₂O-(x)NaCl-0.5Er₂O₃ glass system by using melt quenching technique.
- b) To determine the amorphous nature of (79.5-x)TeO₂-20Na₂O-(x)NaCl-0.5Er₂O₃ glass system.
- c) To determine the optical band gap energy and Urbach energy of (79.5-x)TeO₂-20Na₂O-(x)NaCl-0.5Er₂O₃ glass system.
- d) To determine the luminescence properties of (79.5-x)TeO₂-20Na₂O-(x)NaCl-0.5Er₂O₃ glass system.

1.4 Scope of Study

In order to achieve the objectives, the study has been divided into several scopes as follow;

- a) Preparation of tellurite glass doped with Erbium $(79.5-x)\text{TeO}_2-20\text{Na}_2\text{O}-(x)\text{NaCl}-0.5\text{Er}_2\text{O}_3$ (where $x = 0.0, 2.5, 5.0, 7.5$ and 10.0 mol%) using conventional melt quenching technique.
- b) Determination of the amorphous nature of glass system using X-ray Diffraction.
- c) To determine the optical band gap energy and Urbach energy of the glass system using UV-VIS-NIR spectrophotometer.
- d) Determination of emission spectra of glass system using photoluminescence spectrophotometer.

REFERENCES

- Aitken B.G. and Youngman R.E., NMR Studies Of Aluminum Speciation In Tellurite Glasses, *Journal of Non-Crystalline Solids*, 2001. 284; 9-15.
- Amjad. R.J., Sahar. M.R., Goshal. S.K., Dousti. M.R., Riaz. S., Samavati. A.R., Ariffin. R., Naseem. S., Annealing Time Dependent Up-Conversion Luminescence Enhancement In Magnesium-Tellurite Glass, *Journal Of Luminescence*, 2013. 136; 145-149.
- Chen. D. D., Liu. Y. H., Zhang. Q. Y., Deng. Z. D., Jiang. Z. H., Thermal Stability And Spectroscopic Properties Of Er³⁺-Doped Niobium Tellurite Glasses For Broadband Amplifiers, *Material Chemistry Physics*, 2005. 90; 78-82.
- Chen, D. Wang, Y. Bao, F and Yu, Y., Broadband Near-infrared Emission from Tm³⁺/Er³⁺ Co-Doped Nano-structured Glass Ceramics, *Journal Applied Physics*, 2007. 1001: 113511.
- Dimitrивev. J., Arnaudov. M. and Dimitrov. V., Phase diagram and Infrared-Spectral Investigation of the 2TeO₂-V₂O₅-Na₂O System. *Journal of Solid State Chemistry*, 1981. 38; 55-61.
- Dousti. M.R., Sahar. M.R., Goshal. S.K., Amjad. R.J., and Ariffin. R, Plasmonic Enhanced Luminescence in Er³⁺: Ag Co-doped Tellurite Glass. *Journal of Molecular Structure*, 2013. 1033; 79-83.

- Dousti. M. R, Sahar. M.R., Ghoshal. S.K., Amjad. R J., Samavati. A.R., Effect of AgCl on Spectroscopic Properties of Erbium Doped Zinc Tellurite Glass, *Journal of Molecular Structure*, 2013. 1035; 6-12.
- El-Deen. L. M. S., Al Salhi. M. S., Elkholy. M. M., IR and UV Spectral Studies for Rare Earths-Doped Tellurite Glasses, *Journal of Alloys and Compounds*, 2008. 465; 333-339.
- El-Mallawany. R., Tellurite glasses Part 1: Elastic properties, *Materials Chemistry and Physics*, 1998. 53(2); 93-120.
- El-Mallawany. R., *Tellurite Glasses Handbook: Physical Properties and Data*, CRC Press LLC. 2002.
- El-Mallawany. R., Abdalla. M. D., Ahmed. I. A., New Tellurite Glass: Optical Properties, *Journal Materials Chemistry and Physics*, 2008. 109; 291-296.
- Fares. H., Jlassi. I., Elhouichet. H., Férid. M., Investigations of Thermal, Structural And Optical Properties Of Tellurite Glass With WO₃ Adding, *Journal Non Crystalline Solid*, 2014. 396–397; 1–7.
- Fortes. L. M., Santos. L. F., Goncalves. M. C., Almeida. R. M., Mattarellib. M., Montagna. M., Chiasera. A., Ferrari. M., Monteil. A., Chaussedent. S., Righini. G. C., Er³⁺ Ion Dispersion In Tellurium Oxychloride Glasses, *Optical Materials*, 2007. 29; 503–509.
- Fortes. L. M., Santos. L. F., Goncalves. M. C., Almeida. R. M., The Effects of ZnCl₂ And ErCl₃ on The Vibrational Spectra and Structure of Tellurite Glasses, *Journal Non Crystalline Solid*, 2006. 352; 690-694.
- Fortes. L. M., Santos. L. F., Goncalves. M. C., Almeida. R. M., Preparation And Characterization of Er³⁺-doped TeO₂-Based Oxyhalide Glasses, *Journal Non Crystalline Solid*, 2003. 324; 150-158.

- Hou. Z., Xue. Z., Wang. S., Hu. X., Lu. H., Niu. C., Wang. H., Wang. C. and Zhou. Y., Thermal Stability and Structure of Tellurite Glass. *Key Engineering Materials*, 2012. 512-515; 994-997.
- Ivanova. I., Glass Formation in Oxide-Halide System, *Journal of Material Science*, 1990. 25; 2087-2090
- Jihong. Z., Haizheng. T., Yu. C., Xiujian. Z., Structure, Upconversion and Fluorescence Properties of Er³⁺-Doped TeO₂-TiO₂-La₂O₃ Tellurite glass, *Journal of Rare Earths*, 2007. 25(1); 108-112.
- Jlassi. I., Elhouichet. H., Ferid. M., Chtourou. R., Oueslati. M., Study of Photoluminescence Quenching in Er³⁺-Doped Tellurite Glasses, *Optical Materials*, 2010. 32; 743–747.
- Jlassi. I., Elhouichet. H., Ferid. M., Thermal and Optical Properties of Tellurite Glasses Doped Erbium, *Journal Material Science*, 2011. 46; 806-812.
- Kostka. P., Lezal. D., Poulain. M., Pedlikova. J., Novotna. M., Glass Formation in The PbCl₂-Sb₂O₃-TeO₂ System, *Solid State Phenomena*, 2003. 90-91; 235-240.
- Kumar. G.A., De la Rosa. E., Desirena. H., Radiative And Non Radiative Spectroscopic Properties Of Er³⁺ Ion In Tellurite Glass, *Optics Communications*, 2006. 260(2); 601-606.
- Lin. H., Meredith. G., Jiang. S. B., Peng. X., Luo. T., Peyghambarian. N. and Pun. E. Y., Optical Transitions and Visible Upconversion In Er³⁺ Doped Niobic Tellurite Glass, *J. Appl. Phys*, 2003. 93; 186.
- Liu. Y. H., Chen. H., Chen. D. D., Zhang. Q. Y. and Jiang. Z. H., Infrared -to-Visible Upconversion Emissions in Er³⁺ doped TeO₂-based Oxyhalide Glasses, *Key Engineering Materials*, 2005. 280-283; 953-956.

- Malik. M. S. and Hogarth. C. A., Control of Electrical Conductivity With The Admixture of Chlorine In Copper Tellurite Glasses, *Journal of Materials Science*, 1990. 25; 116.
- Marjanovic. S., Toulouse. J., Jain. H., Sandmann. C., Dierolf. V., Kortan. A. R., Kopylov. N., Ahrens. R. G., Characterization Of New Erbium-Doped Tellurite Glasses And Fibers, *Journal of Non-Crystalline Solids*, 2003. 322; 311–318.
- Mott N., Davis E., *Electronic Process in Non-Crystalline Materials*, Second Edition, Clarendon Press, Oxford, UK, 1979.
- Neindre. L. L., Jiang. S., Hwan. B. C., Luo. T., Watson. J., Peyghambarian. N., Effect of Relative Alkali Content on Absorption Line Width In Erbium-Doped Tellurite Glasses, *Journal Non-Crystalline Solids*, 1999. 255; 97-102.
- Nii. H., Ozaki. K., Herren. M., and Morita M., Up-Conversion Fluorescence of Er³⁺- and Yb³⁺- Doped TeO₂ Based Oxide Glass and Single Crystals, *Journal Luminescence*, 1998. 76-77, 116-119.
- Rosmawati, S. Sidek, H.A.A. Zainal, A.T. and Zobir, H. M.. IR and UV Spectral Studies of Zinc Tellurite Glasses, *J. Applied Sci*, 2007. 7 (20). 3051-3056.
- Sahar M.R. ‘Sains Kaca’. Universiti Teknologi Malaysia Skudai. 1998.
- Sahar,M., and Noordin, N.. Oxychloride Glasses on the TeO₂-ZnO-ZnCl₂ System, *J. Non-Cryst. Solids*, 1995. 184, 137-140.
- Sahar. M.R., Arifin. R., Ghosal. S.K., Effects of Chloride Ion in TeO₂-ZnO-ZnCl₂-Li₂O-Eu₂O₃ Glass System, *Solid State Phenomena*, 2012. 181-182; 383-387.
- Shen. X., Nie. Q., Xu. T., Dai. S., Wang. X., Investigation on Energy Transfer From Er³⁺ to Nd³⁺ in Tellurite Glass, *Journal of Rare Earths*, 2008. 26; 899-903.

- Shen. X., Nie. Q., Xu. T., Dai. S., Li. G., Wang. X. Effect of Ce^{3+} on The Spectroscopic Properties in Er^{3+} Doped $TeO_2-GeO_2-Nb_2O_5-Li_2O$ Glasses, *Journal of Luminescence*, 2007. 126: 273.
- Sudo. S., *Optical Fiber Amplifiers—Materials, Devices, and Applications*, Artech House.1997.
- Sreekanth C. R. P., Sivaramaiah. G., Lakshmana R. J., Gopal. N. O., EPR and Optical Investigations Of Manganese Ions In Alkali Lead Tetraborate Glasses, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2005. 62; 761-768.
- Stambouli. W., Elhouichet. H., Ferid. M., Study Of Thermal, Structural and Optical Properties of Tellurite Glass With Different TiO_2 Composition, *Journal of Molecular Structure*, 2012. 1028; 39-43.
- Tincher. B., Massera. J., Petit. L., Richardson. K., Viscosity Properties of Tellurite-Based Glasses, *Materials Research Bulletin*, (2010). 45(12), 1861-1865.
- Uhlmann. D. R. and Kreidl. N. J., *Glass: science and technology*, Academic Press: New York,, vol 1; 1983.
- Upender. G. and Mouli. V. C., Optical, Thermal and Electrical Properties of Ternary TeO_2-WO_3-PbO Glasses, *Journal of Molecular Structure*, 2011. 1006; 159-165.
- Upender, G., Ramesh, S., Prasad, M., Sathe, V. G., Mouli, V. C., Optical Band Gap, Glass Transition Temperature and Structural Studies of $(100-2x)TeO_2-xAg_2O-xWO_3$ glass system, *Journal of Alloys and Compounds*, 2010. 504; 468-474.

Wang. Y.H., Osaka. A., Miura. Y., Takada. J., Oda. K. and Takahashi. K., Glass Forming Range and Properties of New Oxyhalide Glasses in The System TeO_2 - PbO - PbCl_2 , *Material Science Forum*, 1988. 32-33; 161-166.

Weber. M. J., Myers. J. D., and Blackburn. D. H., Optical Properties of Nd^{3+} In Tellurite and Phosphotellurite Glasses, *Journal Applied Physics*, 1981. 52, 2944.

Zhang. J., Tao. H., Cheng. Y., Zhao X., Structure, Upconversion and Flourescence Properties of Er^{3+} -Doped TeO_2 - TiO_2 - La_2O_3 Tellurite Glass, *Journal of Rare Earth*, 2007. 25; 108.