



UNIVERSITI PUTRA MALAYSIA

**ELASTIC, OPTICAL AND THERMAL PROPERTIES OF TeO₂-ZnO AND
TeO₂-ZnO-AlF₃ GLASS SYSTEMS**

ROSMAWATI BINTI SHAHARUDDIN

FS 2008 9



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By

ROSMAWATI BINTI SHAHARUDDIN

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

August 2008



In The Name of Allah, The Beneficent, The Merciful

Special Dedication

Husband

Othman Bin Jailani

Beloved Children

Liyana Nabilah
Iskandar Najmuddin
Syazana Masturah
Luqman Ul-Hakim

Mom

Rahima Yahya

Dad

Shaharuddin Shamsuddin

Brothers and Sisters



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

**ELASTIC, OPTICAL AND THERMAL PROPERTIES OF $\text{TeO}_2\text{-ZnO}$
AND $\text{TeO}_2\text{-ZnO-AlF}_3$ GLASS SYSTEMS**

By

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August 2008

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This thesis presents the study of binary zinc tellurite, $\text{TeO}_2\text{-ZnO}$ and ternary oxyfluorotellurite, $\text{TeO}_2\text{-ZnO-AlF}_3$ glass system which have been prepared using melt quenching technique. The TeO_2 , ZnO and AlF_3 contents have been changed based on their mole fraction. The physical properties were measured and their amorphous nature was confirmed by x-ray diffraction technique.

Additional increment of ZnO in binary and ternary glass systems caused the decreasing of ultrasonic velocity. The values of velocity in ternary glass system are higher as compared to the values in binary glass system. Addition of fluorine into TeO_2 -based glass system resulted the reduction of Te-O-Te linkages due to a gradual transformation of trigonal bipyramid TeO_4 (tbp) through TeO_{3+1} to trigonal pyramid TeO_3 which decreasing the connectivity of the tellurite glass former network. Similar pattern in elastic moduli in both glass systems was observed where the values decreased linearly.



Both Young's modulus and bulk modulus were related to the cross-linking density with large influence on the propagation of ultrasonic velocities. All glass samples were found to have high cross-link densities. The values of Poisson's ratio lie between 0.1 to 0.2. The elastic properties of these glasses are closely related to the strength of glass networks and structures.

The refractive index of the TeO_2 -ZnO glasses was found to increase from 1.99 – 2.07 for mole fraction of 0.10-0.40 ZnO content with an interval of 0.05. The refractive indices for ternary glass system show an increasing trend in all series of glass and varying between 2.01 – 1.76. The behaviour of the refractive index can be explained in either electron density or polarizability of the ions. In this study, the positions of the fundamental absorption edge shift to higher energy (shorter wavelength) with increasing ZnO content in binary tellurite glasses. The shifting of wavelength was related to the amount of production of the non-bridging oxygen (NBO) in TeO_2 -ZnO glass system and the effect of fluorine ions replacement to the non-bridging oxygen ions in ternary glass system.

Experimental data shows that the values of E_{opt} decreased with increasing content of ZnO for both glass systems where the values of E_{opt} for binary glass system varied from 2.34 eV to 1.88 eV for indirect allowed transition. The variation of E_{opt} with glass composition can be explained by suggesting that the non-bridging oxygen ion content increases with increasing ZnO content, shifting the band edge to lower energies and leading to a decrease in the value of E_{opt} . FTIR spectra revealed broad, weak and strong absorption bands in the investigated range of wavenumbers from 4000 to 400 cm^{-1}



which associated with their corresponding bond modes of vibration and the glass structure. For pure TeO_2 glass, the strong absorption band is located at 626 cm^{-1} . The addition of ZnO to TeO_2 shifted the major band from 626 cm^{-1} to the band at around 669 cm^{-1} . AlF_3 greatly affects the binary structure of TeO_2 - ZnO glasses by shifting the absorption bands to the lower wavenumbers.

The thermal properties such as thermal expansion coefficient, glass transformation temperature, T_g , acoustic Debye temperature and softening temperature were collected for both glass systems. Generally, the increase of the thermal expansion coefficient in both glass systems might be due to the changes of the coordination number of TeO_2 from 4 to 3 and associated with the creation of non-bridging oxygen that caused the decrease in rigidity. Experimental results showed that values for glass transition temperature were closely related to the chemical bond in the system. The decrease in the glass transition temperature, acoustic Debye temperature and softening temperature values implies that number of bridging oxygen group decreases. This is mainly due to the addition of ZnO which weaken the bond between each atom sample (increases the number of NBOs atom). The bond easier to break and hence the T_g of the sample decreased. The fluorine ions tend to break up the strong TeO_2 covalent network of the glass by forming ionic, non-bridging M-F bonds, where M is a metal cation.



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

**SIFAT-SIFAT ELASTIK, OPTIK DAN TERMA BAGI SISTEM
KACA $\text{TeO}_2\text{-ZnO}$ DAN $\text{TeO}_2\text{-ZnO-AlF}_3$.**

Oleh

ROSMAWATI BINTI SHAHARUDDIN

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Tesis ini mempersembahkan kajian mengenai sistem kaca binari zink tellurit, $\text{TeO}_2\text{-ZnO}$ dan sistem kaca ternari oksiflorotellurit, $\text{TeO}_2\text{-ZnO-AlF}_3$ yang telah di sediakan melalui teknik pelindapan leburan. Kandungan TeO_2 , ZnO dan AlF_3 berubah dalam setiap siri berdasarkan pecahan mol. Sifat amorfus bahan kaca telah dipastikan terlebih dahulu dengan menggunakan teknik pembelauan sinar-X sebelum pengukuran ciri-ciri fizikalnya dilakukan.

Penambahan peningkatan ZnO dalam sistem kaca binari dan ternari menyebabkan pengurangan halaju. Nilai-nilai halaju dalam sistem kaca ternari adalah lebih tinggi jika dibandingkan dengan nilai-nilai halaju dalam sistem kaca binari. Penambahan fluorin ke dalam sistem kaca berasaskan tellurit menghasilkan pengurangan pautan Te-O-Te disebabkan transformasi trigonal bipiramid TeO_4 (tbp) melalui TeO_{3+1} ke trigonal piramid TeO_3 , mengurangkan hubungan rangkaian kaca pembentuk tellurit. Corak yang



sama diperhatikan di dalam modulus elastik bagi kedua-dua sistem kaca, di mana nilai-nilainya mengurang secara linear. Kedua-dua modulus Young dan modulus pukal adalah berkaitan dengan ketumpatan pemaualsilang yang sangat mempengaruhi perambatan halaju ultrasonik. Kesemua sampel kaca didapati mempunyai ketumpatan pemaualsilang yang tinggi. Nilai-nilai nisbah Poisson adalah diantara 0.1 dan 0.2. Sifat-sifat kenyal kesemua kaca ini adalah berkait rapat dengan struktur dan kekuatan rangkaian kaca.

Indeks biasan kaca $\text{TeO}_2\text{-ZnO}$ didapati meningkat daripada 1.99 – 2.07 untuk pecahan mol 0.1 – 0.4 kandungan ZnO dengan sela 0.05. Indeks biasan sistem kaca ternari menunjukkan peningkatan dalam semua siri dan berubah di antara 2.01 – 1.76. Sifat indeks biasan boleh diterangkan samada melalui ketumpatan elektron atau kebolehkutuban ion. Di dalam kajian ini, kedudukan pinggir penyerapan fundamental menganjak ke tenaga yang lebih tinggi (jarak gelombang yang lebih rendah) dengan peningkatan kandungan ZnO di dalam kaca binari tellurit. Anjakan jarak gelombang adalah berkait dengan jumlah penghasilan oksigen tanpa titian (NBO) di dalam sistem kaca $\text{TeO}_2\text{-ZnO}$ dan kesan penggantian ion-ion florin kepada ion oksigen tanpa titian di dalam sistem kaca ternari.

Data eksperimen menunjukkan nilai E_{opt} mengurang dengan peningkatan kandungan ZnO untuk kedua-dua sistem kaca di mana nilai E_{opt} untuk sistem kaca binari berubah daripada 2.34 eV ke 1.88 eV untuk transisi tidak langsung yang dibenarkan. Perubahan E_{opt} dengan komposisi kaca boleh di terangkan dengan mengandaikan bahawa kandungan ion oksigen tanpa titian meningkat dengan kandungan ZnO, menganjak pinggir jalur ke tenaga yang lebih rendah dan seterusnya mengurangkan nilai E_{opt} .



Spektra FTIR menunjukkan jalur-jalur penyerapan yang lebar, lemah dan kuat di dalam julat penyiasatan jarak gelombang dari $4000 - 400 \text{ cm}^{-1}$ yang mana menghubungkan jalur-jalur yang ditentukan berdasarkan mod-mod getaran ikatan dengan stuktur kaca. Untuk kaca TeO_2 , jalur penyerapan utama terletak dilokasi 626 cm^{-1} . Penambahan ZnO ke TeO_2 menganjak jalur utama daripada 626 cm^{-1} ke jalur lebih kurang 669 cm^{-1} . Kehadiran AlF_3 sangat mempengaruhi struktur binari kaca $\text{TeO}_2\text{-ZnO}$ dengan menganjak jalur penyerapan ke nombor gelombang yang lebih kecil.

Sifat-sifat terma seperti pekali pengembangan terma, suhu transisi kaca, T_g suhu akustik Debye dan suhu pelembutan telah dikumpulkan untuk kedua-dua sistem kaca. Pada umumnya, peningkatan pekali pengembangan terma di dalam kedua-dua sistem kaca mungkin disebabkan perubahan nombor koordinasi TeO_2 daripada 4 kepada 3 dan ia berhubungkait dengan penghasilan oksigen tanpa-titian yang menyebabkan pengurangan ketegaran. Keputusan eksperimen menunjukkan bahawa nilai-nilai suhu transisi kaca adalah berkait rapat dengan ikatan kimia di dalam sistem. Pengurangan nilai-nilai suhu transisi kaca, suhu akustik Debye dan suhu pelembutan menunjukkan bahawa bilangan kumpulan oksigen titian berkurangan. Ini disebabkan oleh penambahan ZnO yang melemahkan ikatan antara setiap sampel atom (peningkatan bilangan atom NBO). Ikatan lebih mudah putus dan akhirnya mengurangkan T_g . Ion-ion fluorin cuba untuk memutuskan rangkaian kovalen kaca TeO_2 yang kuat dengan membentuk ikatan ionik tanpa titian M-F, di mana M adalah kation logam.



ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to Allah swt, the Creator of the Universe, for His blessings and consent, had granted me strength and perseverance till the completion of my thesis within the allocated time frame. ‘Selawat’ and ‘Salam’ to the Prophet Muhammad, Peace upon him, his family and his companion.

I have always admired this statement from the Al-Quran: “*A hundred times, everyday, I remind myself, that my inner and outer life is based on the labors of others to give in the same measure as I have received and am still receiving*”. This research work is also the result of the support and encouragement from many whom I would like to acknowledge in the process of getting a PhD degree.

First of all, I am greatly indebted to my advisor, Professor Dr Sidek Hj Abd Aziz who has always been a constant source of inspiration to me. He encouraged me to be a better researcher and was patient enough during my hard times. Without his guidance I would never have been able to complete my research. My utmost appreciation for all the emotional support, care and advice from him. Also to Associate Professor Dr Zainal Abidin Talib and Professor Dr Mohd Zobir Hussein, I am very thankful for their valuable comments and for being members of my advisory and reading committee.

I, hereby, also extend my highest thanks to Professor Dr Sidek Hj Abd Aziz, Professor Dr W Mahmood Mat Yunus, Associate Professor Dr Wan Mohd Daud Wan Yusoff,



Associate Prof Dr Azmi Zakaria, Dr Mahdi Abd Wahab, Professor Dr Mohd Yusof Sulaiman, Associate Professor Dr Norhana Yahya and Professor Dr Abd Halim Shaari who have passed me with excellent grades in my compulsory PhD papers/courses.

To my employer, The Ministry of Education of Malaysia, thank you for the financial support which has made this work possible and to The Ministry of Science, Technology and Innovation of Malaysia who funded this research project under the IRPA Research Program (54275/54061). My thanks also go to the past and present Directors of Institut Perguruan Teknik, for their support. Added to the list is the editorial board of international publications, “Journal of Applied Sciences”, who accepted and acknowledged my papers into their journal.

I would like to express my deepest gratitude to my friends, Mr Hamezan Muhammad, Mr Noor Azhar Mohd Sayuti, Dr Khamirul Amin Matori, Dr Halimah Mohamed Kamari and Associate Prof Dr Jumiah Hassan, for without their help and support I could never be at this place I am today. I am also thankful to Associate Prof Dr Norhana for her advice, help and support for the meaningful conversations during the times of my personal hardship. I would also like to thank my colleagues, especially Mdm Nordiana Mohd Yusof, Mdm Norfazilah Jaafar Sidek, Mdm Suzaini Sihar and Mdm Nurul Asyikin Abd Hamid for being my dearest friends who had helped me from the start till the present.

I am grateful to my family, husband, Othman bin Jailani and children, Liyana Nabilah, Iskandar Najmuddin, Syazana Masturah and Luqman Ul-Hakim who have supported all



of my decisions and for being so understanding with my work. Without their love, support and encouragement I could have never reached this point.

In the course of this work, there have been many people who had kindly assisted me with their knowledge and experience in using various techniques and equipment. I would like to thank Miss Yusnita Othman and Mdm Wan Yusmawati Wan Yunus for their assistance with the X-Ray diffraction and thermal expansion data collections and data analysis. I would also like to thank Mdm Rosnah Nawang, the science officer of Institut Teknologi Maju for her assistance with the FTIR experiments. My thanks also go to Mdm Noraini Mohd Ain for her assistance in SEM and EDX studies which were performed at the Institute of Bioscience.

Finally, I want to thank all the other people whose names are not listed here, for their direct and indirect involvement in dealing with my thesis work.



I certify that an Examination Committee has met on 19th August 2008 to conduct the final examination of Rosmawati bt Shaharuddin on her Doctor of Philosophy thesis entitled “Elastic, Optical and Thermal Properties of TeO₂-ZnO and TeO₂-ZnO-AlF₃ Glass Systems” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee were as follows:

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DECLARATION

I declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

ROSMAWATI BT SHAHARUDDIN

Date:



TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	vi
ACKNOWLEDGEMENTS	ix
APPROVAL	xiii
DECLARATION	xiv
LIST OF TABLES	xviii
LIST OF FIGURES	xxi
LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS	xxxii
CHAPTER	
1 INTRODUCTION	1
1.1 General Introduction	1
1.2 Application of Tellurite Glass in Fibre Optics	4
1.3 Problem Statements	5
1.4 Research Objectives	7
1.5 Chapter Organisation	8
2 LITERATURE REVIEW	11
2.1 Introduction	11
2.2 Nature of Glass	11
2.3 General Properties of Tellurite Glass	13
2.3.1 Structure of Tellurite Glasses	13
2.3.2 Formation Range and Bonding Nature in Tellurite Glasses	17
2.4 Ultrasonic Studies on Tellurite Glass	21
2.5 Optical Studies on Tellurite Glass	25
2.5.1 Refractive Index	25
2.5.2 Optical Absorption	25
2.5.3 Infrared Absorption	27
2.6 Thermal Studies on Tellurite Glass	30
2.7 Summary	31
3 THEORY	32
3.1 Introduction	32
3.2 Some Fundamental Theories of Glass Structure and Glass Formation	32
3.2.1 Zachariasen's Random Network Theory	32
3.2.2 Network Former and Network Modifier	35
3.2.3 Structural Model	40
3.3 Density and Molar Volume	44



3.4	Elastic Properties	47
3.4.1	Stress and Strain	48
3.4.2	Relationship between Ultrasonic Velocity and Elastic Moduli	54
3.4.3	Qualitative Analysis of Elastic Properties	58
3.5	Optical Properties	68
3.5.1	Refractive Index, Polarization and Molar Refractivity	69
3.5.2	Optical Absorption	73
3.6	Thermal Properties	83
3.6.1	Thermal Analyses of Glasses	83
3.6.2	Thermal Expansion	84
3.6.3	The Glass Transition	85
3.6.4	Thermal Stability	90
3.6.5	Acoustic Debye and Softening Temperature	91
3.7	Summary	93
4	EXPERIMENTAL TECHNIQUES	94
4.1	Introduction	94
4.2	Glass Sample Preparation Method	94
4.3	X-Ray Diffraction Analysis	99
4.4	Density and Molar Volume Determination	99
4.5	Ultrasonic Properties	101
4.5.1	Ultrasonic Transduction	101
4.5.2	Quartz Piezoelectric Transducer	102
4.5.3	Acoustic Bonding Agent	103
4.5.4	Ultrasonic Method of Measurement	104
4.5.5	The MBS-8000 System	105
4.6	Optical Properties	108
4.6.1	Refractive Indices	109
4.6.2	Optical properties in the Ultraviolet Region	110
4.6.3	Fourier Transform Infrared Spectroscopy (FTIR)	113
4.7	Thermal Properties Method of Measurement	116
4.7.1	Thermal Expansion Coefficient	116
4.7.2	Glass Transition Temperature	117
4.7.3	Principle of Differential Thermal Analysis (DTA)	119
4.8	Summary	120
5	RESULTS AND DISCUSSION	121
5.1	Introduction	121
5.1.1	Structural Model for Tellurite Glasses	126
5.1.2	Chemical Compositions Analysis	129
5.1.3	Glasses Samples	134
5.1.4	X-Ray Diffraction Analysis on Zinc Tellurite and Oxyfluorotellurite Glasses System	137
5.2	Density and Molar Volume of Zinc Tellurite Glasses	143



5.2.1	The Influence of Minor Constituents	145
5.2.2	The Effect of Annealing	147
5.3	Molar Volume of Zinc Tellurite Glasses	147
5.4	Elastic Properties of Zinc Tellurite Glass	150
5.4.1	Velocity of Wave Propagation	150
5.4.2	Elastic Moduli	152
5.4.3	Fractal Bond Connectivity	158
5.4.4	Quantitative Analysis of Zinc Tellurite Glasses System	161
5.5	Optical Properties of Zinc Tellurite Glasses	173
5.5.1	Refractive Indices	175
5.5.2	Ultraviolet Absorption Edge	178
5.5.3	FTIR Spectral Studies	183
5.5.4	Infrared Theoretical Consideration for Zinc Tellurite Glasses	189
5.6	Thermal Properties of Zinc Tellurite Glasses	190
5.6.1	Thermal Expansion Coefficient, α_{th}	190
5.6.2	Glass Transition Temperature	192
5.6.3	Acoustic Debye and Softening Temperature	194
5.7	Density and Molar Volume of Oxyfluorotellurite Glasses	197
5.8	Elastic Properties of Oxyfluorotellurite Glasses	203
5.8.1	Velocity of Wave Propagation	203
5.8.2	Elastic Moduli	211
5.8.3	Fractal Bond Connectivity	218
5.9	Optical Properties of Oxyfluorotellurite Glasses	223
5.9.1	Refractive Indices	223
5.9.2	Ultraviolet Absorption Edge	227
5.9.3	FTIR Spectral Studies	244
5.10	Thermal Properties of Oxyfluorotellurite Glasses	254
5.10.1	Thermal Expansion Coefficient, α_{th}	254
5.10.2	Glass Transition Temperature	257
5.10.3	Acoustic Debye and Softening Temperature	260
5.11	Summary	265
6	CONCLUSIONS	269
6.1	Suggestions	272
	REFERENCES	273
	APPENDICES	284
	BIODATA OF THE STUDENT	293
	LIST OF PUBLICATIONS	295



LIST OF TABLES

Table		Page
2.01	Distances between components in structure of α -TeO ₂	14
3.01	Characteristics of Q _n units	44
5.01	Mole fraction and weight percentage of components for zinc tellurite glasses, (TeO ₂) _{1-x} (ZnO) _x	122
5.02	Mole fraction and weight percentage of components for oxyfluorotellurite glasses, (TeO ₂) _x -(ZnO) _y -(AlF ₃) _z	123
5.03	Fraction of oxygen type (BO and NBO) for ZnO _x (TeO ₂) _{1-x} glass system	127
5.04	BO and NBO per tetrahedra for ZnO _x (TeO ₂) _{1-x} glass system	128
5.05	Chemical compositions from three sources	130
5.06	EDX data of glass compositions and the contamination of alumina compositions	136
5.07	Density and molar volume of zinc tellurite glasses, (TeO ₂) _{1-x} (ZnO) _x	144
5.08	Comparison of ZnO-TeO ₂ glasses preparation techniques	146
5.09	Ultrasonic velocities and elastic moduli of zinc tellurite glasses, (TeO ₂) _{1-x} (ZnO) _x	153
5.10	Microhardness of (ZnO) _x (TeO ₂) _{1-x} glass system	158
5.11	Fractal bond connectivity of (ZnO) _x (TeO ₂) _{1-x} glass system	160
5.12	Regression analysis of the variables (density, ρ ; molar volume, V ; longitudinal and shear ultrasonic velocities, v_l , v_s ; elastic moduli, L , G , K , E ; Poisson's ratio, σ ; microhardness, H and elastic internal energies, Mv_l , Mv_s)	162



5.13	Bond length (r), first order stretching force constant (F), coordination number (n_f) of the oxides TeO_2 and ZnO and n_c	165
5.14	Average crosslink density (n_c^-), Young's modulus (E), shear modulus (G), (E/G) ratio	166
5.15	Glass composition, calculated values for bulk modulus (K_{bc}), ratio of (K_{bc}/K_{exp}), number of bonds per unit volume (N_b) and average stretching force constant (F)	168
5.16	Glass composition, average crosslink density, ring diameter (l) and theoretical Poisson's ratio (σ_{th})	168
5.17	Theoretical elastic moduli of ZnO-TeO_2 glasses	170
5.18	Packing density (V_t), dissociation energy (G_t), elastic moduli (E_m , K_m and G_m) and Poisson's ratio, σ , calculating according to Makishima and Mackenzie model of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glasses	172
5.19	Experimental elastic moduli (E_e , G_e , K_e), bond compression model (E_{bc} , G_{bc} , K_{bc}) and Makishima and Mackenzie (E_m , G_m , K_m) for Young's, shear and bulk modulus, respectively and Poisson's ratio (σ_e , σ_{bc} , σ_m) of $(\text{TeO}_2)_{1-x} (\text{ZnO})_x$	174
5.20	Refractive indices, molar refractivity and polarizability of zinc tellurite glasses, $(\text{TeO}_2)_{1-x} (\text{ZnO})_x$	178
5.21	Optical band gap of zinc tellurite glasses, $(\text{TeO}_2)_{1-x} (\text{ZnO})_x$	181
5.22	FTIR peaks position of the $(\text{Zn O})_x (\text{TeO}_2)_{1-x}$ glasses	187
5.23	The theoretical IR band positions compared with the experimental wavenumber for the stretching force constant for the $\text{TeO}_2\text{-ZnO}$ glass system	189
5.24	Transition temperature and thermal expansion of zinc tellurite glasses, $(\text{TeO}_2)_{1-x} (\text{ZnO})_x$	192



5.25	Transition temperature, Debye temperature and softening temperature in Kelvin of zinc tellurite glasses, $(\text{TeO}_2)_{1-x} (\text{ZnO})_x$	195
5.26	Density and molar volume of tellurite oxyfluorotellurite glasses, $(\text{TeO}_2)_x (\text{ZnO})_y (\text{AlF}_3)_z$	198
5.27	Ultrasonic velocities and elastic moduli of tellurite oxy-fluoride glasses, $(\text{TeO}_2)_x (\text{ZnO})_y (\text{AlF}_3)_z$	204
5.28	The variation of ultrasonic velocities due to the addition of AlF_3 in the TeO_2 - ZnO - AlF_3 network	210
5.29	Microhardness of oxyfluorotellurite glass system	219
5.30	Fractal bond connectivity of oxyfluorotellurite glass system	221
5.31	Refractive indices, molar refractivity and polarizability of tellurite oxy-fluoride glasses, TeO_2 - ZnO - AlF_3	224
5.32	Optical band gap of tellurite oxy-fluoride glasses, $(\text{TeO}_2)_x (\text{ZnO})_y (\text{AlF}_3)_z$	235
5.33	FTIR peaks position of the $(\text{TeO}_2)_x(\text{ZnO})_y(\text{AlF}_3)_{1-y}$ glasses	253
5.34	Transition temperature and thermal expansion of tellurite oxy-fluoride glasses, $(\text{TeO}_2)_x (\text{ZnO})_y (\text{AlF}_3)_z$	255
5.35	Transition temperature, Debye temperature and softening temperature in Kelvin of tellurite oxy-fluoride glasses, $(\text{TeO}_2)_x (\text{ZnO})_y (\text{AlF}_3)_z$	261



LIST OF FIGURES

Figure		Page
1.01	The overall picture of the research	9
2.01	Schematic illustration of the change in volume with temperature as a supercooled liquid is cooled through the glass-transition temperature (T_g)	14
2.02	Basic coordination polyhedron in vitreous TeO_2 and in crystalline tellurite and paratellurite	16
2.03	Diagram showing the structural recombination model in tellurite glasses (a) α - TeO_2 , (b) TeO_2 chains, (c) deformation and breaking of the TeO_2 chains by a modifier	16
3.01	Schematic two-dimensional representation of (a) an oxide crystal and (b) a glass of the same chemical composition (A_2O_3) due to Zachariasen	34
3.02	Schematic two-dimensional representation of the microscopic structure of binary oxide glass; (a) composed of basic glass former and glass former; (b) showing the effect of network modifying cations on the network of the glass former	38
3.03	Illustration of the three components of forces acting along the x direction; σ_{xx} is a tensile stress; τ_{xy} and τ_{xz} are shear stresses; τ_{xy} represents a force acting along the x-axis in a plane perpendicular to the y-axis, etc. Similar forces act along the y- and z-axis.	49
3.04	Illustrated definitions of constants of elasticity, (a) Young's modulus; (b) shear modulus; (c) bulk modulus	51
3.05	Force-distance curve illustrating the origin of the elastic modulus	53
3.06	An example of a simple cubic or single crystal, the required elements for isotropic materials are adapted from the simple cubic as illustrated. The directional arrows show the particle direction for the shear waves	57



3.07	The variation of Poisson's ratio. (lateral strain / longitudinal strain) with cross-link density (n_c) for tensile stresses applied parallel to oriented chains. The forces resisting lateral contraction increase with crosslink density	66
3.08	The case of absorption of light through an optical filter includes other process	76
3.09	Schematic illustration of the change in volume with temperature as a supercooled liquid is cooled through the glass-transition temperature (T_g)	86
3.10	Schematic illustration of the experimental determination, by extrapolation, of the fictive temperature (T_f)	87
3.11	Illustration of the change in fictive temperature (or glass transition temperature) with cooling rate (curling rate curve 1 is less than curve 2)	88
3.12	Schematic illustration of the change in specific heat at constant pressure (C_p) on cooling through the glass transition temperature (T_g)	90
4.01	Schematic diagram of glass making process for both binary and ternary tellurite glass samples	98
4.02	Block diagram of the MBS-8000 with all the equipment employed in the ultrasonic measurement	107
4.03	Schematic diagram of ultrasonic measurement process for both types of glass samples	108
4.04	Schematic diagram of the typical spectrophotometer	112
4.05	Schematic diagram of refractive index, optical absorption and FTIR spectroscopy measurement process for both types of glass samples	115
4.06	Schematic DTA trace showing the glass transition, (1), crystallization, (2) and melting (3)	120



5.01	Composition of binary zinc tellurite ($\text{TeO}_2\text{-ZnO}$) and ternary oxyfluorotellurite ($\text{TeO}_2\text{-ZnO-AlF}_3$) glass samples and glass forming region. Glasses are presented with the circle solid point	125
5.02	Fraction of NBO and BO of $\text{ZnO}_x (\text{TeO}_2)_{1-x}$ glass system	128
5.03	BO and NBO per Te for $\text{ZnO}_x (\text{TeO}_2)_{1-x}$ glass system	129
5.04	EDX Analysis of TeO_2 (Technical Grade)	130
5.05	XRD Analysis of TeO_2 (Technical Grade)	131
5.06a	SEM photo for chemical powder of TeO_2	131
5.06b	SEM photo for chemical powder of ZnO	132
5.06c	SEM photo for chemical powder of AlF_3 .	132
5.06d	SEM photo for TeO_2 glass	133
5.06e	SEM photo for binary $\text{TeO}_2\text{-ZnO}$ glass	133
5.06f	SEM photo for ternary $\text{TeO}_2\text{-ZnO-AlF}_3$ glass	134
5.07	Primary network former TeO_2	135
5.08a	XRD pattern of chemical powder of TeO_2 (Technical Grade)	138
5.08b	XRD pattern of Chemical Powder of ZnO (99.9%)	138
5.08c	XRD pattern of Chemical Powder of AlF_3 (97.0%)	139
5.09	XRD patterns of binary zinc tellurite and pure tellurite glass	139
5.10a	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.90$ glass series	140
5.10b	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.85$ glass series	140
5.10c	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.80$ glass series	141



5.10d	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.75$ glass series	141
5.10e	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.70$ glass series	142
5.10f	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.65$ glass series	142
5.10g	XRD patterns of ternary oxyfluorotellurite for $\text{TeO}_2 = 0.60$ glass series	143
5.11	Variation results of glass density as reported by Mochida <i>et al.</i> (1978), Burger <i>et al.</i> (1992) and Mallawany (1993)	146
5.12	Density of ZnO- TeO_2 glasses	149
5.13	Molar volume of ZnO- TeO_2 glasses	149
5.14	Ultrasonic velocities of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glasses	151
5.15	Elastic moduli of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glass series	154
5.16	Poisson's ratio of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glass system	157
5.17	Micro-hardness of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glasses	159
5.18	The fractal bond connectivity, d of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glasses at room temperature	161
5.19	Elastic strain energy of $(\text{ZnO})_x (\text{TeO}_2)_{1-x}$ glass system	163
5.20	(E/G) ratio versus ZnO mole fraction for TeO_2 -ZnO glasses	166
5.21	Agreement between the experimental values of bulk modulus and that calculated using bond compression model.	171
5.22	Agreement between the experimental values of Young's modulus and that calculated using Makishima and Mackenzie's model.	173

