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 TeO_2-ZnO AND TeO_2-ZnO-AlF_3 GLASS SYSTEMS

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ROSMAWATI BINTI SHAHARUDDIN

August 2008

Chairman: **Sidek Hj Abd Aziz, PhD**

Faculty: **Science**

This thesis presents the study of binary zinc tellurite, TeO_2-ZnO and ternary oxyfluorotellurite, TeO_2-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 refactive 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 netrwork 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 TeO_2-ZnO DAN TeO_2-ZnO-AlF_3.

Oleh

ROSMAWATI BINTI SHAHARUDDIN

August 2008

Pengerusi: **Sidek Hj Abd Aziz, PhD**

Fakulti: **Sains**

Tesis ini mempersembahkan kajian mengenai sistem kaca binari zink tellurit, TeO_2-ZnO dan sistem kaca ternari oksiflorotellurit, TeO_2-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 florin 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 pemautsilang yang sangat mempengaruhi perambatan halaju ultrasonik. Kesemua sampel kaca didapati mempunyai ketumpatan pemautsilang 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 TeO_2-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 TeO_2-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 cm^{-1} yang mana menghubungkaitkan 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 TeO_2-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 florin 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 TeO_2-ZnO and TeO_2-ZnO-AlF_3 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:

Hishamuddin Zainuddin , PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Wan Mohd Daud Wan Yusoff, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Halimah Mohamed Kamari, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Md. Rahim Sahar, PhD
Professor
Faculty of Science
Universiti Teknologi Malaysia
(External Examiner)

HASANAH MOHD GHAZALI, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Sidek Hj. Abdul Aziz, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zainal Abidin Talib, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohd Zobir Hussein, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

AINI IDERIS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 13 November 2008

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:

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