



UNIVERSITI PUTRA MALAYSIA

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

ROSMAWATI BINTI SHAHARUDDIN

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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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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 TeO₂-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 TeO₂-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.



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**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.



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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:



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