UNIVERSITI PUTRA MALAYSIA

PHYSICAL CHARACTERIZATION OF LEAD BISMUTH BORATE AND LEAD BISMUTH PHOSPHATE GLASSES

HAMEZAN BIN MUHAMMAD @ AHMAD.

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Master of Science

December 2005

In The Name of Allah, The Beneficent, The Merciful

This Thesis is Dedicated to My Beloved Dad, Mom and Family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

PHYSICAL CHARACTERIZATION OF LEAD BISMUTH BORATE AND LEAD BISMUTH PHOSPHATE GLASSES

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Chairman: Associate Professor Sidek Haji Abdul Aziz, PhD

Faculty: Science

Systematic series of lead bismuth borate ($PbO - Bi_2O_3 - B_2O_3$) and lead bismuth phosphate ($PbO - Bi_2O_3 - P_2O_5$) glasses were prepared using melt quenching technique, where PbO, Bi_2O_3, B_2O_3 and P_2O_5 contents changed in every series based on their weight percentage. Some physical properties were measured and their amorphous natures were confirmed earlier by the X-ray diffraction technique.

The experimental results showed that the density (ρ) of both glasses increased, for examples from 3920 kg/m^3 to 6325 kg/m^3 for A1 – A5 series in $PbO - Bi_2O_3 - B_2O_3$ glasses and from 4331 kg/m^3 to 5698 kg/m^3 for E1 – E5 series in $PbO - Bi_2O_3 - P_2O_5$ glasses. This was due to the replacement of Bi_2O_3 and PbO in the B_2O_3 and P_2O_5 in glassy networks. Additional increment of Bi_2O_3 and PbO in both types of glasses causing more discontinuity and hence, decreased in their rigidity and velocity. Meanwhile,

there was also a similar pattern in elastic moduli in both glass systems, where the values increased at the earlier stage and then decreased subsequently. Both Young's and bulk modulus were related to the cross-linking density with large influence on the propagation of ultrasonic velocities. All glass samples were also found to have crosslink density of 1 and Poisson's ratio ~ 3 which was typical for the B_2O_3 and P_2O_5 glasses.

In optical properties for both types of glasses, it was found that the shifting of wavelength was related to the amount of production of the non-bridging oxygen (NBO). The existence of less disorder in phosphate network contributed to higher values of glass optical band gap (E_{opt}). Conversely, the introduction of PbO and Bi_2O_3 cause great disorder happen in the borate network which results in lower E_{opt} values. In this study, the values of E_{opt} decreased uniformly with increasing content of PbO and Bi_2O_3 for examples from 2.61 eV to 2.25 eV for B1 – B5 series in PbO – Bi_2O_3 – B_2O_3 glasses and from 3.71 eV to 3.06 eV for G1 – G4 series in PbO – Bi_2O_3 – P_2O_5 glasses. The increases in NBOs will be accompanied by an increase in polarizability and refractive index (n). In most cases, the variation of n increases when the molar volume (V_m) decreases, however for PbO – Bi_2O_3 – B_2O_3 glasses, the increasing value of n for an example from 1.62 to 1.86 for C1 – C5 series is accompanied by an increased in V_m. This discrepancy can be explained by assuming the increase in both of the V_m and ρ, was attributed to change occurred in the volume concentration of BO_3 units.

Results from thermal studies of the glass showed that values for glass transition temperature (T_g) was closely related to the chemical bond in the system. For PbO – Bi_2O_3 – B_2O_3 glasses, the ionic bond character became more dominant in the system with the addition of more Pb^{2+} and Bi^{3+} and hence decreases the T_g of sample. However, in PbO – Bi_2O_3 – P_2O_5 glasses, the addition of Pb^{2+} and Bi^{3+} not only failed to weaken the covalent character in P–O–P bonds, but strengthened it further which leads to an increment in T_g values for an example from 309°C to 352°C for F1 – F4 series.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

PENCIRIAN SIFAT FIZIKAL BAGI KACA PLUMBUM BISMUTH BORAT DAN PLUMBUM BISMUTH FOSFAT

Oleh

HAMEZAN BIN MUHAMMAD @ AHMAD

Disember 2005

Pengerusi: **Profesor Madya Sidek Haji Abdul Aziz, PhD**

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Siri sistematik kaca plumbum bismuth borat ($PbO - Bi_2O_3 - B_2O_3$) dan plumbum bismuth fosfat ($PbO - Bi_2O_3 - P_2O_5$) telah disediakan melalui teknik pelindapan leburan, di mana kandungan PbO, Bi_2O_3, B_2O_3 dan P_2O_5 telah berubah dalam setiap siri berdasarkan kepada peratusan berat bahan. Beberapa ciri fizikal telah diukur dan sifat amorfus bahan terlebih dahulu telah disahkan menggunakan teknik pembelauan sinar-X.

Keputusan ujikaji menunjukkan ketumpatan (ρ) bagi kedua jenis kaca telah meningkat, sebagai contoh dari 3920 kg/m^3 ke 6325 kg/m^3 untuk siri A1 – A5 dalam kaca $PbO - Bi_2O_3 - B_2O_3$ dan dari 4331 kg/m^3 ke 5698 kg/m^3 untuk siri E1 – E5 dalam kaca $PbO - Bi_2O_3 - P_2O_5$. Ini berlaku hasil penggantian Bi_2O_3 dan PbO ke dalam rangkaian kaca B_2O_3 dan P_2O_5. Pertambahan Bi_2O_3 dan PbO di dalam kedua-dua jenis kaca, menyebabkan banyak ketidaksinambungan dan dengan itu, telah berlaku penurunan dalam sifat

kekakuan dan halaju. Sementara itu, terdapat juga corak sama dalam modulus elastik bagi kedua-dua sistem kaca, di mana nilai-nilai telah meningkat pada peringkat awal dan kemudiannya menurun. Modulus Young dan pukal adalah berkait kepada ketumpatan pemautsilangan dengan memberi kesan besar ke atas penyebaran halaju ultrasonik. Kesemua sampel kaca mempunyai ketumpatan pemautsilang bersamaan 1 dan nisbah Poisson ~ 3 di mana ini adalah tipikal untuk kaca B_2O_3 dan P_2O_5.

Di dalam pencirian optik untuk kedua-dua jenis kaca, didapati bahawa anjakan jarak gelombang adalah berkait dengan jumlah penghasilan oksigen tanpa titian (NBO). Kewujudan kurang ketidakseragaman dalam rangkaian fosfat telah menyumbang kepada nilai-nilai sela jalur optik (E_{opt}) yang tinggi. Sebaliknya, pengenalan PbO dan Bi_2O_3 menyebabkan lebih ketidakseragaman berlaku di dalam rangkaian borat yang mana menghasilkan nilai-nilai E_{opt} yang rendah. Melalui kajian ini, nilai-nilai E_{opt} telah menurun secara seragam dengan peningkatan kandungan PbO dan Bi_2O_3 sebagai contoh dar 2.61 eV ke 2.25 eV untuk siri B1 – B5 dalam kaca PbO – Bi_2O_3 – B_2O_3 dan dari 3.71 eV ke 3.06 eV untuk siri G1 – G4 dalam kaca PbO – Bi_2O_3 – P_2O_5. Peningkatan dalam NBO disertai dengan kenaikan dalam kebolehkutuban dan indeks biasan (n). Di dalam kebanyakan situasi, variasi n meningkat apabila isipadu molar (V_m) menurun, bagaimanapun bagi kaca PbO – Bi_2O_3 – B_2O_3, peningkatan nilai n sebagai contoh dari 1.62 ke 1.86 untuk siri C1 – C5 telah disertai dengan peningkatan dalam V_m. Ketidakpatuhan ini dapat dijelaskan dengan menganggap peningkatan dalam kedua-dua ρ dan V_m, adalah merujuk kepada perubahan yang telah berlaku di dalam kepekatan isipadu unit-unit BO_3.

Keputusan dari kajian ciri terma untuk kaca telah menunjukkan bahawa nilai-nilai suhu transisi kaca (T_g) adalah berkait rapat dengan ikatan kimia di dalam sistem. Bagi kaca PbO – Bi_2O_3 – B_2O_3, sifat ikatan ionik telah menjadi lebih dominan di dalam sistem dengan penambahan lebih banyak Pb^{2+} dan Bi^{3+} dan menyebabkan penurunan pada T_g sampel. Bagaimanapun, dalam kaca PbO – Bi_2O_3 – P_2O_5, penambahan Pb^{2+} dan Bi^{3+} bukan sahaja telah gagal melemahkan sifat kovalen pada ikatan P–O–P, malah telah menjadikannya lebih kuat di mana membawa kepada peningkatan dalam nilai-nilai T_g, sebagai contoh dari 309°C ke 352°C untuk siri F1 – F4.

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I certify that an Examination Committee met on 5th December 2005 to conduct the final examination of Hamezan Bin Muhammad @ Ahmad on his Master of Science thesis entitled "Physical Characterization of Lead Bismuth Borate and Lead Bismuth Phosphate Glasses" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby 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 or concurrently submitted for any other degree at UPM or other institutions.

HAMEZAN BIN MUHAMMAD @ AHMAD

Date: 28 DEC 2005

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LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimeter
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared
NBO	Non-bridging oxygen
NMR	Nuclear Magnetic Resonance
TMA	Thermo Mechanical Analyzer
UV	Ultraviolet
Vis	Visible
XAFS	X-ray Absorption Fine Structure
XPS	X-ray Photoelectron Spectroscopy
A	Absorbance
B	Bulk modulus
C_p	Heat capacity
C_{11}	Longitudinal modulus
C_{44}	Shear modulus
E	Electric field
E_{opt}	Optical band gap
ΔE	Urbach energy
F	Applied force
J	Current density
L	Length
M	Molecular weight

M_s	Mean velocity
N_A	Avogadro's number
P	Power of light
T	Transmittance
T_c	Glass crystallization temperature
T_g	Glass transition temperature
T_m	Glass melting point
T_f	Fictive temperature
V	Velocity
V_L	Longitudinal velocity
V_s	Shear velocity
V_m	Molar volume
W_{air}	Weight of sample in the air
$W_{acetone}$	Weight of sample in acetone
Y	Young modulus
Z	Number of atoms
Z	Acoustic impedance
c	Speed of light in vacuum
d	Thickness of the sample
f	Frequency
h	Planck's constant
k	Boltzmann's constant
n	Index of refraction
q	Cooling rate
v	Speed of light in a medium

α	Absorption coefficient
α_T	Thermal expansion
δ_{ij}	Kronecker delta
ε	Linear strain
θ	Angle of refraction
θ_D	Debye temperature
λ	Wavelength
ρ	Mass density
$\rho_{acetone}$	Absolute density of acetone
ρ_{sample}	Density of sample
σ	Poisson's ratio
σ	Conductivity
σ	Linear stress
ω	Angular frequency
$\hbar$	Reduced Planck's constant
κ_T	Compressibility