UNIVERSITI TEKNOLOGI MARA

DIELECTRIC, ELASTIC AND OPTICAL PROPERTIES OF $80TeO_2$-(20-x)MnO_2-$x$$Fe_2O_3$ AND $30Li_2O$-$4MoO_3$-(66-x)TeO_2-$x$$V_2O_5$ MIXED OXIDE TELLURITE GLASSES IN THE CONDUCTIVITY ANOMALY REGION

ROSDIYANA BINTI HASHAM@HISAM

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This project has not been submitted to any other academic institution or non-academic institution for any other degree or qualification.

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Name of Student	:	Rosdiyana Binti Hasham @ Hisam
Student ID No.	:	2013446266
Programme	:	Doctor of Philosophy (Science) – AS950
Faculty	:	Applied Sciences
Thesis Title	:	Dielectric, Elastic and Optical Properties of $80TeO_2$-$(20$-$x)MnO_2$-xFe_2O_3 and $30Li_2O$-$4MoO_3$-$(66$-$x)TeO_2$- xV_2O_5 Mixed Oxide Tellurite Glasses in the Conductivity Anomaly Region
Signature of Student	:	....
Date	:	March 2017

ABSTRACT

In this study, two series of mixed oxide tellurite based glasses with composition $80TeO_2$-(20-x)MnO_2-xFe_2O_3 (x = 5 mol% to 20 mol%) and $30Li_2O$-$4MoO_3$-(66-x)TeO_2-xV_2O_5 (x = 0.2–1.2 mol%) were prepared using melt-quenching method to investigate their dielectric, AC conductivity, elastic and optical properties. For the $80TeO_2$-(20-x)MnO_2-xFe_2O_3 glass samples, the dielectric constant showed strong variation with Fe_2O_3 at a frequency ≥10 kHz, where ε' decreased to a minimum value at x = 10 mol% before increasing for x >10%. The decrease in ε' may be attributed to some form of hindrance effect on heavy dipoles caused by the mixed transition-ion effect (MTE). Meanwhile, variation of AC conductivity with Fe_2O_3 showed non-linear increase for x ≤10 mol% before dropping to a minimum at 15 mol% Fe_2O_3. This result is attributed to Anderson localization because of the disorder in the glass system. On the other hand, DC conductivity for the same glass system showed a strong increase for x ≤10 mol% Fe_2O_3 before reaching a saddle-like behavior between 10 mol % ≤x ≤15 mol%, followed by a large increase for x > 15 mol%. Independent longitudinal modulus (C_L), shear modulus (μ) and bulk modulus (K_e) showed increased values for x ≤10 mol% with an anomalous drop at x = 15 mol% Fe_2O_3, followed by a large increase at x > 15 mol%. The anomalous region between 10 mol% ≤x ≤15 mol% coincided with DC conductivity saddle-like region and is suggested to be related to the MTE. Meanwhile, in the same region, optical band gap (E_{opt}) exhibited a maxima, whereas refractive index showed a minima, thereby indicating a variation in polarizability due to changes in concentration of bridging and non-bridging oxygens. For the $30Li_2O$-$4MoO_3$-(66-x)TeO_2-xV_2O_5 glasses, the variation of AC conductivity with V_2O_5 showed a non-linear increase for x ≤0.6 mol% before decreasing to a minimum at 0.8 mol% V_2O_5. The decrease in σ_{AC} is attributed to some forms of blocking effect on Li^+ ions caused by the mixed ionic-electronic (MIE) effect. Meanwhile, dielectric constant showed a general increase for x ≤0.6 before an anomalous decrease at x = 0.8 mol% V_2O_5, which was followed by a large increase at x > 0.8 mol%. The decrease at x = 0.8 mol% coincided with the σ_{AC} drop at the same location. This decrease was also suggested to be related to the MIE that induced a blocking effect, which caused the restricted dipole movement. Meanwhile, DC conductivity showed initial weak increase for x ≤0.6 mol% V_2O_5 before decreasing sharply at x = 0.8 mol% followed by a large increase for x > 0.8 mol%. Independent longitudinal modulus (C_L), shear modulus (μ) and related elastic modulus also exhibited non-linear behavior where their values decreased to a minimum at x = 0.8 mol% before increasing beyond x = 0.8 mol% with the addition of V_2O_5. The decrease in elastic modulus for x ≤0.8 mol% indicated a decrease in stiffness and rigidity of the glasses due to increase in non-bridging oxygen (NBO) contributed by TeO_3 and MoO_3 which weakened the glass network. Subsequently, a large increase at x > 0.8 mol% is suggested to be due the increase in BO contributed by VO_5 together with the formation of strong covalent V-O bond. The anomalous region at x = 0.8 mol% which coincided with the DC conductivity minimum region is suggested to be related to the (MIE) effect. Meanwhile, in the same region, optical band gap (E_{opt}) and refractive index (n) exhibited an off-trend behavior indicating variation in polarizability due to changes in concentration of bridging and non-bridging oxygen.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF RESEARCH

Oxide glasses have been extensively studied because of their unique properties and potential applications in many industries. Interestingly, among the oxide glasses, tellurium oxide-based glasses have drawn technical interest because of their low melting point (Cardillo, Montani, & Frechero, 2010; Mohamed, Ahmad, & Aly, 2012; Reddy & Anavekar, 2008; Saddeek, 2005; Sidkey & Gaafar, 2004; Sidkey, R. El-Mallawany, Nakhla, & El-Moneim, 1997) and high glass forming ability (Sidkey, El-Moneim, & El-Latif, 1999; Souri, 2010; Souri, 2011b). Tellurium oxide-based glasses are non-hygroscopic, unlike phosphate and borate glasses (Mallawany, 1998). These glasses possess a high refractive index (El-Mallawany, Abdalla, & Ahmed, 2008; El-Mallawany, Abousehly, & Yousef, 2000; Khafagy, El-Adawy, Higazy, El-Rabaie, & Eid, 2008b; Lakshminarayana, Yang, & Qiu, 2009; Ovcharenko & Smirnova, 2001; Yousef, Hotzel, & Rüssel, 2007), significant third-order nonlinear optical susceptibility (Xu et al., 2011; Yousef et al., 2007), low maximum phonon energy (Nandi & Jose, 2006), and high dielectric constant (Ahmad, Yousef, & Moustafa, 2006; Kumar & Veeraiah, 1998; Sankarappa, Kumar, Devidas, Nagaraja, & Ramakrishnareddy, 2008), which make these glasses a potential material for optical devices. In addition, tellurite glasses are stable against devitrification, non-toxic, and resistant to moisture for long periods (Gandhi, Mohan, & Veeraiah, 2011). The basic structure of the glass is characterized by a TeO_4 trigonal bipyramid (tbp) and TeO_3 trigonal pyramid (tp) unit structure with a lone pair at the equatorial position (Sabadel et al., 1997). Interestingly, TeO_2 is a recognized conditional glass former, which requires the addition of a modifier oxide, such as alkali, alkaline earth, and transition metal oxides or other glass formers (Moraes et al., 2010; Rajendran, Palanivelu, Chaudhuri, & Goswami, 2003b).

Recent studies on the spectroscopic, mechanical, and electrical properties of tellurite-based glasses mixed with different network formers and modifiers are available in the literature (Azianty, Yahya, & Halimah, 2012; Szu & Chang, 2005;