UNIVERSITI TEKNOLOGI MARA

ELASTIC, CONDUCTIVITY AND DIELECTRIC PROPERTIES OF SODIUM LEAD GERMANATE GLASS AND OPTICAL INTERACTION MECHANISM STUDIES OF ERBIUM DOPED AT GERMANATE ANOMALY REGION

MOHD FAUZI BIN MAULUD

Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Science)

Faculty of Applied Sciences

August 2022

ABSTRACT

A phenomenon known as germanate anomaly has drawn much attention due to the unique characteristic of germanate glass which can cause anomalous behavior in the physical properties of the glass. In this study, glasses with composition $x$$Na_2O$-(99−$x$)[80$GeO_2$:20PbO]-1$Er_2O_3$ (x = 0, 5, 10, 15, 20 and 25 mol%) were prepared by melt-quenching method to elucidate the elastic, optical, dielectric and optical interaction of erbium ions of the glass around the germanate anomaly region. Structural investigation of glass samples was carried out by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy while optical properties by UV-VIS spectroscopy and elastic properties were studied by ultrasonic pulse-echo method. FTIR analysis revealed that the conversion of GeO_4 to GeO_6 which indicates the glass system possesses germanate anomaly characteristic. Elastic measurements showed longitudinal modulus (C_L), shear modulus (μ), bulk Modulus (K) and Young's modulus (Y) increased to maximum value at x=10 mol% but decreased for higher Na_2O addition revealing the elastic nature of the germanate anomaly. The germanate anomaly also affected optical properties where optical energy gap, E_{opt} decreased with the addition of Na_2O up to 10 mol% and slightly increased beyond 10 mol%, while Urbach energy, E_U and refractive index, n showed opposite trends to E_{opt}.. For dielectric and ac conductivity studies, both were increased as Na_2O was substituted into the glass samples up to x = 20 mol% while further substitution of Na_2O for x=25mol% showed both properties decreased. However, for x≤10 mol% the dielectric constant, ε' shows an increase with a slower rate at the germanate anomaly region compared to a larger increase of ε' for x>10 mol% beyond the anomaly while the variation of ac conductivity, σ_{ac} with Na_2O also shows higher dispersion compared to 15 ≤ x ≤ 25 mol% samples. Analysis of conductivity exponent s1 and s2 at low and high frequency region of ac conductivity for 10≤x≤25 mol% indicates CBH mechanism model while for 0≤x≤10 mol% the exponents showed unsystematic variation which did not agree with any single known conductivity mechanism. The results suggest that conversion of GeO_4 to GeO_6 in the germanate anomaly region for 0≤x≤10 mol% affects dielectric properties and ac conductivity of the glass. For x=25 mol% the drop in ac conductivity and dielectric properties is due to the blocking effect involving Pb^{3+} present in the glass network. For absorption studies of erbium in the glass system, the oscillator strength (f_{exp}) of the glass samples exhibits almost all transitions reached the maxima at x = 10 mol% of Na_2O, with the highest value occurs at two hypersensitive transitions (HST) of $^4G_{11/2}$ and $^2H_{11/2}$. Only two Judd–Ofelt parameters (Ω_2 and Ω_6) showed a similar trend with f_{exp} of HST. The variations in f_{exp}, Ω_2 and Ω_6 were explained in terms of the changes in the asymmetry of the ligand fields at Er^{3+} and the changes in covalence nature upon germanate anomaly. The down–conversion (DC) photoluminescence (PL) spectra for the glass series at a 378 nm excitation displayed three emissions bands at 420, 501 and 554 nm due to electron transition from excited energy levels to ground state $^4I_{15/2}$ energy levels of Er^{3+}. The DC emission followed spectroscopic quality factor (SQF) trend where the maxima emission intensity for 554 nm occurred at x = 5mol% while 420 nm and 500 nm at x = 20 mol%. The knowledge gained from these studies may provide useful information towards the development of novel lead germanate glass for various photonic applications.

ACKNOWLEDGEMENT

First and foremost, thanks to ALLAH for giving me the opportunity and health so that I can complete my PhD research and thesis successfully. I would like to express my deep and sincere gratitude to my respected research supervisor Assoc. Prof. Ts. Dr Rosdiyana Hasham@Hisam for her willingness to accept me as a student under her supervision at the end of my journey. I am very grateful for her kindness, support, valuable opinion, advice on my research work and precious time towards me.

My warm regards to my respected former supervisor Prof. Dr. Ahmad Kamal Hayati Yahya. His wisdom, dedication, knowledge and valuable opinion throughout fruitful discussions contribute greatly to the completion of this project. I would always appreciate all of his contributions of time, ideas and patience. Also, I am truly thankful for the opportunities he had provided me and I have learned a lot.

My grateful appreciation goes to all my co–supervisors, Prof. Dr. Halimah Mohamed Kamari (UPM) and Dr. Ezza Syuhada Sazali (UTM) for countless suggestions and providing necessary laboratory facilities as well as assistance in carrying out the present project.

I feel pleasure in extending my thanks to my colleagues and friends for sharing their ideas and motivation throughout this project. I also thank all the laboratory staff for their help and cooperation. The financial support provided by the Universiti Teknologi Mara (UiTM) and Ministry of Higher Education through staff scholarship and research grant are also gratefully acknowledged and appreciated.

Finally, this thesis is dedicated to my beloved parents and siblings. Without their endless prayers, unconditional love and encouragement, it might be impossible for me to achieve my success. Special thanks to my wife and children who are always enriched my life with their patience, sacrifice and constant support behind me at every stage of my personal and academic life, which became my true source of strength and enthusiasm. I love you all.

Alhamdulillah and thank you.

TABLE OF CONTENTS