

ABSTRACT

This study synthesized three unique quaternary glass systems: $V_2O_5-Na_2O-ZnO-P_2O_5$ (VNZP), $Bi_2O_3-BaO-V_2O_5-P_2O_5$ (BBVP) and $Bi_2O_3-Fe_2O_3-V_2O_5-P_2O_5$ (BFVP) via the standard melt-quenching method, and systematically modified each by variable doping to observe the material structure and optical, dielectric, electrical, mechanical, and thermal properties. The focus was to have some precise structure-property correlations to determine the effects of compositional tuning to functional performance to application in optoelectronics, high-temperature dielectrics and energy-related devices. X-ray diffraction (XRD) structural analysis established that all compositions are predominantly amorphous, as evident in the broad diffuse halo, with nanocrystalline phases in dopant-rich samples detected and quantified through Rietveld refinement. Systematic phosphate- and vanadate-based structural unit modifications were systematically characterized optically using Raman and Fourier-transform infrared (FTIR) spectroscopy, where additions of V_2O_5 favoured network depolymerization. UV-visible absorption spectroscopy revealed that the optical band gap (E_{opt}) reduced systematically in a consistent way, and Urbach energy (E_u) increased, suggesting increased structural disorder and increased density of defect states. Composition-dependent changes in the refractive index, molar polarizability and extinction coefficient demonstrated that the optical performance could be tuned to deliver photonic applications. Different behaviours were shown in the dielectric analysis in all three systems. In VNZP, the dielectric constant (ϵ') and dielectric loss (ϵ'') were both frequency dependent and temperature dependent, where the former declined with frequency and rose with temperature. In electric modulus scaling, non-exponential behaviour was interpreted as temperature-independent and (relatively) composition-dependent relaxation, with the exponent ($n < 1$) in the Bergman representation of relaxation proving to be non-Debye behaviour. BBVP glasses had the same trends, with scaling behaviour that was independent of temperature and composition and relaxation that depends on the re-organization of structure. In BFVP, ϵ' increased up to 15 per cent at 413 K at low frequencies and was thermally stable; ϵ'' revealed optimal dipolar relaxation at $x = 0.3$. The activation energy of dielectric relaxation decreased by 0.67 eV ($\times 0.1$) to 0.49 eV ($\times 0.4$), and the electric modulus spectra were consistent with the lack of Debye relaxation in all systems. Electric conductivity measurements showed that the AC conductivity was correlated with a modified correlated barrier hopping (CBH) model, and DC conductivity showed a flux in ionic conduction to small-polaron hopping with the

increased temperature and the doping density. The addition of Bi_2O_3 led to increased DC conductivity because of reduced hopping distances and the high density of defect pairs. The assessment of mechanical properties was done both at the micro- and nanoscale. Vickers microhardness (H_v) declined systematically with increasing concentration of V_2O_5 in the VNZP series, consistent with a progressively softer, less rigid network that is formable but less ideal in higher-durability applications. In this series, too, there was a sharp indentation size effect (ISE); the value of H_v was nearly linearly dependent upon the load applied. Conversely, both the micro- and nano hardness of BBVP and BFVP glasses monotonically enhanced with higher Bi_2O_3 content because of the packing density of the network, a decrease in the number of non-bridging oxygens and the creation of robust Bi–O–P/Bi–O–V linkages. Nano-mechanical properties, determined via the Oliver and Pharr method with a Continuous Stiffness Measurement (CSM) nano-indenter, confirmed increases in instrumented hardness (HIT) and elastic modulus (EIT). In the case of BBVP, fracture toughness (K_{IC}) and stored elastic strain energy (U_r) increased with Bi_2O_3 loading and increased elastic constants were confirmed by ultrasonic pulse 2D echo measurements.

Thermal stability, determined by Differential Scanning Calorimetry (DSC), increased consistently with Bi_2O_3 incorporation across the BBVP and BFVP series, with systematic rises in glass transition temperature (T_g), crystallisation onset temperature (T_c), and peak crystallisation temperature (T_p). The T_g increased by 34% at 35 mol% Bi_2O_3 , showing that cross-linking occurred in the network through strong Bi–O bonding, enhancement of the network cross-link density and decreased tendency to devitrify. The overall findings show that careful compositional engineering, especially via Bi_2O_3 enrichment, is capable of optimising mechanical strength, dielectric stability, electrical transport, optical tunability, and thermal resistance all at once. The VNZP glasses have increased formability, BBVP glasses are superior in mechanical and thermal resilience, and BFVP glasses are stiff with the added property of improved dielectric. These results form a strong foundation to build the next generation of optoelectronic devices, thermally stable dielectrics, mechanically robust optical windows and energy-storage interfaces to future electronic, photonic and sustainable energy technologies.