Influence of Chemical Bonding and Physical Properties on the Nonlinear Optical Properties of La^{3+}-Doped Tellurite-Zinc Glasses

J L Clabel H[1], J V P Valverde[1], and C R Mendonça[1]

[1]*São Carlos Institute of Physics, University of São Paulo, São Carlos, Brazil*
Contact Email: jclabel@ifsc.usp.br

Tellurite glasses are highly valued in optoelectronics for their unique electronic structures and processing versatility. They exhibit high refractive indices, low phonon energies, and broad infrared transmittance. Incorporating La_2O_3 into TeO_2-ZnO (TZ) glass compositions results in high-density, high surface hardness, and good transparency, making lanthanum (La)-containing glasses valuable in various fields, from optics and electronics to specialty glass manufacturing. A series of TeO_2-ZnO-La_2O_3 (TZL) glasses were fabricated with increasing fractions of La_2O_3 using the melt-quenching technique. The relationship between the nonlinear optical properties and the glass structures, associated with the chemical bonding and physical properties, was investigated. The chemical bonding was analyzed using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Density increased from 5.469 g/cm^3 (TZL0) to 5.585 g/cm^3 (TZL9), and direct bandgap ($E_{\text{gap}}^{\text{dir}}$) values increased from 3.52 eV (TZL0) to 3.62 eV (TZL9). The nonlinear refractive index (n_2) was measured over a wide wavelength range (590–1500 nm) using the femtosecond Z-scan technique. The nonlinear refractive index increased with La_2O_3 content, from an average of 0.21×10^{-18} m^2/W (TZL0) to 0.65×10^{-18} m^2/W (TZL9) at 600 nm. The optical nonlinearity of these tellurite glasses increased as the stretching Raman band and O 1s core level spectra (XPS) of Te^{4+}-O_{ax} or bridging oxygen (BO) in TeO_4 decreased, while the stretching band of Te^{3+}-O or non-bridging oxygens (NBOs) in TeO_3 increased. This indicates that the amount of TeO_3 units or NBO was deeply related to the n_2 value, consistent with theoretical calculations showing higher hyperpolarizabilities for TeO_3 compared to TeO_4 units. When trivalent cations (La^{3+}) were doped into the TeO_2–ZnO binary network system, the formation of TeO_{3+1} structures with Zn^{2+} modifier cations created additional environments for La^{3+}. These environments increased the possible bond configurations for lone-pair electrons, favoring the formation of NBOs. Therefore, the high nonlinear refractive index and polarizability underscore the potential of these glasses for advanced nonlinear optical (NLO) device applications.

Acknowledgements: The authors acknowledge financial support from the Brazilian Institutions: São Paulo Research Foundation (FAPESP) under the grant 2020/04835-3, 2018/11283-7, and 2021/11484-5, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Código de Financiamento 001, Air Force Office of Scientific Research – AFOSR (FA9550-23-1-0664) and US ARMY (W911NF2110362).