Correlation between tungsten coordination, structure, and optical properties of P_2O_5–WO_3–Na_2O glasses

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Phosphate-based glasses have attracted significant attention as functional materials due to their low melting temperatures, high solubility of rare-earth elements, and flexible glass network structures. In such glasses, tungsten may behave as either a network former or a network modifier, giving rise to distinct structural units, such as tetrahedral WO_4 and octahedral WO_6 species. The coexistence and possible interconversion between tetrahedral and octahedral WO_x units significantly affect the short-range order of the glass network, which can be reflected in characteristic features of infrared (IR) and Raman spectra, as well as in the photoluminescence properties of the materials. The incorporation of rare-earth ions, namely Eu^{3+}, into tungsten-containing phosphate glasses further expands their functional potential.

In the present work, a series of glasses in the P_2O_5-WO_3-Na_2O-Eu_2O_3 system was prepared to elucidate the effect of WO_3 on the structural and luminescence properties of the glasses. Detailed IR and Raman spectroscopic analyses were performed to identify changes in phosphate and tungstate structural units. The presence of WO_6 units is confirmed throughout the entire compositional range, while the relative contribution of WO_4 groups increases with WO_3 content. This result indicates a coexistence of different tungsten-oxygen polyhedra and progressive modification of the glass network. Diffuse reflectance analysis also revealed the formation of absorption bands associated with WO_4 and WO_6 units, and a pronounced reduction in both direct and indirect optical band gaps, even at low WO_3 concentrations. The peculiarities of the Eu^{3+} ions' emission have been used to evaluate the influence of tungsten-related species on excitation energy transfer and luminescence efficiency. The evolution of photoluminescence excitation spectra and the increase in the asymmetry ratio with WO_3 content indicate a growing distortion of the Eu^{3+} local environment, consistent with phosphate network depolymerization and an increasing participation of tungsten-oxygen units. This behavior reflects significant changes in network connectivity and electronic structure induced by tungsten incorporation into the glass network.

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