IMPACT OF STRUCTURE COMPLEXITY ON OPTOELECTRONIC AND NON-LINEAR OPTICAL PROPERTIES

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Chalcogenide crystals are a unique class of materials distinguished by their complex anion substructures, often consisting of up to eight chalcogen atoms. These intricate arrangements significantly influence the crystals' optoelectronic characteristics and nonlinear optical (NLO) behaviors. The present study examines the relationship between structural complexity and the physical properties of quaternary compounds. By altering the chemical composition and employing laser irradiation, researchers have demonstrated the ability to precisely tune the optical properties across an expansive spectral range, which is of critical importance for tailoring materials to specific optoelectronic applications.

A transition from ternary to quaternary structures has shown a marked enhancement in NLO efficiency, primarily due to the increased density of NLO-active units such as chalcogen-centered tetrahedra. These units exhibit high polarizability and non-centrosymmetric geometries, making them highly effective for second and third harmonic generation (SHG and THG). Synthesis techniques like the Bridgman–Stockbarger method and the gradient freeze technique have proven essential in cultivating high-quality, defect-minimized single crystals. Such advancements are crucial for producing materials suitable for infrared (IR) laser systems and photonic devices.

The study further explores the electronic band structures through density functional theory (DFT) simulations and X-ray photoelectron spectroscopy (XPS) analyses. These techniques reveal how elemental substitutions—specifically the replacement of lead (Pb) with silver (Ag), or gallium (Ga) with indium (In)—affect the electronic band gap, density of states, and nonlinear susceptibilities. Changes in composition also influence the Urbach energy, indicative of structural disorder and defect density, which in turn impacts optical absorption edges and carrier mobility. Finally, based on the analysis of our results and literature data, we determined the relationships between the crystallographic structure, the complexity of the chemical composition and the band gap width on the SHG intensity.

Ultimately, this research underscores the importance of crystal engineering in the development of advanced nonlinear optical materials. Through a comprehensive understanding of structural-electronic-property relationships, it is possible to design tailored materials that meet the stringent requirements of modern optoelectronics, including wide IR transparency, high damage thresholds, and tunable band gaps.

References

1. M. Piasecki et al., Journal of Alloys and Compounds 909 (2022) 164636.