**γ-NaAsSe\textsubscript{2}: a 1-D Chain-like Crystal with Giant Nonlinear Optical Susceptibility Enhanced by Lone-Pair Electrons**

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Novel nonlinear optical (NLO) crystals are of great interest for infrared laser applications in recent years because they can convert the frequency/color of a given laser line to the one of interest by combining or splitting photons. Second harmonic generation (SHG), for instance, is a second-order NLO effect that combines two identical photons into a photon with twice the frequency. Currently, only a few infrared NLO crystals are commercially available such as AgGaS\textsubscript{2} and AgGaSe\textsubscript{2}, which limits the advancements of infrared lasers. Hence, new NLO crystals with superior properties are needed to address this technological gap.

γ-NaAsSe\textsubscript{2} crystal is promising toward this goal for its outstanding polycrystalline SHG performance (75×AgGaSe\textsubscript{2}); however, for commercialization, it is crucial to study the complete optical properties and understand the structure-property relationship. Here, we systematically assessed γ-NaAsSe\textsubscript{2} as a future infrared NLO crystal. First, the anisotropic linear optical tensor was examined by spectroscopic ellipsometry and Fourier-Transform Infrared (FTIR) spectroscopy. Next, the NLO susceptibilities of γ-NaAsSe\textsubscript{2} were studied using a self-designed SHG polarimetry setup. Through systematic optical modeling, we extracted a giant SHG coefficient of \(d_{11}=590\text{pm V}^{-1}\text{ at 2μm}\) (highest among all known materials). Moreover, it has a wide transparency range extending from 0.66μm to at least 16μm, which allows broadband tunability. The non-phase-matched NLO conversion efficiency of γ-NaAsSe\textsubscript{2} was calculated to be over 500 times greater than AgGaSe\textsubscript{2}, making it promising for orientation patterned quasi-phase-matching devices. Furthermore, we explored the origin of the large SHG response to understand the structure-property relationship. We found that the lone pairs electrons of As, Se, and Se in the [AsSe\textsubscript{2}]\textsubscript{−} chains significantly enhanced the NLO performance. The lone pair vector addition suggested that \(d_{11}\) has the largest value, consistent with the experiment. These outstanding optical properties make γ-NaAsSe\textsubscript{2} a promising NLO crystal for future infrared laser applications.