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Ultrafast Nonlinear Absorption and Second Harmonic Generation in $Cu_{0.33}In_{1.30}P_2S_6$ van der Waals Layered Crystals

Aamir Mushtaq,* Liam Clink, Mohamed Yaseen Noor, Conrad Kuz, Emma DeAngelis, Ryan Siebenaller, Adam Fisher, Darpan Verma, Roberto C. Myers, Benjamin S. Conner, Michael A. Susner, and Enam Chowdhury*

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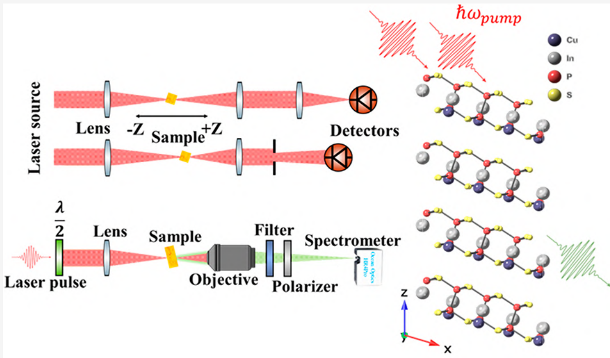
ABSTRACT: The advancement of ultrafast photonics and optoelectronic devices necessitates the exploration of new materials with optical and chemical stability to implement practical applications. Layered quaternary metal-thio/selenophosphate has attracted much interest over the past few years. Ferroelectric $CuInP_2S_6$ (CIPS) is an emerging material that belongs to this family. When synthesized with Cu deficiencies, CIPS forms self-assembled in-plane heterostructures, which in turn exhibit properties that are both compositionally and thermally dependent. These characteristics can be explored for applications in nonlinear optoelectronic and photonic devices. Herein, we study the second and third order nonlinear optical behavior of $Cu_{0.33}In_{1.30}P_2S_6$ bulk heterostructure. We observed large two photon induced nonlinear absorptions and self-defocusing at 1032 nm pulsed laser excitation using the Z-scan technique. Furthermore, we identified a polarization-dependent second harmonic signal and determined the laser-induced optical damage threshold. Our observations allow for the designing of optoelectronic and ultrafast photonic devices based on these materials.



Over the past several years, graphene and other two-dimensional (2D) materials which contain a van der Waals (vdW) gap have become hotspots for their novel ferroic and optical properties,[1−5] which make them attractive for various applications, e.g., LEDs, lasers, photodiodes, and photovoltaics.[6−10] These materials systems include hexagonal boron nitride (hBN), molybdenum disulfide (MoS_2), molybdenum telluride ($MoTe_2$), rhenium disulfide (ReS_2), black phosphorus, and their heterostructures. This latter category is a new emerging field where two or more atomically thin 2D layers of the same (or different) atomic crystal species are stacked either by adhesion (stamping one layer over the other) or by chemical deposition techniques. These vdW heterostructures have opened a wide swath of possibilities for the exploration of new emerging physics, including fascinating electric, magnetic, thermal, and optical properties,[11−14] among which ferroelectricity has been extensively explored for potential applications in memories, capacitors, sensors, and actuators.[15,16]

Recently, a complementary approach involving thermochemistry and sublattice melting was utilized to create in-plane heterostructures on a bulk scale using metal thiophosphates (MTP) which are a structural analogue of metal dichalcogenides in which 1/3 of the metal atoms are replaced by a diphosphorous entity which binds six adjacent sulfur atoms into the anionic $[P_2S_6]^{4-}$ subgroup, which is then charge-balanced against the positive charge carried by the metal cations which sit in the other 2/3 of the octahedral sites. These metal cations are also responsible for the various ferroic properties observed in MTP compounds, including magnetism, ferroelectricity, and even superconductivity. It is this incipient ferroic behavior that has led to much interest for the development of next generation multifunctional devices with this material system. Layered $CuInP_2S_6$ (CIPS) is one of the representative materials which could be used in heterostructure-based electronics and optoelectronics[13] due to its room temperature ferroelectricity and chemical stability. CIPS is also appealing due to its fascinating physical properties, such as spontaneous polarization, second harmonic generation (SHG), and a quadruple potential well.[17]

As interesting as pure-phase CIPS is from a fundamental perspective, the synthesis of Cu-deficient CIPS results in spontaneously phase-separated $CuInP_2S_6$ (ferroelectric) and

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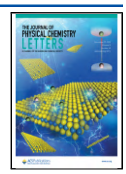

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