

## Vibrational properties of $\text{CuInP}_2\text{S}_6$ across the ferroelectric transition

Sabine N. Neal <sup>1</sup>, Sobhit Singh <sup>2</sup>, Xiaochen Fang <sup>2,3</sup>, Choongjae Won <sup>4</sup>, Fei-ting Huang <sup>2,3</sup>, Sang-Wook Cheong <sup>2,3,4</sup>, Karin M. Rabe <sup>2</sup>, David Vanderbilt <sup>2</sup>, and Janice L. Musfeldt <sup>1,5,\*</sup>

<sup>1</sup>*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*

<sup>2</sup>*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*

<sup>3</sup>*Rutgers Center for Emergent Materials, Rutgers University, Piscataway, New Jersey 08854, USA*

<sup>4</sup>*Laboratory for Pohang Emergent Materials and Max Plank POSTECH Center for Complex Phase Materials, Pohang University of Science and Technology, Pohang 790-784, Korea*

<sup>5</sup>*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*



(Received 31 July 2021; revised 26 January 2022; accepted 28 January 2022; published 28 February 2022)

In order to explore the properties of a two-sublattice ferroelectric, we measured the infrared and Raman scattering response of  $\text{CuInP}_2\text{S}_6$  across the ferroelectric and glassy transitions and compared our findings to a symmetry analysis, calculations of phase stability, and lattice dynamics. In addition to uncovering displacive character and a large hysteresis region surrounding the ferroelectric transition temperature  $T_C$ , we identify the vibrational modes that stabilize the polar phase and confirm the presence of two ferroelectric variants with opposite polarizations. Below  $T_C$ , a poorly understood relaxational or glassy transition at  $T_g$  is characterized by local structure changes in the form of subtle peak shifting and activation of low frequency out-of-plane Cu- and In-containing modes. The latter are due to changes in the Cu/In coordination environments and associated order-disorder processes. Moreover,  $T_g$  takes place in two steps with another large hysteresis region and significant underlying scattering. Combined with imaging of the room temperature phase separation, this effort lays the groundwork for studying  $\text{CuInP}_2\text{S}_6$  under external stimuli and in the ultrathin limit.

DOI: [10.1103/PhysRevB.105.075151](https://doi.org/10.1103/PhysRevB.105.075151)

### I. INTRODUCTION

The past decade has witnessed exceptional progress in revealing the potential and inner workings of complex chalcogenides, especially those belonging to the metal phosphorous trisulfide family ( $\text{MPS}_3$ , with  $M = \text{Mn, Fe, Ni}$ ) [1–3]. Exciting properties under external stimuli include sliding, metallicity, piezochromism, and superconductivity under pressure [4–7], reentrant phases in high magnetic fields [8–11], tunable band gaps [12], and strongly anisotropic thermal conductivity [13]. These systems can also be exfoliated into few- and single-layer sheets that host novel magnetic excitations and states as well as symmetry breaking [14–23]. While simple metal site substitution is well studied in the  $\text{MPS}_3$  series, bimetallic substitution is relatively unexplored even though lower symmetry may promote useful properties such as ferroelectricity [24–28] along with different types of structural phase transitions. Dual-sublattice analogs such as bimetallic  $\text{CuInP}_2\text{S}_6$  and  $\text{AgInP}_2\text{S}_6$  offer flexible platforms for the discovery of tunable states of matter under external stimuli and the development of structure-property relations.  $\text{CuInP}_2\text{S}_6$ , for instance, hosts a quadruple-well potential with two distinct polar phases and four different polarization states under strain [29,30].

$\text{CuInP}_2\text{S}_6$  is a layered van der Waals system with a paraelectric  $\leftrightarrow$  ferroelectric transition near  $T_C = 310$  K [31–37].

Although the terms “ferrielectric” and “ferroelectric” are both used in the  $\text{CuInP}_2\text{S}_6$  literature [29,31,32,36,38–41], we have adopted the latter usage here. Our choice is motivated by the observation that there is no In off-centering instability in the absence of Cu off-centering. This contrasts with the case of a ferrimagnet, in which magnetic moments would still appear on either magnetic sublattice even if suppressed on the other sublattice. Here, instead, the small In displacements seem more analogous to the anionic displacements that are also induced by the Cu off-centering. In any case, the polarization in  $\text{CuInP}_2\text{S}_6$  is stable and switchable, although switching under high bias is associated with  $\text{Cu}^+$  ion mobility [36,42]. The latter has a two-step path that involves both in-plane and out-of-plane hopping of  $\text{Cu}^+$  ions [42]. In the high temperature paraelectric phase, the system is in the  $C2/c$  space group, whereas the polar phase has  $Cc$  symmetry [38]. Individual layers of  $\text{CuInP}_2\text{S}_6$  consist of  $\text{Cu}^+$  and  $\text{In}^{3+}$  ions surrounded by sulfur octahedra with P-P dimers filling the octahedral voids. Along with the primary driver—which is distortion of cations from their centrosymmetric positions—the symmetry reduction from  $C2/c \rightarrow Cc$  is thought to occur with ordering of the copper occupancies [38]. This provides a natural explanation for the high bias ionic conductivity. Variable temperature Raman scattering suggests an order-disorder component to the ferroelectric transition as well [43].

Because  $T_C$  is just above room temperature, there are a number of intriguing properties at 300 K. For example,  $\text{CuInP}_2\text{S}_6$  displays a room temperature electrocaloric effect that may prove useful for solid-state refrigeration [44]. The

\*musfeldt@utk.edu

system also hosts sizable intrinsic negative longitudinal piezoelectricity [29,45]. Further,  $\text{CuInP}_2\text{S}_6$  single crystals exhibit polar domain structure that gets smaller and then disappears in flakes thinner than 50 nm [36,46,47].  $\text{CuInP}_2\text{S}_6$  is also being prepared in thin film form. In fact, when sandwiched with germanene as a two-dimensional van der Waals heterostructure, electric field can drive a metal-semiconductor transition via control over the polarization direction [48].  $\text{CuInP}_2\text{S}_6$  has been incorporated (along with  $\text{MoS}_2$ ) in a negative capacitance field effect transistor as well [49]. Dielectric dispersion studies reveal a broad relaxation near 150 K, although the exact position, amplitude, and shape depend upon the measurement frequency [38]. This relaxation is attributed to a dipolar glass transition due to freezing of the electric dipole [38]. Finally, we note that this system hosts a first order monoclinic  $\leftrightarrow$  triclinic structural transition at 4 GPa [31].

In this paper, we combine infrared absorption and Raman scattering spectroscopies to reveal symmetry-breaking and local lattice distortions across the ferroelectric and relaxational or glassy phase transitions in  $\text{CuInP}_2\text{S}_6$ . We compare our findings with complementary lattice dynamics calculations, mode displacement patterns, and an analysis of the energy landscape. Interestingly, we identify several different infrared- and Raman-active modes in this system that appear below the ferroelectric transition, although of course only the odd-symmetry features contribute to the development of electric polarization. The mechanism of the  $C2/c \rightarrow Cc$  transition is displacive, and comparison with the  $\text{MPS}_3$  family of materials reveals that bimetallic *A*-site substitution is what enables the polar ground state to emerge [27,28]. The 150-K order-disorder transition, on the other hand, does not take place with a change in space group. Yet, it is characterized by subtle peak shifting and activation of low-frequency out-of-plane Cu- and In-containing modes that arise due to differences in the local bonding environment. Thus in addition to order-disorder and glassy character to the transition near 150 K, there is a weak structural component due to Cu site disorder. The strong hysteresis as well as the two-step character of  $T_g$  are also consequences of bimetallic substitution and the resulting Cu site disorder. We further investigate the tendency toward chemical-phase separation using a combination of vibrational spectroscopies as well as piezoforce and transmission electron microscopies uncovering the signatures of the highest quality  $\text{CuInP}_2\text{S}_6$  crystals and imaging their two polarization domains. Going forward, these studies will enable rapid verification of crystal quality.

## II. METHODS

### A. Crystal growth and characterization

$\text{CuInP}_2\text{S}_6$  single crystals were grown by vapor transport methods as follows. Copper powders, indium shots, a phosphorus lump, and sulfur flakes were loaded into an evacuated quartz tube with  $\approx 10^{-5}$  torr pressure and then heated with a temperature gradient between both ends of the quartz ampule. The sealed tube was held at  $\approx 1023$  K for ten days and then cooled to room temperature. The single crystal flakes were mechanically extracted from the entangled bulk. As detailed in the Supplemental Material [50], there is a strong tendency

toward chemical phase separation in  $\text{CuInP}_2\text{S}_6$ -like materials. In fact, until the crystals are rigorously tested, they should be regarded as  $\text{Cu}_{1-x}\text{In}_{1+x/3}\text{P}_2\text{S}_6$ . Chemical vapor transport growth of  $\text{CuInP}_2\text{S}_6$  results in thin, orange, transparent flakes. We call these single phase platelets type I crystals. Type II crystals on the other hand contain  $\text{CuInP}_2\text{S}_6$  + nonferroelectric  $\text{In}_{4/3}\text{P}_2\text{S}_6$  as a secondary phase. All of the spectroscopic work reported here was performed with type I single crystals.

The exceptional phase complexity makes growth of high-quality stoichiometric crystals quite challenging, and we strongly urge that each crystal be tested for phase purity as discussed in the Supplemental Material [50]. There are a number of tests that can be used to confirm sample quality and purity. In this paper, we performed energy dispersive x-ray analysis, piezoforce microscopy, and transmission electron microscopy. The vertical piezoforce microscopy (PFM) experiments were performed on freshly exfoliated surfaces of  $\text{CuInP}_2\text{S}_6$  using the MultiMode atomic force microscope by Veeco/Digital Instruments. Thermally cured gold paste was used to mount the sample and act as the bottom electrode. All PFM measurements were conducted using between 3 and 5 V ac. The voltage was applied to a conducting contact mode atomic force microscope tip, and the bottom electrode was grounded. The vertical piezoelectric response signal was extracted using a NanoScope controller and a lock-in amplifier. Crystal structure, electron diffraction, and domain character were examined by JEOL-2010F field-emission transmission electron microscopy in plane-view specimens.  $\text{In}_{4/3}\text{P}_2\text{S}_6$ -containing regions were observed by selecting (002) spots of  $\text{In}_{4/3}\text{P}_2\text{S}_6$ .

### B. Vibrational spectroscopies

Prior to our spectroscopic measurements, a type I single crystal of  $\text{CuInP}_2\text{S}_6$  was exfoliated to reveal a clean, smooth *ab*-plane sample surface. This crystal was adhered to a round pinhole aperture. Infrared measurements were performed in transmittance mode using a Bruker IFS 113V infrared spectrometer equipped with a low noise He-cooled bolometer detector over the frequency range of 20–700  $\text{cm}^{-1}$  with 2- $\text{cm}^{-1}$  resolution. The measured transmittance was converted to absorption:  $\alpha(\omega) = -\frac{1}{d}\ln[\mathcal{T}(\omega)]$ , where  $\mathcal{T}(\omega)$  is measured transmittance, and  $d$  is the crystal thickness. This measurement was carried out on the *ab* plane, without polarizers. Note that the *c* axis is not perpendicular to the *ab* plane, so there is a residual contribution from the *c* axis in our spectroscopic results. This is fortunate, because we were unable to polish a crystal to fully expose the *c* axis. Raman scattering measurements were performed in a back-scattering geometry on a Horiba LabRAM HR Evolution Raman spectrometer over a 50–750- $\text{cm}^{-1}$  frequency range. We used an excitation wavelength of 532 nm at a power of 0.1 mW, an 1800 line/mm grating, a 50  $\text{cm}^{-1}$  notch filter, and a liquid  $\text{N}_2$  cooled CCD detector. We used the same orientation of the  $\text{CuInP}_2\text{S}_6$  crystal on the pin hole as described above, with light incident onto (and scattered from) the *ab* plane. No polarizers or analyzers were employed because the instrument does not have them. As a result, the spectra average over the Raman tensor components. Table S1 in the Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80]) summarizes the symmetries of the allowed excitations in the high and low

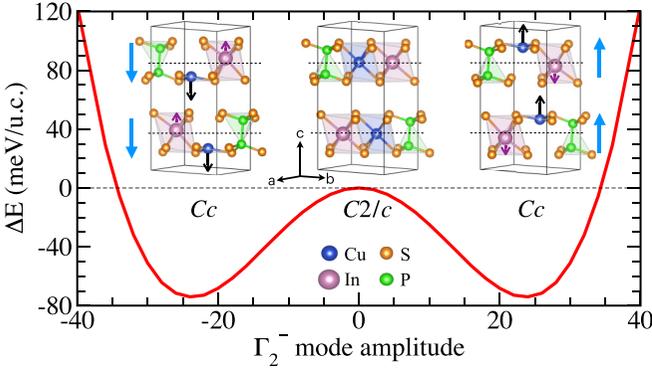


FIG. 1. The double-well potential energy profile computed by freezing the polar  $\Gamma_2^-$  phonon mode in the paraelectric phase as a function of the phonon distortion amplitude. Crystal structures of the paraelectric ( $C2/c$ ) and ferroelectric ( $Cc$ ) phases of  $\text{CuInP}_2\text{S}_6$  are shown in the inset. Black arrows denote the displacement of Cu ions corresponding to the  $\Gamma_2^-$  mode distortion. Purple arrows denote the relatively small displacement of In ions. The net polarization of individual  $\text{CuInP}_2\text{S}_6$  layers is along the direction of the blue arrows.

temperature phases of  $\text{CuInP}_2\text{S}_6$ . In each case, an open flow cryostat provided temperature control.

### C. Electronic structure calculations

All the first-principles density-functional theory (DFT) calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP) [51–53]. The number of valence electrons in the considered PAW pseudopotentials were 11 ( $3d^{10} 4s^1$ ), 3 ( $5s^2 5p^1$ ), 5 ( $3s^2 3p^3$ ), and 6 ( $3s^2 3p^4$ ) for Cu, In, P, and S atoms, respectively. The exchange-correlation functional was computed using the generalized-gradient approximation as parametrized by Perdew-Burke-Ernzerhof (PBE) [54]. The zero-damping D3 method of Grimme (PBE-D3) was employed to describe the weak van der Waals interactions between the  $\text{CuInP}_2\text{S}_6$  layers [55]. This method has been reported to correctly predict a wide range of physical and chemical properties of  $\text{CuInP}_2\text{S}_6$  [56,57]. The energy convergence criterion for self-consistent DFT calculations was set at  $10^{-7}$  eV and force convergence criterion for relaxation of atomic coordinates was set at  $10^{-3}$  eV/Å. The reciprocal space was sampled using a Monkhorst-pack  $k$  mesh [58] of size  $8 \times 8 \times 4$  along with a kinetic energy cutoff of 650 eV for the plane waves.

The optimized lattice parameters and cell angles of the paraelectric  $C2/c$  phase are  $a = b = 6.069$  Å,  $c = 13.159$  Å,  $\alpha = \beta = 94.5^\circ$ , and  $\gamma = 119.9^\circ$ . The ferroelectric  $Cc$  phase was obtained using after applying a polar  $\Gamma_2^-$  distortion on the high-symmetry  $C2/c$  phase. A further free relaxation was performed of the local minimum structure ( $Cc$ ) shown in Fig. 1. The resulting cell parameters and cell angles of the  $Cc$  phase are  $a = b = 6.112$  Å,  $c = 13.360$  Å,  $\alpha = \beta = 94.3^\circ$ , and  $\gamma = 120.0^\circ$ , which are in good agreement with the experimental data reported at 296 K [59]. The PHONOPY package was employed to calculate the zone-center phonon frequencies and phonon eigenvectors of the DFT optimized structures at 0 K using the finite-displacement approach [60].

The Bilbao Crystallographic Server was utilized to analyze the symmetry of phonon modes [61]. The theoretical infrared (IR) spectra were calculated by computing the mode dynamical charge associated with each phonon eigendisplacement, and the theoretical Raman spectra were simulated by appropriately averaging the Raman activity tensor calculated for each Raman-active phonon eigenmode at zone center [62].

## III. RESULTS AND DISCUSSION

### A. Analyzing the symmetries and properties of $\text{CuInP}_2\text{S}_6$

#### 1. Energy landscape and ferroelectricity

Before we present our infrared and Raman spectroscopies, let us start by briefly describing the essential details of the crystal structure, ferroelectricity, and vibrational properties of the paraelectric and ferroelectric phases of  $\text{CuInP}_2\text{S}_6$ . The inset of Fig. 1 shows the crystal structure of the paraelectric and two equivalent ferroelectric phases of  $\text{CuInP}_2\text{S}_6$ , which belong to space groups  $C2/c$  (no. 15) and  $Cc$  (no. 9), respectively. The bulk unit cell of both phases contains two weakly interacting single layers of  $\text{CuInP}_2\text{S}_6$ , i.e., 2 f.u., stacked along the  $c$  axis. In the paraelectric phase, the vertically stacked  $\text{CuInP}_2\text{S}_6$  layers are related by an in-plane  $C_2$  rotation followed by a translation  $\tau(c/2)$  operation along the  $c$  axis. This structure resembles a lamellar structure composed of a sulfur framework in which the metal cations and P-P dimers fill the octahedral voids within each layer [32–34,39,63,64]. The P-P dimers act as vertical pillars separating the top and bottom sulfur planes in each layer. By contrast, the Cu and In metal cations reside exactly at the midplane of the layers, marked by dashed horizontal black lines in the inset of Fig. 1, lying between two vertically stacked sulfur planes and passing through the P-P dimer at its half bond length within each  $\text{CuInP}_2\text{S}_6$  layer.

The paraelectric phase is stable only at high temperatures ( $T > 310$  K) [32–34,36,38–40]. Below 310 K, this phase transforms into a ferroelectric  $Cc$  phase having a net polarization primarily along the out-of-plane direction of each  $\text{CuInP}_2\text{S}_6$  layer [32–34,39,64], which occurs due to the polar displacements of the Cu and In sublattices in an antiparallel fashion relative to the midplane of each  $\text{CuInP}_2\text{S}_6$  monolayer, as shown in Fig. 1.

From the group theory perspective, the paraelectric and ferroelectric phases are related by a zone center polar optic phonon mode distortion,  $\Gamma_2^-$  mode ( $B_u$  symmetry). This mode is unstable in the paraelectric phase having frequency  $50.3i \text{ cm}^{-1}$  and it primarily represents an in-phase vertical displacement of two Cu ions located in the adjacent  $\text{CuInP}_2\text{S}_6$  layers, as denoted using two parallel black arrows in the insets of Fig. 1 (left and right panels). The calculated potential energy profile obtained by freezing the the  $\Gamma_2^-$  mode as a function of the phonon distortion amplitude is shown in Fig. 1. The magnitude of the energy barrier is comparable with the data reported in Refs. [29,30]. Notably, in Refs. [29,30], the authors reported the presence of two polar phases ( $Cc$ ) with four different (two high and two low) polarization states under local strain conditions. No local strain was applied in our paper.



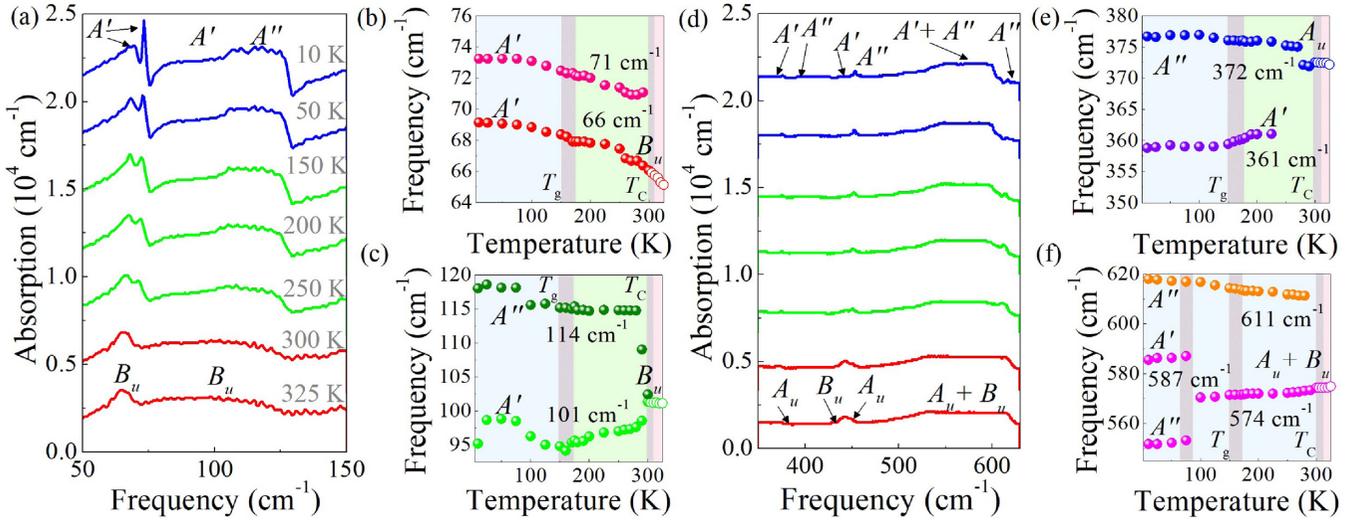


FIG. 3. (a, d) Close-up view of the far infrared response of  $\text{CuInP}_2\text{S}_6$  as a function of temperature. High temperatures are indicated in red, and low temperatures are indicated in blue. The peaks are labeled using  $C2/c$  and  $Cc$  space group symmetries in the high and low temperature phases, respectively. Panels (b) and (c) highlight the behavior for the ferroelectric modes in panel (a), whereas panels (e) and (f) display peak position vs temperature of the ferroelectric modes highlighted in panel (d). The vertical gray bars define the transition regions, and the open to closed data points denote the  $C2/c \rightarrow Cc$  space group change. There is a significant hysteresis depending upon direction of temperature sweep. The measurements shown here are taken with increasing temperature.

modes is practically negligible owing to the weak coupling between the adjacent  $\text{CuInP}_2\text{S}_6$  layers. The simulated Raman spectra of the paraelectric and ferroelectric phases appears to be in reasonable agreement with our experimental data as well as with the data reported by Vysochanskii *et al.* [43]. A detailed comparison of the experimental and theoretical data is provided in the Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80]).

## B. Vibrational properties of $\text{CuInP}_2\text{S}_6$ across the ferroelectric transition

### 1. Infrared spectroscopy probing inversion symmetry breaking

Figure 3 summarizes the infrared response of  $\text{CuInP}_2\text{S}_6$  as a function of temperature. In order to analyze the development of polar phonons across  $T_C$ , we focus on the two frequency windows displayed in panels (a) and (d). At 325 K, there are two distinct phonons in the low frequency infrared response. These include a sharp  $B_u$  mode near  $65 \text{ cm}^{-1}$  as well as a very broad  $B_u$  mode centered around  $101 \text{ cm}^{-1}$ . As temperature decreases across  $T_C = 310 \text{ K}$ , there is a noticeable activation of the lower frequency  $B_u$  mode and the development of a shoulder on the  $101 \text{ cm}^{-1}$  feature [Figs. 3(b) and 3(c)]. The appearance of new modes below  $310 \text{ K}$  is due to a change in the space group from  $C2/c$  in the high temperature paraelectric phase to  $Cc$  in the low temperature ferroelectric phase. While the  $65 \text{ cm}^{-1}$  feature has  $B_u$  symmetry above  $T_C$ , the peaks in the low temperature phase are assigned as  $A' \oplus A'$ . This doublet sharpens and continues to blueshift with decreasing temperature. At the same time, the once-broad  $B_u$  symmetry mode at  $101 \text{ cm}^{-1}$  develops a shoulder below  $T_C$ . The lower frequency component evolves as an  $A'$  mode, and the higher frequency component at  $114 \text{ cm}^{-1}$  transforms to  $A''$  symmetry [Fig. 3(c)]. The  $A'$  branch redshifts below  $310 \text{ K}$ —a trend that continues to the relaxational or glassy

phase transition near  $150 \text{ K}$ —below which it blueshifts again. By contrast, the  $A''$  branch has a sharp blueshift immediately below room temperature and continues to harden systematically to  $10 \text{ K}$ .

Figure 3(d) summarizes the infrared properties of  $\text{CuInP}_2\text{S}_6$  in the  $350$  to  $625 \text{ cm}^{-1}$  range. Of the many vibrational modes present in the high temperature phase, only one is sensitive to  $T_C$ : the  $A_u$  symmetry mode at  $372 \text{ cm}^{-1}$  [Figs. 3(d) and 3(e)]. A slight hardening occurs across  $T_C$  due to the change in space group, below which the  $A_u$  feature converts to an  $A''$  symmetry mode. Below  $T_C$ , this mode downshifts slightly before rising near  $275 \text{ K}$ , continuing to blueshift toward base temperature. Activation of a small  $A'$  symmetry mode at  $361 \text{ cm}^{-1}$  can be seen in the low temperature phase near  $225 \text{ K}$ , with an overall redshift toward base temperature. Figures 3(d) and 3(f) also show a broad phonon centered at  $574 \text{ cm}^{-1}$ , assigned as an  $A_u \oplus B_u$  symmetry mode. This feature redshifts slightly across  $T_C$  below which the new symmetries are assigned as  $A' \oplus A''$ . Systematic redshifting persists through  $\approx 100 \text{ K}$ , where this broad feature separates slightly into two individual symmetry components:  $A'$  ( $587 \text{ cm}^{-1}$ ) and  $A''$  ( $553 \text{ cm}^{-1}$ ). Both features redshift slightly to  $10 \text{ K}$ . The spectra also reveal an  $A''$  mode at  $611 \text{ cm}^{-1}$  that emerges just below  $300 \text{ K}$ . The appearance of this feature is in line with our theoretical predictions. This mode sharpens and increases in frequency toward  $10 \text{ K}$ . A comprehensive table of mode assignments and displacement patterns is available in the Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80]).

The development of a polar state requires inversion symmetry breaking, so we are naturally interested in the behavior of the odd-symmetry vibrational modes across  $T_C$ . Our infrared work demonstrates that  $\text{CuInP}_2\text{S}_6$  hosts five polar modes in reasonable overall agreement with the theoretical results in Fig. 2(a). These include features near  $65$  and

TABLE I. Infrared-active vibrational modes that are sensitive to the ferroelectric phase transition in  $\text{CuInP}_2\text{S}_6$ . Frequencies shown for  $C2/c$  are at  $T > 310$  K. For the  $Cc$  phase,  $T < 300$  K. All values are in  $\text{cm}^{-1}$ . Corresponding DFT calculated frequencies ( $\omega$ ) are given in parentheses.

$C2/c$		$Cc$		Displacement patterns
$\omega$ experiment	Symmetry	$\omega$ experiment	Symmetry	
65 (63)	$B_u$	66 (64)	$A'$	In-plane twist of P-P dimers + out-of-plane vibration of S Out-of-plane polar displacement Cu In-plane Cu + In + P + out-of-plane S
		71 (71)	$A'$	
101 (100)	$B_u$	102 (102)	$A'$	(in-phase adjacent layers) + out-of-plane vibration of S In-plane Cu + In + out-of-plane S In-plane Cu + S and out-of-plane P-P stretching In-plane Cu + S and out-of-plane stretching of P-P dimers (opposite phase in adjacent layers)
		114 (114)	$A''$	
		361 (354)	$A'$	
372 (359)	$A_u$	373 (355)	$A''$	In-plane P-P + in-plane S vibration
574 (540, 541)	$B_u, A_u$	553, 587, 611 (558, 563, 563)	$A'', A', A'$	

$103 \text{ cm}^{-1}$  that appear to split below  $T_C$  due to the activation of new modes, the  $372 \text{ cm}^{-1}$  feature which blueshifts across the ferroelectric transition, and two additional features near  $361$  and  $611 \text{ cm}^{-1}$  are activated in the low temperature phase. All infrared-active polar modes, along with their symmetries and displacement patterns, are listed in Table I. The predicted  $A'$  symmetry soft mode near  $50 \text{ cm}^{-1}$  is not unambiguously observed in our spectra—probably due to the low frequency limit of our instruments.

## 2. Raman scattering spectroscopy across $T_C$

Figure 4(a) summarizes the Raman scattering response of  $\text{CuInP}_2\text{S}_6$  along with mode assignments for the various phonons as a function of temperature. Even-symmetry modes

also change across  $T_C$  although they do not break inversion symmetry. For instance, the  $68 \text{ cm}^{-1}$   $B_g$  symmetry mode in the high temperature paraelectric phase transforms to give  $A' \oplus A''$  symmetry modes in the low temperature ferroelectric phase [Fig. 4(b)]. The upper frequency branch is relatively consistent in terms of size and position until  $150$  K, below which the peak position hardens toward  $75$  K and then softens again. The lower frequency branch systematically blueshifts toward base temperature. Figure 4(c) displays the behavior of the  $A_g \oplus B_g$  high temperature doublet. The  $B_g$  component near  $103 \text{ cm}^{-1}$  hardens toward  $T_C$  and then remains relatively constant (although the symmetry becomes  $A'$ ). Below  $300$  K, the  $A_g$  peak converts to an  $A'$  branch near  $113 \text{ cm}^{-1}$  and an  $A''$  branch near  $116 \text{ cm}^{-1}$ . Moving on to the  $A_g$  feature at  $162 \text{ cm}^{-1}$  [Fig. 4(d)], we note a  $4 \text{ cm}^{-1}$  blueshift across the

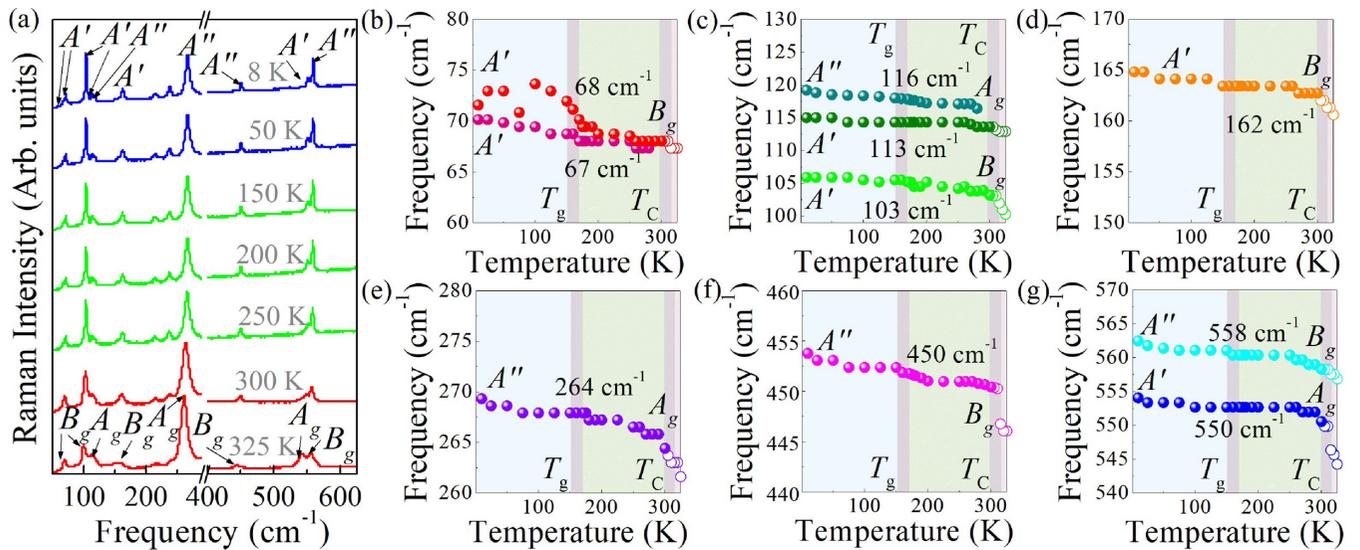


FIG. 4. (a) Raman scattering of  $\text{CuInP}_2\text{S}_6$  as a function of temperature. High temperatures are indicated in red, and low temperatures are indicated in blue. The peaks are labeled using  $C2/c$  and  $Cc$  space group symmetries in the high and low temperature phases, respectively. Panels (b)–(g) highlight the behavior of several different Raman-active modes, many of which are sensitive to  $T_C$ . The vertical gray bars define  $T_C$  and  $T_g$ . The open to closed data points indicate the  $C2/c \rightarrow Cc$  transition. There is a significant hysteresis effect depending upon direction of temperature sweep. This is seen very clearly in the Raman scattering response when rendered as a contour plot (Fig. S3, Supplemental Material [50]). The measurements shown here correspond to a temperature up-sweep.

TABLE II. Raman-active vibrational modes that are sensitive to the ferroelectric phase transition in  $\text{CuInP}_2\text{S}_6$ . Frequencies shown for  $C2/c$  are at  $T > 310$  K. For the  $Cc$  phase,  $T < 300$  K. All values are in  $\text{cm}^{-1}$ . Corresponding DFT calculated frequencies ( $\omega$ ) are given in parentheses.

$C2/c$		$Cc$		Displacement patterns
$\omega$ (experiment)	Symmetry	$\omega$ (experiment)	Symmetry	
67 (66)	$B_g$	68 (64), 67 (70)	$A', A''$	In-plane Cu + P and out-of-plane S vibration Out-of-plane Cu + S vibration
100 (108)	$B_g$	103 (102)	$A'$	Out-of-plane In + P + S
113 (130)	$A_g$	114 (114), 116 (117)	$A', A''$	In-plane displacement Cu + In + S, out-of-plane S
161 (175)	$A_g$	162 (160)	$A'$	In-plane Cu + P and out-of-plane S Out-of-plane P-P + in-plane S
262 (254)	$A_g$	264 (263)	$A''$	In-plane Cu + P + out-of-plane S In-plane S motion
446 (429)	$B_g$	450 (435)	$A''$	Out-of-plane P + S
544 (534)	$A_g$	550 (558, 558)	$A', A''$	In-plane P-P stretching + S vibration
557 (539)	$B_g$	558 (562, 563)	$A', A''$	In-plane P-P + S vibration

ferroelectric transition as the mode changes to  $A'$  symmetry. The peak position remains relatively constant, shifting only slightly with decreasing temperature. Figure 4(e) displays the frequency vs temperature trend for the  $A_g$  symmetry mode near  $264 \text{ cm}^{-1}$ . It hardens across the  $C2/c \rightarrow Cc$  transition and is reclassified as  $A''$  which has a fairly continuous up-shift to base temperature. The blueshift near the ferroelectric transition is even more noticeable in the  $B_g$  symmetry mode near  $450 \text{ cm}^{-1}$  [Fig. 4(f)]. Below 310 K, the feature hardens steadily until 150 K where there is a slight cusp and then an overall blueshift toward base temperature. Finally, we turn our attention to Fig. 4(g) which tracks the high frequency  $A_g \oplus B_g$  doublet. The higher frequency branch has an even clearer blueshift across  $T_C$  although both features move systematically below 310 K, with a slight frequency upturn below 25 K. A full list of symmetries and mode assignments as well as the relevant mode displacement patterns are available in the Supplemental Material [50] (see, Refs. [29,31,35,41,43,67,72–80]).

As previously mentioned, several even-symmetry Raman-active modes change across  $T_C$  although they do not break inversion symmetry or contribute to the electric polarization in  $\text{CuInP}_2\text{S}_6$ . Our Raman scattering work reveals activation of additional modes related to the 67 and  $113 \text{ cm}^{-1}$  phonons below  $T_C$ . This is in line with theory for a displacive transition, which predicts new peaks in the ferroelectric phase. Other Raman-active phonons including those at the 100, 161, 262, 446, and the  $544\text{--}557 \text{ cm}^{-1}$  doublets reveal sharp frequency shifts near 310 K as well. Frequency shifts are also evident in the predicted Raman spectra [Fig. 2(b)]. All Raman-active modes that are sensitive to  $T_C$ , along with their symmetries and displacement patterns, are summarized in Table II. Raman scattering nicely shows the hysteresis across  $T_C$  as well (Fig. S3, Supplemental Material [50]).

### 3. Bimetallic A-site substitution introducing ferroelectricity

Returning to a comparison of  $\text{MPS}_3$  systems ( $M = \text{Mn}, \text{Ni}, \text{Fe}$ ) and dual sublattice analogs such as  $\text{CuInP}_2\text{S}_6$  and  $\text{AgInP}_2\text{S}_6$ , we immediately see that the most important consequence of the bimetallic nature is the introduction of

ferroelectricity. A-site size disorder has been predicted to produce polar behavior in other materials as well [27,28]. That  $T_C$  is slightly above room temperature is already providing the basis for a number of applications. Examples include electrocaloric effects for refrigeration, negative longitudinal piezoelectricity, and a negative capacitance field effect transistor [44,67]. Unfortunately, Cu site disorder demonstrably broadens the ferroelectric and relaxational or glassy phase transitions. This is seen very clearly in the Raman scattering response when rendered as a contour plot [Fig. 5(d) and Fig. S3, Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80])]. It also hinders the formation of larger polarization in  $\text{CuInP}_2\text{S}_6$ . The  $\text{MPS}_3$  materials obviously do not have A-site disorder. They also lack ferroelectricity (although  $\text{MnPS}_3$  may be ferrotorroidic) [68]. Another useful point of comparison in these structure-property relationships is  $\text{CrPS}_4$ , a related chalcogenide with slightly different stoichiometry and  $C2$  symmetry [69]. This system appears to be both polar and chiral. There is no A-site disorder, and the P-P dimer is absent. Clearly, subtle structural changes have important consequences for properties in this family of materials.

### C. Vibrational properties of $\text{CuInP}_2\text{S}_6$ across the low temperature relaxational transition

In addition to the well-defined ferroelectric transition,  $\text{CuInP}_2\text{S}_6$  displays a weak relaxational or glassy transition ( $T_g$ ) near 150 K. By comparison, this transition is more subtle and much less studied than the displacive  $C2/c$  to  $Cc$  ferroelectric transition. Although  $T_g$  does not alter the  $Cc$  space group, there is a local rearrangement of the structure in which the relative interatomic coordinates of Cu and In are different. The weak structural component is probably due to the existence of multiple competing  $Cc$  phases with varying monoclinic cell angle [59]. This gives the transition local structure aspects as well as order-disorder or glassy character due to freezing of ferroelectric domains [38].

Figure 5 summarizes the infrared absorption and Raman scattering response of  $\text{CuInP}_2\text{S}_6$  across the relaxational transition. We can track how the various modes evolve across

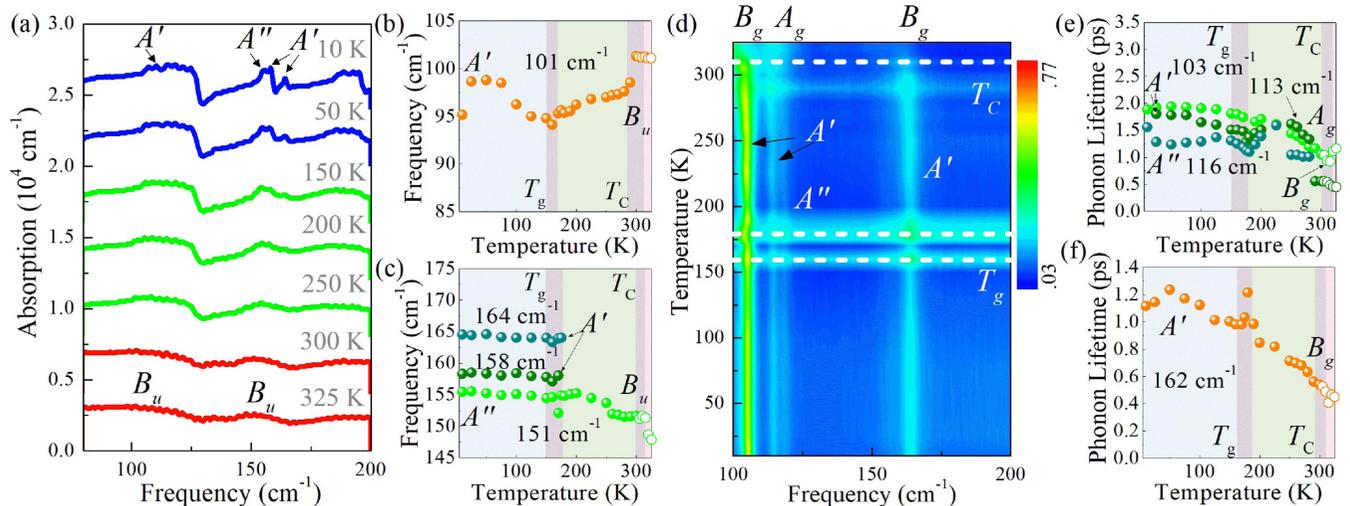


FIG. 5. Infrared (a–c) and Raman scattering (d–f) response of  $\text{CuInP}_2\text{S}_6$  across the relaxational or glassy phase transition,  $T_g$ . High temperatures are shown in red, and low temperatures are shown in blue. The peaks are labeled using symmetries of the  $C2/c$  and  $Cc$  space groups in the high and low temperature phases, respectively. Panel (a) summarizes the infrared spectrum as a function of temperature, and panels (b) and (c) show peak position vs temperature to highlight the infrared-active modes most influenced by  $T_g$ . The curves in panel (a) are offset for clarity. Panel (c) summarizes the variable temperature Raman scattering response as a contour plot, and panels (e) and (f) deepen our understanding of the local structure transition at  $T_g$  by examining phonon lifetime trends as discussed in the text. There is a significant hysteresis effect in both  $T_C$  and  $T_g$  depending upon direction of temperature sweep (Fig. S3, Supplemental Material [50]). These measurements correspond to a temperature up-sweep.

$T_g$  using frequency vs temperature and phonon lifetime vs temperature plots. The latter is calculated from the phonon linewidth and is an expression of Heisenberg uncertainty principle [70]. The spectroscopic signatures of  $T_g$  tend to appear below  $200 \text{ cm}^{-1}$ . These modes are mostly due to out-of-plane motions of indium and copper [Tables S2 and S3, Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80])]. They are labeled with symmetries of the  $Cc$  space group.

Interestingly, Raman scattering spectroscopy reveals that the structural aspects of  $T_g$  may take place in two distinct steps. This is particularly noticeable in the contour plot [Fig. 5(d)] as well as Fig. S3 in the Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80]). Significant broadening of all three phonons is observed around 175 and 150 K—in addition to underlying scattering intensity consistent with order-disorder processes [43]. The increase in the background scattering across  $T_g$  may be due to critical scattering (opalescence) from the microdomains.

Taken together, we see that while many infrared- and Raman-active phonons drive the ferroelectric transition, the relaxational or glassy transition in  $\text{CuInP}_2\text{S}_6$  is discernible only through subtle peak shifting and mode activation. This is because  $T_g$  is not associated with a change in the space group. Instead, our spectroscopic work reveals local lattice distortions associated with Cu site disorder. These effects appear only in phonons below  $200 \text{ cm}^{-1}$ , suggesting that  $T_g$  involves local rearrangements of the  $\text{Cu}^+$  and  $\text{In}^{3+}$  coordination environments (which may impact the polarization) as well as order-disorder processes that involve freezing of the  $\text{Cu}^+$  ions. Interestingly, the two-step character of  $T_g$  [Fig. 5(d) and Fig. S3 in the Supplemental Material [50] (see, also, Refs. [29,31,35,41,43,67,72–80])] is consistent with the low

frequency dielectric dispersion of  $\text{CuInP}_2\text{S}_6$  which shows a broad transition region near 155 K along with evidence for a possible two-step aspect to the relaxation embedded in the overall shape of the response at certain frequencies [38]. In the  $\text{MPS}_3$  family of materials ( $M = \text{Mn, Fe, Ni}$ ), only  $\text{MnPS}_3$  hosts a comparable process with spin-phonon coupling across the antiferromagnetic ordering transition [71].

#### IV. SUMMARY AND OUTLOOK

In order to explore the properties of complex chalcogenides, we measured the infrared absorption and Raman scattering response of  $\text{CuInP}_2\text{S}_6$  across the ferroelectric and glassy phase transitions and compared our findings with a symmetry analysis and complementary lattice dynamics calculations. Several different infrared- and Raman-active modes drive the ferroelectric transition whereas the relaxational or glassy phase transition involves local lattice distortions and is characterized by much more subtle peak shifting and activation. This is because  $T_C$  is a displacive transition whereas  $T_g$  is due to Cu site disorder. Both transitions have large hysteresis regions—probably on account of the bimetallic nature of this system. The glassy transition is especially interesting because, while there is no change in space group, order-disorder processes lead to local structure differences at the Cu and In sites that arise from varying coordination environments. In addition to providing evidence for a two-step transition, the spectral response across  $T_g$  is hysteretic and has significant underlying scattering intensity—consistent with glassy character. We also investigated the tendency toward chemical phase separation in these materials and, using a combination of optical microscopy, piezoforce microscopy, transmission electron microscopy, and vibrational spectroscopies, we

unravel the signature of the highest quality crystals. This paper provides guidance on how to identify high quality single crystals and, at the same time, places the vibrational properties of ferroelectric  $\text{CuInP}_2\text{S}_6$  on a firm foundation to support future work to reveal the symmetry and dynamics of few- and single-layer systems [35,72–77].

### ACKNOWLEDGMENTS

Research at the University of Tennessee is supported by the U.S. Department of Energy, Office of Basic Energy

Sciences, Materials Science Division under Grant No. DE-FG02-01ER45885. Work at Rutgers University is funded by the NSF-DMREF program (Grant No. DMR-1629059) and ONR Grants No. N00014-16-1-2951 and No. N00014-19-1-2073. Work at Pohang University of Science and Technology was supported by the National Research Foundation of Korea funded by the Ministry of Science and ICT (Grant No. 2016K1A4A4A01922028). This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Grant No. DE-SC0020353 (S.S.).

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