# Size-effect in layered ferrielectric $CuInP_2S_6$

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ABSTRACT. We report on polarization switching properties of thin flakes of van der Waals ferrielectric $CuInP_2S_6$ (CIPS). We observe mesoscale polarization domains, ferroelectric switching and the Curie temperature above 299K down to a thickness of ~50 nm. However, the electromechanical response is progressively suppressed below 50 nm, and vanishes at room temperature at a thickness of ~10 nm. Though larger than a single layer, 10 nm is still a very small value compared to the expectations for an intrinsic ferroelectric semiconductor. We therefore propose a model for a doped surface layer that screens spontaneous polarization in this material. The charges in the screening layer may also participate in secondary chemical reactions, which may explain domain pinning observed in thermal cycling of the flakes above the Curie temperature. At the same time, ferroelectric switching is intertwined with ionic diffusion, resulting in erratic and damaging switching at room temperature. Owing to much stronger temperature dependence of ionic diffusion, the two phenomena can be decoupled allowing more reliable switching to be obtained at low temperatures.

The interest in ultrathin layered ferroelectrics is motivated by the prospect of integrating piezoelectric, ferroelectric, memory and high-k dielectric functionalities with 2D electronic materials through van der Waals interfaces.[1,2] At the same time, 2D and quasi-2D ferroelectrics may facilitate the quest toward nanoscale electronic elements utilizing switchable ferroelectric barriers[3,4] and ferroelectric control of optoelectronic properties.[5,6]

Most of the layered van der Waals semiconductors, such as transition metal dichalcogenides, have centrosymmetric lattices, excluding existence of spontaneous atomic ordering leading to ferroelastic and/or ferroelectric order parameters. In addition, the large depolarizing energy in 2D ferroelectric materials should suppress spontaneous out-of-plane polarization of a single layer.[7–9] Yet recent theoretical proposals point to the possibility of in-plane atomic displacements within single $MoS_2$ layers[10], and weak out-of-plane polarization induced by an electronic mechanism.[11]

An alternative route to a 2D ferroelectric, pursued primarily with complex oxides, is size-reduction of bulk ferroelectrics. Transition metal thiophosphate (TMTP) family, with a general formula of $M^{I}_{x}M^{II}_{y}P_2(S/Se)_6$ offer a number of materials that are ferroelectric in the bulk [12, 13]. TMTP are characterized by relatively thick single layers (~0.8 nm) and ionic bonding within each layer.[14] Given that these are van der Waals crystals, they can be exfoliated to nanoscale flakes.

In a series of recent papers, ferroelectric domains were characterized in $CuInP_2S_6$[1,2] – the only layered ferroelectric so far with the transition above room temperature ($T_c$ ~ 309 K). Intriguingly, using chemical phase separation, the $T_c$ of this material is increased up to 340K due to the effect of coherence strain in phase-separated layers.[2] Ferroelectric domains in $CuInP_2S_6$ were detected down to 20 nm thickness. Here were report on the ferroelectric size-effect and ferroelectric switching in $CuInP_2S_6$ down to a few nanometers thickness, utilizing variable-temperature piezoresponse force microscopy (PFM). At the time of writing of this paper, Liu et al.[15] reported ferroelectricity in flakes of $CuInP_2S_6$ as thin as 4 nm, at least half the value of the minimum thickness reported here. Based on our direct measurement of the thickness dependence of piezoresponse and the extrinsic screening model, such a small thickness can be achieved but it requires either very efficient extrinsic screening of polarization charge and/or sufficient doping. At the same time, we show that $CuInP_2S_6$ is electrochemically active at room temperature, particularly in local measurements, which should also be taken into account when exploring size-effects in this or similar material systems.

## Results and discussion

**Fig.1** shows ferroelectric domains on $CuInP_2S_6$ flakes of varying thicknesses (84.4 ± 26.2, 33.4 ± 2.3, and 10.4 ± 0.6 nm. The error bars are due to height variation within each flake). Clear contrast due to ferroelectric domains is observed in phase and amplitude of local piezoresponse[16] on ~84 nm and ~33 nm thick flakes. It is also notable that the size of polarization domains in the flakes far exceeds the thickness of the flakes themselves. Thin flakes of $CuInP_2S_6$ therefore essentially stabilize uniform, monodomain polarization.

At the same time, the piezoresponse amplitude decreases by about three-fold (Fig. 1j) from 50 nm to 10 nm thickness. The phase signal shows no contrast for the ~10 nm flake at 298K (Fig. 1f). We therefore infer that ferroelectricity is suppressed below ~10 nm.

Confocal Raman spectroscopy also supports the existence of ferroelectric state down to least 45 nm (Fig.S1). The intensity of the Raman signal is quite quickly diminished with decreasing thickness, which prevents us from characterization of the ultrathin films at this point. Nevertheless, the data in Fig. S1 show the general similarity of the Raman spectrum between bulk crystallites and flakes in the 30-70 nm range. Under the reasonable assumption that this similarity will also persist above ferroelectric $T_c$, we surmise that the ultrathin films below 10 nm will be in an unpolarized, disordered state at room temperature. This is also consistent with the absence of meaningful piezoresponse from such films as shown in Fig. 1c, as well as no hysteresis loop opening as discussed below. Note that if the film was ferroelectric, but with polarization domains too small to resolve, switching hysteresis should still be observed, perhaps as an apparent double-hysteresis loop.

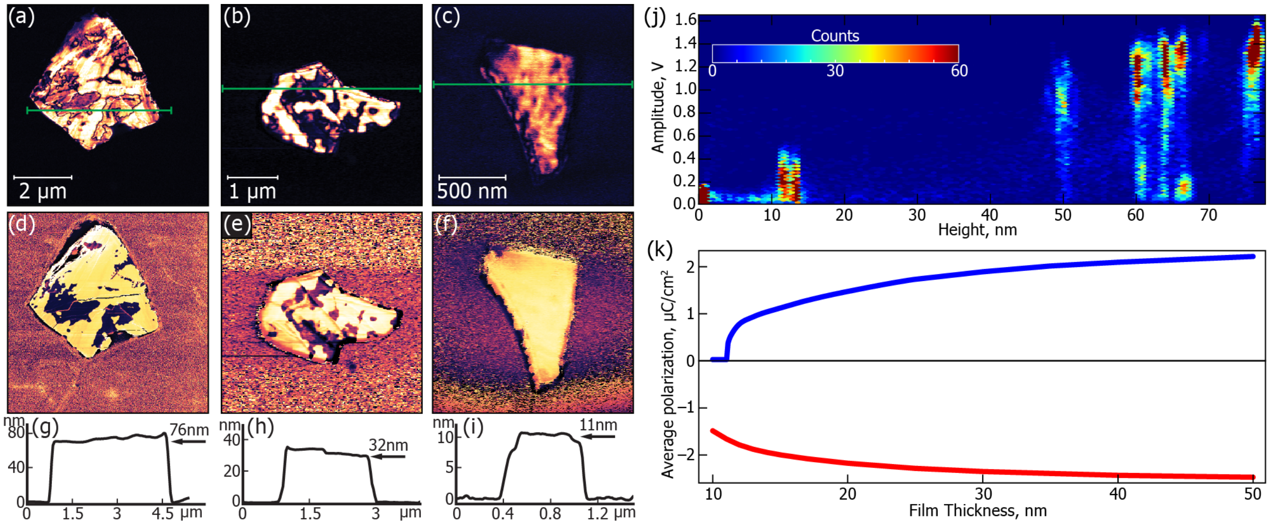

**Figure 1.** Amplitude (a,b,c) and phase (d,e,f) of local piezoresponse as well as topography profiles (g,h,i) for a series of $CuInP_2S_6$ flakes at room temperature (298 K, flake thickness of 84.4 ± 26.2, 33.4 ± 2.3, and 10.4 ± 0.6 nm, respectively). Ferroelectric domains are not observed for ~10 nm thick flake. (j) 2D histogram plot of the PFM amplitude on CIPS flakes of different height acquired during experiment depicted in **Fig.3(k).** (k) Calculated thickness dependence of up- and down- directed polarizations.

Although ~12 unit cell limit for $CuInP_2S_6$ implies that the material itself will not be a 2D ferroelectric at room temperature, at least in a pure form, 10 nm is still a very small value from the perspective of a wide-band gap semiconductor. In our earlier work, we analyzed the stability of spontaneous polarization in $CuInP_2S_6$ against depolarizing field within the framework of the Landau-Ginzburg-Devonshire applied to a proper ferroelectric semiconductor.[1] It was found that the ferroelectricity in ~50 nm thick crystal at room temperature requires mobile charge density of ~$10^{20}$ $cm^{-3}$. However, the intrinsic carrier density in $CuInP_2S_6$ with a band-gap of ~2.9 eV[13] is negligible.

An alternative screening scenario is that of a "polar catastrophe" induced by band-bending across the sample due to uncompensated polarization charge. We suppose that ferroelectric media contains screening charges of both signs so that in the equilibrium total charge is zero (i.e. we consider ferroelectric as a semiconducting media). Under the application of electric field (either external or depolarization one) the abovementioned charges are separated and screening charge layer is formed near the interface. A similar concept was invoked to predict existence of a free-electron gas on the surface of $BaTiO_3$[17] and the formation of two-dimensional electron gas (2DEG) in polar (but not ferroelectric) $LaAlO_3/SrTiO_3$ system.[18] In our case, spontaneous polarization would be screened by charges localized in a thin layer (we assume ~1-2 nm thick). Since $CuInP_2S_6$ surface is hydrophilic and experiments were performed in dry but ambient environment, mobile screening charges may also participate in chemical reactions upon crystal cleaving. In this case, polarization domains would likely be pinned by chemical charges. Chemical screening was previously suggested for monodomain $PbTiO_3$[8] and generic ultrathin ferroelectric films.[19]

We calculate the critical thickness of $CuInP_2S_6$ with moderate intrinsic carrier concentration placed on a conducting bottom electrode. The minimum concentration of ~$10^{18}$ $cm^{-3}$ is required to stabilize polarization charge down to 10-nm (see **Fig.1(k)** and Supporting information). At this thickness the screening acquires a non-linear (i.e. non-Debye) behavior and regions depleted or enriched by the space charge carriers originate in the vicinity of the electrically open surface (Fig. S3). Furthermore, the critical thickness significantly depends on the direction of spontaneous polarization (see **Fig.1(k)**), because of specific doping. The screening scenario would be symmetric with respect to polarization direction for an intrinsic semiconductor. Notably, the large screening carrier density can make the surface of $CuInP_2S_6$ electronically conducting, similar to $BaTiO_3$[17] surface and $LaAlO_3/SrTiO_3$[18] interface, an intriguing possibility for a van der Waals crystals that is compatible with 2D materials.

The validity of the above screening-controlled size-effect model is qualitatively supported by the similarity of the predicted thickness dependence of spontaneous polarization and the measured thickness dependence of the piezoresponse. **Fig.1(j)** shows a 2D histogrammatic plot of PFM amplitude versus flake thickness, where the histogram of the piezoresponse from a large area PFM image is plotted as function of the thickness of the corresponding flake. Indeed, the piezoresponse gradually decreases below 50 nm qualitatively resembling the calculated polarization profile in Fig. 1(k). Notably, the extrinsically controlled screening observed in our case does not rule out that ferroelectricity will be stabilized in better screening environments[9], particularly in light of the second order Jan-Teller electronic mechanism that favors off-center displacements within each lamella of $CuInP_2S_6$.

At the same time, the existence of secondary chemical processes that may participate in the screening can be supported by pinning of the as-grown domain structure, even when the crystal is thermally cycled across the ferroelectric phase transition. As seen in **Fig.2**, thermal cycling of an 88 nm flake across $T_c$ leaves nearly all domains unchanged. This is in contrast to domains created with DC electric field on the tip which disappear after thermal cycling, reverting largely to the as-grown structures (**Fig.2**). These observations can be rationalized by assuming chemical pinning in $CuInP_2S_6$ and a lack of reliable control over this pinning by local electric fields.

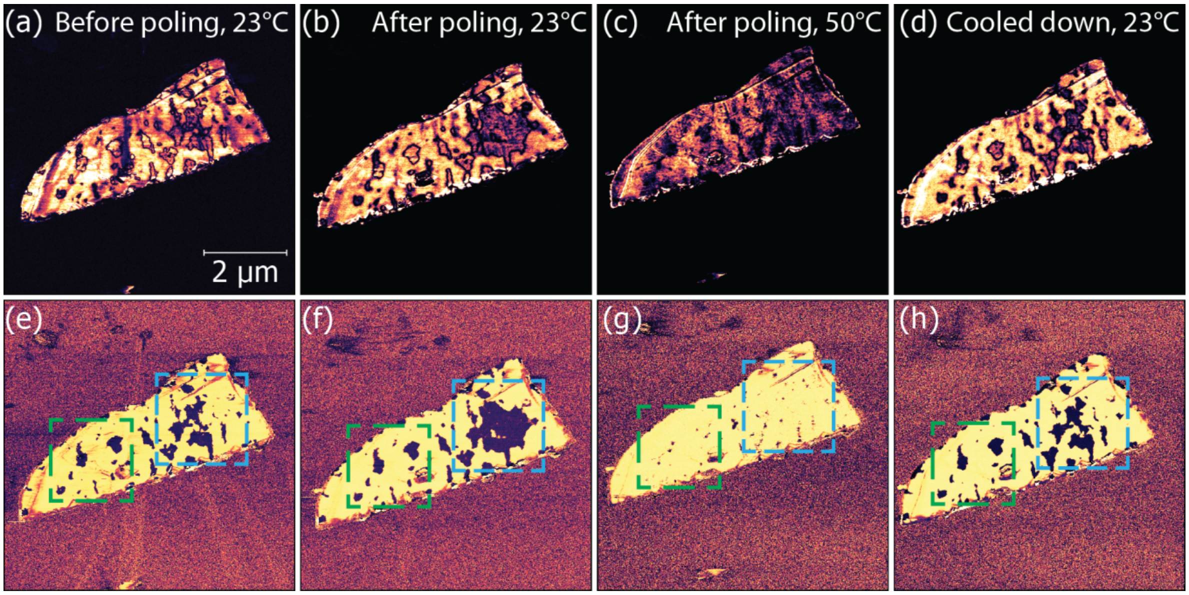

**Figure 2.** Ferroelectric domains of 88 nm flake subjected to thermal cycling. Piezoresponse amplitude (top) and phase (bottom): as prepared flake (a,e); after poling with 4V bias (b,f); after heating above $T_c$ (c,g) and cooling back to 299K (d,h). After heating, the domains switch back to the initial state. Green and cyan areas indicate pristine and poled regions of the flake, respectively.

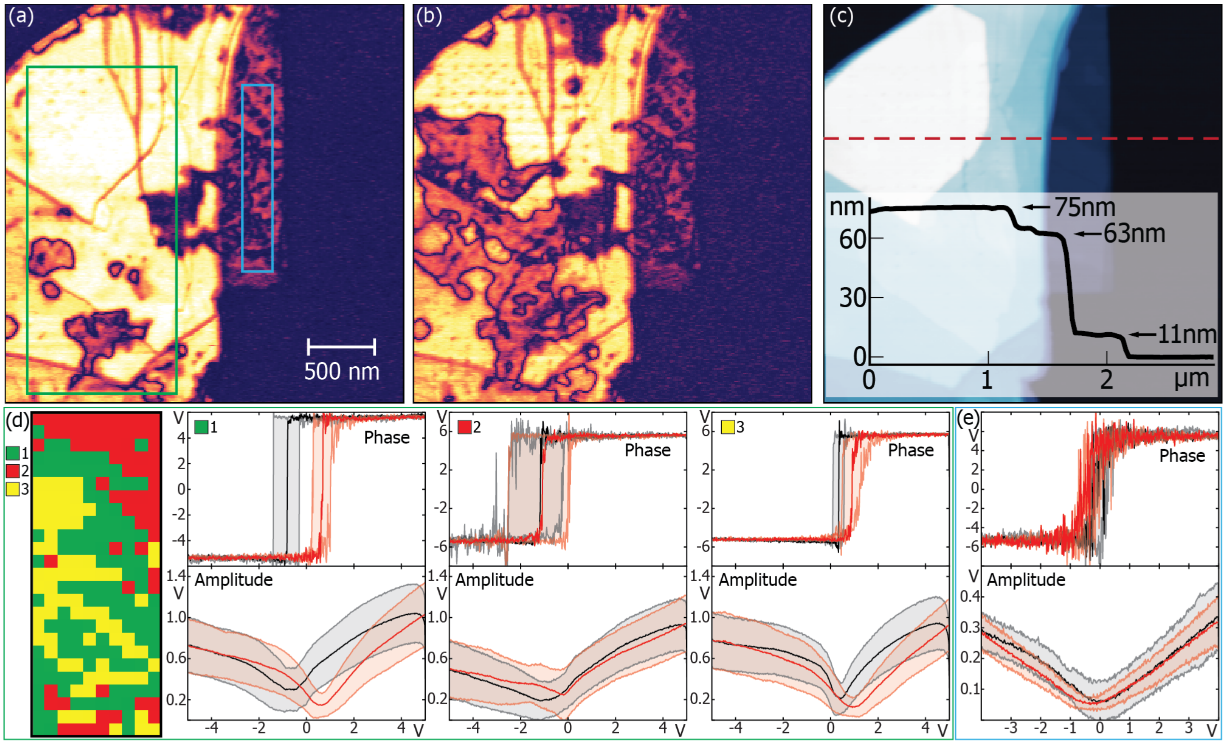

**Figure 3.** Switching experiments on $CuInP_2S_6$ flakes. Piezoresponse amplitude before (a) and after (b) switching, with the green and cyan rectangles denoting areas where local switching was performed. (c) topography of the same flake – note that the lowest part of the flake is ~ 11 nm thick. (d) Map of piezoresponse loops (25 x 10 pixels) showing three types of loops: 1 – moderately symmetric loops, 2, 3 –strongly imprinted loops. Each loop type from the thicker region (green outline) is shown in (d). Bright solid lines correspond to average signal, while shaded regions - to standard deviation of the phase and amplitude. (e) Average (bright solid lines) and standard deviation (shaded lines) of the phase and amplitude variation for 150 loops collected on the ~11 nm thick area of the flake (cyan rectangle).

Local ferroelectric switching of a representative flake was subsequently characterized with an in-field switching methodology[14] where the piezoresponse is measured as a function of increasing DC potential on the tip. The flake shown in **Fig.3** had variable thickness, from 11 nm to 75 nm. We observed a rather large variation of switching parameters (see 3 representative loop shapes in **Fig. 3(d)**) The 11 nm flake did not reveal loop opening (**Fig.3(e)**), which further confirms the absence of ferroelectricity at this thickness. Phase switching near 0 V (**Fig.3(e)**) is due to the contact electrostatic contribution to the overall measured signal[20]. This contribution should be comparable to piezoresponse in $CuInP_2S_6$ given its small net polarization.

To understand the origin of variability in ferroelectric switching on thick flakes, we repeated switching experiments on the surface of a bulk (>400$\mu$m thick) $CuInP_2S_6$ crystal. As seen in **Fig.4(a)** (and Fig. S4), switching of the bulk crystal is also inhomogeneous across the surface.

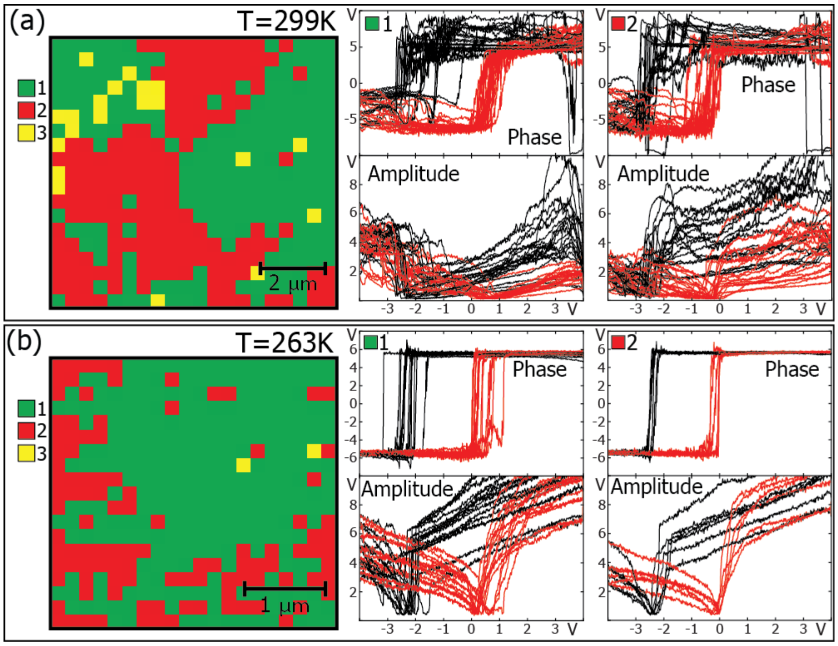

**Figure 4.** (a) In-field switching of >400$\mu$m thick $CuInP_2S_6$ crystal at 299 K. 20x19 map of piezoresponse hysteresis loops clustered in two categories with varying degree of imprint (1 – remnant loops, 2 – loops with unstable upward polarization, 20 randomly selected representative loops shown). (b) The same experiment in repeated at 263 K.

An important consideration for $CuInP_2S_6$ is possible displacement of Cu ions beyond the layer[17,18] into van der Waals gap, as evidenced by ionic conductivity at room temperature with an activation barrier of 1.16 eV.[20]

We acquired consecutive switching maps systematically increasing switching envelope from –2/+2V to –5/+5V recording PFM images between the maps (See **Fig.S5**, Supporting Information). Although the topography remains virtually unchanged after –2/+2V bias, the PFM signal registers increased amplitude at biased locations. The change can be rationalized by the change of surface potential due to ionic displacements.[20] The persistence of these changes indicates that ionic diffusion is partially irreversible in $CuInP_2S_6$. However, at ~5V we begin to observe substantial topographic changes (Fig. S6).

The comparatively large activation barrier for ionic motion suggests that even with mild cooling ionic conductivity can be suppressed. In contrast, ferroelectric switching in the localized electric field of the SPM tip is nearly intrinsic,[24] which implies that temperature changes should not affect the critical fields significantly. To verify this hypothesis, we repeated switching experiments on the surface of $CuInP_2S_6$ at 263 K. As seen in **Fig.4(b)**, ferroelectric hysteresis did become much more regular, with switching in all probed locations and switching bias closely nested around -2.5 V and ~0 V. The asymmetry of the hysteresis loops may be indicative of large built-in bias, or poor screening of downward oriented polarization, qualitatively similar to polarization switching of $PbZr_xTi_{1-x}O_3$ in ultra-high vacuum.[25]

In conclusion, we identified size effects of the layered ferroelectric $CuInP_2S_6$ with scanning probe microscopy. Ferroelectric polarization is suppressed below ~10 nm in thin $CuInP_2S_6$ flakes supported by silicon substrate. At the same time, the Curie temperature remains bulk-like down to at least 80 nm. Analytical model of a ferroelectric semiconductor reveals that efficient extrinsic screening mechanism must exist to stabilize spontaneous polarization in $CuInP_2S_6$. We propose the existence of a thin layer on the open surface, that may either be charge-doped or contain ionic charges (due to secondary chemical reactions). Experiments confirm pinning of domains consistent with immobile charge present on the surface. Polarization switching is intertwined with ionic motion at room temperature, but can be decoupled in bulk crystals by cooling just below 273 K, enabling reproducible local ferroelectric switching. It is clear that $CuInP_2S_6$ is a rather complex ferroelectric system, where ionic and ferroelectric degrees of freedom and preexisting disorder have to be considered simultaneously to explain and predict size-effect and switching properties. This coupling can be potentially exploited to create nanoscale ferroelectrics or even bistable ionic systems that themselves are not ferroelectric. At the same time, this system blends some of the interesting properties of complex oxides with flexible van der Waals crystal structure, providing future opportunities for complex van der Waals heterostructures.

## Methods

$CuInP_2S_6$ crystals were prepared using chemical transport reaction with elements in stoichiometric proportions as detailed in our previous work.[2] Ultrathin flakes were prepared by peeling crystals using scotch tape method[26] and deposited onto the substrate (doped silicon wafers and conductive epoxy). Measurements were performed using a commercial microscope (Bruker Dimension V) with a DS345 Synthesized Function Generator (Stanford Research Systems) and Thermal Applications Controller.[20] Preparation and measurements were performed inside Ar filled glovebox (MBraun).

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## Supplementary Material

Supplementary material includes Raman spectroscopy of CuInP2S6 flakes, Landau-Ginsburg-Devonshire model for an ultrathin ferroelectric semiconductor, additional piezoresponse hysteresis loops of $CuInP_2S_6$ at room temperature and topographic changes of $CuInP_2S_6$ flakes subjected to large electric field.

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