Local symmetry breaking drives picosecond spin domain formation in polycrystalline halide perovskite films

Photoinduced spin–charge interconversion in semiconductors with spin–orbit coupling could provide a route to optically addressable spintronics without the use of external magnetic fields. However, in structurally disordered polycrystalline semiconductors, which are being widely explored for device applications, the presence and role of spin-associated charge currents remains unclear. Here, using femtosecond circular-polarization-resolved pump–probe microscopy on polycrystalline halide perovskite thin films, we observe the photoinduced ultrafast formation of spin domains on the micrometre scale formed through lateral spin currents. Micrometre-scale variations in the intensity of optical second-harmonic generation and vertical piezoresponse suggest that the spin-domain formation is driven by the presence of strong local inversion symmetry breaking via structural disorder. We propose that this leads to spatially varying Rashba-like spin textures that drive spin-momentum-locked currents, leading to local spin accumulation. Ultrafast spin-domain formation in polycrystalline halide perovskite films provides an optically addressable platform for nanoscale spin-device physics.

Central to the use of spin in solid-state spintronic devices is the ability to lift the energetic degeneracy of spin-polarized electrons—Kramer’s degeneracy. Historically this has been achieved by manipulating the local magnetic environment of electrons through an external magnetic field, which breaks time-reversal symmetry and lifts Kramer’s degeneracy. This degeneracy can also be lifted without the need for an external magnetic field in systems with spin–orbit coupling that break inversion symmetry, leading to spin and momentum eigenvalues that are locked to each other. This is known as either the Bychkov–Rashba effect on the surface or Dresselhaus effect when present in the bulk (collectively referred to as the Rashba effect henceforth). With inversion symmetry broken in the out-of-plane direction, a radially symmetric spin–orbit perturbation splits the initially degenerate spin bands in k-space (Fig. 1a). The two bands that emerge are no longer eigenstates of in-plane spin and they inherit particular k-dependent directions referred to as spin textures (red and blue arrows forming circles in Fig. 1a). Along any cut in the direction perpendicular to the symmetry breaking, the inner and outer bands on opposite sides of the zone centre exhibit the same spin state, labelled by the spin quantum number, $m_s$ (green or orange bands, Fig. 1a). Upon photoexcitation with circularly polarized light from a similarly split valence band, selection rules dictate that $\Delta m_s = \pm 1$ (depending on the light
helicity), populating one semicircle of the Fermi contour of the inner spin texture, and the zone-opposed semicircle of the Fermi contour of the outer spin texture. This leads to a net photoinduced electronic momentum imbalance as the Fermi wavevectors for each spin texture are different. From standard Boltzmann transport treatment, this manifests as an in-plane charge current. Depending on the specific dimensionality and chirality of the spin-induced charge current, this effect is known as the inverse spin Hall, inverse Rashba–Edelstein, circular photogalvanic or anomalous circular photogalvanic effect. In all these effects, the link between the particular selection rule (helicity), and associated charge current direction is dictated by the spin textures—i.e. if the spin textures were exchanged, the charge current would reverse direction.

Reports of such photoinduced spin-to-charge transport have thus far been limited to clean quantum systems with low structural disorder such as two-dimensional electron gases, surface states of topological insulators, single crystals and quantum wells probed via bulk, contact-based measurements. By contrast, emerging polycrystalline semiconductors such as thin films of halide perovskites, which show high-quality optoelectronic properties even in the presence of large structural and electronic disorder, have not been investigated with respect to their local spin properties, despite the presence of strong spin–orbit coupling and claims of bulk and surface Rashba effects. In these materials, it is therefore unclear if such spin-associated charge currents are present and what their role is. Here, using circular-polarization-resolved pump–probe microscopy with 15 fs time resolution, we show that not only are spin-associated charge currents present in these polycrystalline materials on the micrometre scale, but that the inherent inter-grain structural disorder drives these currents through local symmetry breaking, leading to the formation of optically addressable local spin domains that could be tailored through structural material design.

We focus here on studying thin films (100 and 150 nm) of the well-established, high-performing and stable halide perovskite system based on the alloyed composition FA0.79MA0.16Cs0.05Pb(I0.83Br0.17)3 (where FA is formamidinium and MA is methylammonium), which have a high degree of polycrystallinity (typical reported grain sizes ranging from 50 to 1,000 nm) and a bandgap at 764 nm (Supplementary Fig. 1 for absorption and luminescence spectra). To resolve the real-space propagation of spin currents and study the effects of the spatial inhomogeneity inherent to these films on the local spin depolarization, we perform ultrafast circular-polarization-resolved pump–probe imaging in a wide-field microscope geometry at room temperature. Here the studied system is first photoexcited with a pump pulse of a given helicity (Δm_f = +1 or −1; green line, blue/red arrows in Fig. 1b), resulting in a net polarization...
of electronic spin. After a fixed time delay, a probe pulse (orange in Fig. 1b) of the same (co; Δm = +1 or −1) or opposite (counter; Δm = −1 or +1) helicity is incident on the material, and the difference between the transmission of the probe pulses (ΔT/ΔTco − ΔT/ΔTcounter) due to the pump pulse is reported as the photoinduced circular polarization. In halide perovskite films, it is reported that this net ensemble positive photoinduced spin polarization decays to zero in a few picoseconds due to spin scattering events.

We first photoexcite a wide-field region of the film of ~200 μm² with an 11 fs pump pulse (500–650 nm) and probe a 100 μm × 100 μm region of this sample with an 8.5 fs broadband probe pulse (700–900 nm; Supplementary Figs. 2–6 for pulse compression, temporal and polarization characterization). All the experiments are repeated by switching the probe polarization helicity on alternate sweeps to ensure no systematic errors appear as a net circularly polarized transient absorption signal (Supplementary Figs. 7–9). We study a homogeneously excited region of 7 μm × 7 μm, choosing to image at a wavelength of 750 ± 10 nm, near the bandgap, where there is a large ground-state bleach signal and where previous studies on spin lifetimes in perovskites have focused. We label right (left) circularly polarized light as σ+ (σ−). To study the spatial photoinduced circular polarization signal, we subtract wide-field ΔT/ΔT images of the probe co- and counter-polarized to the pump helicity at each time delay and report this as the local spin polarization image (Supplementary Fig. 10 for wide-field ΔT/ΔTco images and ΔT/ΔTcounter images). As we make no comment on the polarization magnitude in this report and focus solely on the kinetics and signal sign, we normalize the signals to the average image signal to get an estimate of the transmission of the probe pulses (ΔT/ΔTco or +1) helicity is incident on the material, and report this as the local spin polarization (Supplementary Text 2 for equation).

**Figure 1c** shows that, upon fitting the kinetics of the measured wide-field excited polarization images, we retrieve large spatial variations in the sign of the polarization signal, with regions of positive and negative polarization. This is surprising as a net counter-polarized signal is not expected to occur based on the previously reported spin dynamics of these systems. If we average over all spatial points, we do indeed retrieve the previously reported ensemble average behaviour, as shown in Fig. 1d (green line). Considering all points individually, however, we observe a binary behaviour, with domains of positive polarization rising immediately upon photoexcitation and domains of negative polarization responding with a delayed rise time over a few picoseconds, as exemplified for domains R1 and R2 in Fig. 1c with corresponding kinetics and fits to equation (S2), as shown in Fig. 1d. We note that both types of domains show longer than spatially averaged spin lifetimes (green line in Fig. 1d and Supplementary Figs. 7–9), more consistent with reports of single-crystal spin lifetimes.

**Figure 1e** shows the rise time for each point within the field of view. A clear correlation between the sign of the polarization (shown in Fig. 1c) and its associated rise time (Fig. 1e) can be seen, with domains of negative polarization rising later than domains of positive polarization. This is more clearly seen in the histograms in Fig. 1f. The top panel of Fig. 1f shows a spread in rise times, which comes from locally varying carrier cooling rates as we photoexcite high in the band (Supplementary Fig. 11 for probe energy dependence). However, when compared to the bottom panel, the timescale separation for the positive and negative polarizations is well above this broadening. We repeat this on films prepared by a different synthetic route of different thickness (100 nm) and find the same effect (Supplementary Fig. 12). On repeating the same experiments with linearly polarized pump and probe pulses, we observe no correlation between the local rise times and sign of polarization anisotropy, ruling out the linear birefringence and linear dichroism artefacts (Supplementary Text 1 and Supplementary Figs. 13 and 14).

To study the origin of this rise-time-correlated negative polarization signal, we investigate the spatial transport dynamics of the photoinduced polarization (Fig. 2). Here we perturb the sample with the same circularly polarized pump pulse, but now focused through the microscope objective to a near-diffraction-limited 200 nm spot. This photoinduces a local Gaussian spin-polarized electronic population, the transport of which is then imaged with the co- and counter-polarized wide-field probe pulse as described earlier. To study the motion of the spin-polarized electrons, we directly fit a Gaussian function to the polarization image. While we fit the raw data, for visualization in Fig. 2a, we have chosen to use a Fourier filter to remove spatial fluctuations that are faster than the fastest Fourier component resolvable by our high numerical aperture optical microscope (Supplementary Fig. 15 for raw images). As seen in Fig. 2a, we measure an approximately Gaussian-distributed net polarization at early times (100 fs). Over the first picosecond, however, we find that the photoinduced polarization moves away from the initial spot (as seen in the images at 120 fs, 540 fs and 980 fs). We repeat this on several spots...
and different excitation densities and uniformly observe this behaviour (Supplementary Figs. 16 and 17). At high excitation densities, the lateral shift and formation of counter-polarized spin currents is clear (Supplementary Fig. 18). However, the formation of counter-polarized regions along with spatially varying carrier cooling rates complicates the extraction of an accurate carrier velocity, and hence we chose to focus here on the lowest excitation density measurement. Fitting the change in the Gaussian centre of the net polarization signal as a function of time, we resolve motion of 100 nm over 1 ps, yielding a velocity in the range of $(1.1 \pm 0.3) \times 10^3$ m s$^{-1}$ (Fig. 2b). This velocity is related to the Rashba parameter that gives rise to a momentum imbalance of the carriers near the band edge, setting the drift velocity of spin-momentum-locked currents in Rashba-like bands. This fast, lateral motion suggests that photoinduced spin polarization leads to a lateral current on sub-1 µm length scales and could explain the spatially varying rise of the anomalous negative polarization.

There are two possible scenarios that could explain our observation. The first is the motion of spin-induced lateral currents that arise from Rashba-like spin textures. We note that such spin-pumped lateral charge currents have been previously reported in topological insulators and bulk single-crystal semiconductors using contact-based current measurements. The second is apparent spin transport associated with spin-polarized charges moving in a locally varying energy landscape. As shown in Supplementary Figs. 19–23, we observe a lack of correlation of the measured domains with the spatial photoluminescence, as might be expected for energy-driven transport. To further distinguish between these two scenarios, we perform wide-field experiments for both pump helicities. If the spin transport is caused by charge motion in a locally varying energy landscape, the direction of spin transport will be invariant to the pump helicity. By contrast, in the Rashba-like scenario of spin-associated currents (Fig. 1a), the direction of spin transport must reverse when the pump helicity is inverted.

As shown in Fig. 3a,b, we observe that the local domains of negative and positive polarization reverse sign on changing the helicity of the pump pulse. As expected, however, the sign of the spatially averaged polarization decay depends only on the relative polarization between the pump and probe; that is, it is initially positive and decays to zero as previously reported (Supplementary Fig. 24). The spatial anti-correlation in the polarization on changing the helicity of the pump is made clear in Fig. 3c, where, after the pump pulse arrives ($\Delta t > 0$), the anti-correlation in the signal at each pixel is evident. Crucially, on fitting the kinetics for each pixel, we observe that the domains of slow rise times, which were correlated with negative polarization, switch with the domains of fast rise times upon changing the helicity of the pump pulse, as seen in Fig. 3d,e. This shows that the direction of the underlying lateral transport is reversed. The change in local kinetics on changing the pump helicity conclusively rules out any linear birefringence and linear dichroism artefacts (Supplementary Text 1). This timescale separation is also clearly seen in the histograms in Fig. 3f, which strongly resemble those in Fig. 1f, regardless of the helicity of the pump pulse.

To gain further insight into the microscopic origins of the local spin-locked currents, we investigate these thin films for signatures of local inversion symmetry breaking, as would be needed to produce...
local Rashba-like spin textures\textsuperscript{39}. As shown in Fig. 4, we study the micrometre-scale polycrystallinity (Fig. 4a) using piezoresponse force microscopy (PFM) and uncover signatures of polarized domains (Fig. 4b; Supplementary Fig. 25 for corresponding PFM amplitude)\textsuperscript{38,39}. The images in Fig. 4a,b were taken on the same region of the film to correlate the piezoresponse to topography. We are also able to recover switchable ferroelectric loops on some areas of the film (Supplementary Fig. 26). Local inversion symmetry breaking is further evidenced by micrometre-scale variations in the second-harmonic generation (SHG) intensity measured on the same films, as seen in Fig. 4c. While the presence of SHG is evidence for local symmetry breaking, the large variations in intensity could possibly arise from polar domains or the surfaces of locally canted grains\textsuperscript{40,41}. As the prepared films are spin-coated, the interface with glass should be relatively smooth, suggesting that the spatial heterogeneity arises from variations in inversion symmetry breaking in the bulk.

Our main observations are fourfold. First, there is a photoinduced ultrafast formation of spin-polarized positive and, unexpectedly, negative spin domains on the micrometre scale in real space formed through lateral currents at a velocity of \(v \approx 10^5\) m s\textsuperscript{-1}. Second, the anomalous domains of negative polarization grow in over a few picoseconds, consistently slower than those with positive polarization. Third, the polarization of these domains and lateral transport direction are switched upon switching the polarization of the pump helicity. Fourth, there is strong evidence of local inversion asymmetric phases in these polycrystalline films.

To explain these observations, we propose a model of spin-momentum-locked currents in a micrometre-scale disordered system. Consider two adjacent regions in space where inversion symmetry is broken in opposite directions (Fig. 5a). The local spin textures in the two regions also have opposite directions of the spin-locked lateral currents for a given pump helicity. Immediately upon photoexcitation of these two regions with right-handed circularly polarized light (\(\sigma^+\)), these regions in real space are co-polarized (blue shading). After a few hundred femtoseconds, however, spin-flip mechanisms (Elliott–Yafet or D’yakonov–Perel) cause a subpopulation of the spin-locked currents to reverse in direction (become red in the figure). Propagating these spins with their respective current directions leads to the scattering-limited growth of regions of counter-polarized spins (red) and consequently the formation of spatially segregated regions of co- and counter-polarized (blue and red, respectively) spins. In this scheme, the co- and counter-polarized regions reverse sign upon photoexcitation with left-handed circularly polarized light (\(\sigma^-\)), as do the negatively polarized regions, which show the delayed rise due to spin-scattering-limited growth, entirely consistent with our observations.

While this simple model for two regions shown in Fig. 5a works well at capturing the phenomenology of our observations, it is not clear whether this spin-accumulation effect is robust against the polycrystalline nature of our films, seen in Fig. 4a. We therefore built a stochastic Monte-Carlo-based toy model of the spin transport in a polycrystalline, structurally disordered film (Supplementary Text 3 for details). As input parameters to the model, we use the measured lateral velocities, spin depolarization lifetimes, symmetry breaking length scales consistent with Fig. 4 and picosecond simulation timescales. As seen in Fig. 5b, each region represents a domain with a random direction and magnitude of inversion symmetry breaking, which results in randomized spin-locked currents. We stress that while this disordered landscape can arise from a multitude of microscopic mechanisms—polar/ferroelectric, orientational/canting, interfacial or strain inhomogeneity—its overall effect is to break inversion symmetry locally. In this disordered landscape, we initialize a uniform distribution of \(10^5\) local spin-polarized currents. We then propagate these spin currents in space according to the local spin-momentum locking direction along with the possibility of a Monte-Carlo-style random spin flip, which reverses the current direction for a given region (for video, Supplementary Video 2; for simulated spin depolarization, Supplementary Fig. 27). We find excellent agreement between the features observed in our experiment and this model, which is brought out by convolving the modelled data using a Gaussian kernel density estimate (Fig. 5c). This result suggests that this toy model captures the observed phenomenology.

While the precise microscopic origins of the local inversion symmetry breaking landscape are not understood to date for the case of halide perovskite materials, our results demonstrate that these effects are important in device-relevant polycrystalline films, and we attempt to shed light on the possible mechanisms at play. First, by measuring the same region of the film for SHG and spin-domain formation, we find only a weak correlation between the spin domain regions and polarization rise time and the intensity of the SHG (Supplementary Figs. 30 and 31). This is likely due to the fact that the local SHG intensity is strongly modulated by the local grain orientation and reabsorption losses\textsuperscript{42}. To further investigate this, we study the spin domain formation as a function of film thickness (Supplementary Fig. 32) within our experimental capability and find that the thinner films have a longer spin domain rise time on average, despite similar spatially averaged spin depolarization times (Supplementary Figs. 7 and 8). This suggests that the magnitude of the velocity and consequently the Rashba...
parameter are smaller in the thinner film, suggesting that the relevant symmetry breaking could be related to the material bulk structure.

We note that recent reports of a local symmetry-lowering octahedral tilt responsible for stabilizing the same perovskite film composition may also be responsible for local inversion symmetry breaking phases, despite reports of an inversion symmetric space group. Importantly, strain in halide perovskites has been theoretically predicted to modulate the Rashba parameter. Further, local micrometre-scale strain maps in the same perovskite film composition have reported high uniaxial strain along the grains. Using the inverse Rashba–Edelstein effect framework, the photoinduced momentum imbalance is related to the Rashba parameter $\alpha_R$ as $\Delta k = \frac{2m}{\hbar^2} \alpha_R$, where $m$ is the reduced electron mass and $k$ is the electron wavevector. Hence the measured spin-polarized velocity, $v$, shown in Fig. 2...
offers insight into the magnitude of $\alpha$, as $\alpha = \frac{e}{2m} \nu$, yielding the local Rashba parameter of $\alpha = (0.37 \pm 0.09) \text{ eV}$. This value is well within the range of reported values in the literature on single-crystal halide perovskites and predicted values based on strain, but below that reported for the pure interface Rashba effect in halide perovskites. We can further estimate an upper bound on the electrical polarization of the domains measured using PFM (Fig. 4b and Supplementary Text 4) as $<2 \mu \text{C cm}^{-2}$, in excellent agreement with the calculations of an electric field and strain-induced Rashba effect, suggesting a possible microscopic origin for this local inversion symmetry breaking landscape.

Finally, we note that regardless of the origin of micrometre-scale regions with opposite inversion symmetry breaking (Fig. 5b), our model shows that spin-domain formation will always be observed in a system where the local spin current directions are random. For example, if any two neighbouring regions in Fig. 5b have a component of their spin current along the same direction, this necessarily leads to spin-accumulation domains upon spin-flip scattering events. Crucially, we note that these local spin-accumulation effects spatially average to zero, which explains why they have remained hidden to bulk experimental probes (optical or contact based).

We directly observed the spatio-temporal formation of spin domains in a semiconductor occurring on picosecond timescales. Moreover, these spin domains are fully optically addressable via the choice of pump beam helicity. In the present case of polycrystalline halide perovskite thin films, these spin currents are found to be the consequence of local symmetry breaking on the micrometre scale. This opens up a route to engineer spin domains by micropatterning the symmetry breaking directions through an electric field or elastic strain (as we exemplify in Supplementary Fig. 26 showing ferroelectric hysteresis), benefitting from the facile material processing of halide perovskite films. Our findings therefore unlock applications such as local spin injection for chiral emission of spin-LEDs (LED, light-emitting diode), and polycrystalline, solution-processable semiconductor analogues to magnetic domain wall logic.

Online content
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Methods

Fabrication of 150 nm triple cation halide perovskite film 'A'
The glass substrates were cleaned by a standard four-step (15 minutes each) method. The first step was cleaning the glass slides by sonication in 2% Hellmanex solution followed by 15 minutes of sonication in fresh deionized water. The water-cleaned substrates were then sonicated for 15 minutes in acetone followed by isopropanol. The dried glass slides were cleaned with a treatment of UV–ozone for 15 minutes. UV–ozone-treated substrates were then transferred to a fabrication glove box. The solution of triple cation perovskite \((\text{Cs}_{0.05} (\text{MA}_{0.17} \text{FA}_{0.83})_{0.95} \text{Pb}(\text{I}_{0.84} \text{Br}_{0.16}))_3\) was prepared by dissolving \(\text{PbI}_2\) (0.3112 g, 0.55 M), \(\text{FAI}\) (0.1075 g, 0.5 M), \(\text{PbBr}_2\) (0.0495 g, 0.1 M) and \(\text{MABr}\) (0.0152 g, 0.1 M) in a mixture of \(\gamma\)-butyrolactone (510 µl), anhydrous dimethylsulfoxide (340 µl) and dimethylformamide (150 µl). The resulting solution was continuously stirred at 70 °C for 15 minutes. CsI stock solution was separately prepared by dissolving 194.86 mg of CsI in 0.5 ml of dimethylformamide. Then 30.7 µl (0.0275 M) of CsI was added into the perovskite solution, and the whole perovskite solution was again stirred for 15 minutes at 70 °C. Triple cation perovskite solution (100 µl) was spread on cleaned glass substrates (22 mm × 22 mm) and then spin-coated by using a two-step programme: 1,000 r.p.m. and 6,000 r.p.m. for 10 and 25 seconds, respectively. Nitrogen gas was continuously blown on the spinning samples for the last 15 seconds of spinning time. The fabricated films were annealed at 65 °C for 10 minutes and 100 °C for 30 minutes. The perovskite films were encapsulated by using a glass cover-slip and epoxy resin AB glue.

Fabrication of 150 nm triple cation halide perovskite film 'A' on substrates
The perovskite films on indium tin oxide (ITO) substrates were fabricated by the same process described in the earlier section of halide perovskite thin film fabrication.

Fabrication of 100 nm triple cation halide perovskite film 'B'
Glass slides were cleaned by sonication in 2% Hellmanex solution for 15 min. After rinsing with deionized water, the substrates were sonicated again with acetone and isopropanol for 15 minutes each. The glass slides were treated with UV–ozone for 15 min and transferred immediately to a N₂-filled glove box. Mixed halide triple cation perovskite \((\text{Cs}_{0.05} (\text{MA}_{0.17} \text{FA}_{0.83})_{0.95} \text{Pb}(\text{I}_{0.83} \text{Br}_{0.17}))_3\) was deposited from a precursor solution containing \(\text{FAI}\) (0.42 M), \(\text{PbI}_2\) (0.46 M), \(\text{MABr}\) (0.08 M), \(\text{PbBr}_2\) (0.08 M) and CsI (0.031 M) in anhydrous dimethylformamide/dimethylsulfoxide (4:1. v/v). The perovskite solution was spin-coated using a two-step programme: 1,000 r.p.m. and 6,000 r.p.m. for 10 s and 20 s, respectively. During the second step, 100 µl of chlorobenzene was pipetted onto the spinning substrate 5 s before the end of the programme. The substrates were then annealed at 100 °C for 1 h. The resulting film thickness was 100 nm. The films were encapsulated using a glass coverslip and UV-curable epoxy glue.

Probe generation and compression
The probe pulse was generated using a homebuilt set-up around a Yb:KGW (KGW, potassium gadolinium tungstate) amplifier laser (1,030 nm, 200 kHz, 6 W; Pharos, LightConversion). The pump pulse was a seeded white light continuum created using a 3 mm sapphire crystal that after passing through a 650 nm short-pass filter (FEL650, Thorlabs) spanned from 500 nm to 650 nm. Two pairs of chirped mirrors (109811, Layertec; 17 bounce pairs) were used to pre-compress the white light continuum before it entered a zero-dispersion line, 4-f reflective pulse shaper based on a reflective-grating (Andor, Shamrock SR3-0300-0500), dual-mask liquid crystal spatial light modulator (Jenoptik SLM-S200D). The spatial light modulator voltage-to-phase and pixel-to-wavelength mappings were then calibrated. The white light continuum was then compressed using a Multiphoton Intrapulse Interference Phase Scan (MIIPS) algorithm based on SHG.

MIIPS pulse compression algorithm
Our MIIPS algorithm is based on the sinusoidal variation of the spectral phase through the placement of a programmable spatial light modulator in the Fourier plane of a 4-f pulse shaper, reported by Lozovoy et al.19. First, the uncompressed pump white light continuum is sent through the linear polarizer, the quarter wave plate (polarized parallel to the fast axis), the 500-nm-thin lens (Eksma Optics, Femtoline 110-1233ET+UBBAR, for wide-field measurements only) and the microscope objective and then through a 10 µm beta barium borate crystal for SHG. Care was taken to ensure the exact same optical elements were used in the beam path for compression/characterization and the experiment. The thin beta barium borate crystal is critical to correctly compress such broadband pulses due to its high acceptance bandwidth for SHG. The resulting SHG signal is focused into an OceanOptics UV spectrometer to record its intensity and spectrum. A sinusoidal spectral phase variation with an amplitude of 5 radians and period of 12 fs (target resolution) was then scanned across the spectral phase, and the SHG spectrum for each spectral phase modulation was recorded, keeping the spectral amplitude constant. The maximum intensity line of the two MIIPS traces was extracted, and upon double trapezoidal numerical integration, the phase was retrieved. The inverse phase was applied to the spatial light modulator mask through the voltage-to-phase calibration, and the process was repeated, reducing the amplitude of the spectral phase modulation as appropriate until the total spectral chirp was reduced below a threshold of 50 fs² (ref. 2). The final resulting mask was saved and the resulting pulse characterized using SHG frequency-resolved optical gating20. This phase mask was used for all the experiments reported. The results of the compression are shown in Supplementary Fig. 4.

Characterization of degree of circular polarization
For both the pump and probe beams, the circular polarization was generated using a combination of a broadband linear polarizer (Thorlabs WP25UM-UB) and a super achromatic quarter wave plate (Thorlabs SAQWP0SM-700). This was necessary due to the unavoidable large (transmitting limited) bandwidth of the pulses to ensure their short temporal duration. To characterize the degree of circular polarization of the pulses in the sample, care was taken to ensure all the optical elements during the experiment were present during characterization and that the degree of circular polarization was measured in the sample plane of the microscope. This is critical to understand the limitations in analysing our data due to ellipticity introduced by dichroic beam splitters and non-ideal reflection angles. The degree of circular polarization was measured using a second broadband linear polarizer (analyser) in conjunction with a power meter (Thorlabs PM130D). The power incident on the power meter was monitored as the analyser was rotated. The ratio of the minimum and maximum transmitted power through the second polarizer is reported as the degree of circular polarization.

Microscope design
Our microscope is designed around an inverted 8-f microscope geometry using an oil immersion, high numerical aperture (1.1) objective with...
a 200 nm achromatic doublet imaging lens placed in the infinity space of the objective35. A dual lens beam expander relay system of a 200 mm and 500 mm lens then send the images to an electron-multiplying charge-coupled device (emCCD) camera (Rolera Thunder, QImaging). This yields a total lateral magnification of ×255, that is, 55.5 nm per pixel.

### Wide-field pump–probe microscopy

A clean TEM00 mode for the pump pulse was achieved by using a pinhole. The pump was then collimated using a combination of focusing mirrors at nearly normal incidence and was then focused into the back focal plane of the microscope objective in order to achieve a wide-field pump illumination of approximately 200 μm². The incident fluence was maintained below 5 μJ cm⁻². A counter-propagating wide-field probe pulse, loosely focused to 400 μm², was then incident on the sample and imaged using a 750-10 nm bandpass filter. A closed-looped piezo translation stage (P-625.1CL, Physik Instrumente) was used to delay the probe with respect to the fixed pump, and the pump was modulated at 80 Hz using a mechanical chopper locked to the 200 kHz laser pulse train. The emCCD was triggered at the same rate, and consecutive pump-on and pump-off images were subtracted and normalized to the pump-off image, yielding a spatial ΔT/T signal. This was done for a given circularly polarized pump and the co- and counter-polarized probe beams to measure the photoinduced circular polarization. As shown in Supplementary Fig. 28, the circularity of the beams is adequate to resolve the spin depolarization, which disappears upon exciting with a linearly polarized pump.

### Focused pump–probe microscopy

A clean TEM00 mode for the pump pulse was achieved by using a pinhole. The pump was then collimated using a combination of focusing mirrors at nearly normal incidence and set completely fill the aperture of the microscope objective in order to achieve a focused pump illumination of approximately σ ≈ 200 nm. The incident fluence was maintained below 60 μJ cm⁻², and the maximum ΔT/T signal was matched to the wide-field measurements to ensure an accurate comparison. A counter-propagating wide-field probe pulse, loosely focused to 400 μm², was then incident on the sample and imaged using a 750-10 nm bandpass filter. A closed-looped piezo translation stage (P-625.1CL, Physik Instrumente) was used to delay the probe with respect to the fixed pump, and the pump was modulated at 80 Hz using a mechanical chopper locked to the 200 kHz laser pulse train. The emCCD was triggered at the same rate, and consecutive pump-on and pump-off images were subtracted and normalized to the pump-off image, yielding a spatial ΔT/T signal. This was done for a given circularly polarized pump and the co- and counter-polarized probe beams to measure the photoinduced circular polarization.

### Piezoresponse force microscopy

PFM measurements were performed on a Multimode 8 (Bruker) microscope with Pt-coated NSC35 tips (MikroMasch), and the PFM signal was recorded in polar coordinates. For the PFM measurements, an ITO bottom electrode was deposited on the glass slide prior to sample deposition to enable electrical probing and biasing. We locally detected the PFM response using an alternating voltage of 2 V with a frequency of 15 kHz at nearly normal incidence and was then focused into the back focal plane of the microscope objective in order to achieve a wide-field pump illumination of approximately 200 μm². The incident fluence was maintained below 5 μJ cm⁻². A counter-propagating wide-field probe pulse, loosely focused to 400 μm², was then incident on the sample and imaged using a 750-10 nm bandpass filter. A closed-looped piezo translation stage (P-625.1CL, Physik Instrumente) was used to delay the probe with respect to the fixed pump, and the pump was modulated at 80 Hz using a mechanical chopper locked to the 200 kHz laser pulse train. The emCCD was triggered at the same rate, and consecutive pump-on and pump-off images were subtracted and normalized to the pump-off image, yielding a spatial ΔT/T signal. This was done for a given circularly polarized pump and the co- and counter-polarized probe beams to measure the photoinduced circular polarization.

### Second-harmonic generation microscopy

As the bandgap of the perovskite films investigated is around 760 nm, the fundamental laser of the Yb:KGW amplifier laser system (1,030 nm, 200 kHz, 6 W; Pharos, LightConversion) served as an ideal pulse with which to study the SHG of the films. In the same microscope geometry described earlier, the 1,030 nm laser beam was loosely focused to 400 μm² on the sample. The SHG generated at 515 nm was collected by the objective and imaged onto the emCCD using a 520 nm bandpass filter. For these measurements, the laser fluence was set to 31 mJ cm⁻² and an integration time of 10 min at a gain of 1,000 was used to collect the SHG signal. As a microscope cover-slip was used as the substrate in all of these measurements, this ensured that the SHG could not arise from the substrate and must arise from the perovskite sample. The homogeneity of the TEM00 mode of the fundamental confirmed that the spatial variations measured on the micrometre scale were due to perovskite heterogeneity rather than beam heterogeneity.

### Data availability

The data that support the plots within this paper and other findings of this study are available at the University of Cambridge Repository at https://doi.org/10.17863/CAM.95175.

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### Author contributions

A.A., S.F. and A.R. conceived the project. A.A. performed all the optical experiments and built and programmed the pulse shaper for pulse compression. S.N. and B.R. fabricated the halide perovskite films. N.S. performed the PFM measurements. A.S. contributed to the analysis of possible optical artefacts in the signal. A.A. and A.J.S. built the pump–probe microscope set-up. J.S. supervised the building of the pump–probe microscope set-up. J.L.M.-D. supervised the PFM measurements. S.D.S. supervised the work of S.N. and B.R.; S.F. and
A.R. supervised the project. A.A. wrote the manuscript with input from all authors.

**Competing interests**
The authors declare no competing interests.

**Additional information**

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**Correspondence and requests for materials** should be addressed to Sascha Feldmann or Akshay Rao.

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