### Supporting information

## Ferroelasticity, domain structures and phase symmetries in organicinorganic hybrid perovskite methylammonium lead chloride

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# S1. Optical crystallography and twin domain structure of ferroelastic and ferroelectric (ferroic) crystals.

Here we describe briefly the principles of optical crystallography which is used to interpret the PLM observations. Ferroelastic and most ferroelectric phase transitions are accompanied by a small deformation (spontaneous strain) of the unit cell of the parent phase. As a result, the ferroic phase may belong to another crystal system. The spontaneous strain is typically very small: the dimensions of the parent cell change by no more than a few per cent, and the crystallographic angles may change by a few degrees or less. Therefore, it is possible (and convenient) to characterize the structure of the ferroelastic phase(s) by referring to the crystallographic axes of the parent phase. We adopt this convention in our paper.

All the MAPbX<sub>3</sub> crystals have the cubic (C) perovskite structure as their parent phase, thus in Fig. S1 the possible distortions of the cubic primitive cell are presented. The distortions shown in Figs. S1ac,f,g correspond to transitions into tetragonal (T), rhombohedral (R), orthorhombic (O), monoclinic (M) and triclinic (Tr) phases, respectively. In these cases, the crystallographic axes of a ferroic phase have the same or almost the same orientation as in the parent C phase. Fig. S1d represents the monoclinic distortion of a primitive cell where the parameters *a* and *b* remain equal. In this case, the side-centred cell with two formula-units is conventionally chosen as the unit cell, as delimited by the dash-dotted lines. Its parameters are  $a_0 \neq b_0 \neq c_0$ ,  $\alpha_0 = \beta_0 = \gamma_0 = 90^\circ$  and the resulting symmetry should be classified as orthorhombic. We designate the phases of orthorhombic system with primitive and side-centred cells as  $O_P$  and  $O_S$ , respectively.



Figure S1 Spontaneous lattice distortions which are permitted in the phases of different crystal systems after ferroelastic or ferroelectric transitions from a parent cubic phase with the lattice parameters of a = b = c, and  $\alpha = \beta = \gamma = 90^\circ$ . a, tetragonal with  $a = b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ . b, trigonal (rhombohedral) with a = b = c,  $\alpha = \beta = \gamma < 90^\circ$ , c, orthorhombic with  $a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ . d, orthorhombic with  $a = c \neq b$ ,  $\alpha = \gamma = 90^\circ < \beta$ . e, monoclinic with  $a = b \neq c$ ,  $\alpha = \beta < 90^\circ \neq \gamma$ . f, monoclinic with  $a \neq c \neq b$ ,  $\alpha = \gamma = 90^\circ < \beta$ . g, triclinic with  $a \neq b \neq c$ ,  $\alpha \neq \beta \neq \gamma$ . Crystallographic axes of the parent phase are indicated. Primitive cells which appear as a result of distortions of the primitive cubic cell are shown by solid lines. Red dash-dotted lines show the conventional cells: orthorhombic, O<sub>s</sub>, with  $a_0 \neq b_0 \neq c_0$ ,  $\alpha_0 = \beta_0 = \gamma_0 = 90^\circ$  and monoclinic, M<sub>A</sub> and M<sub>B</sub>, with  $a_M \neq b_M \neq c_M$ ,  $\alpha_M = \gamma_M = 90^\circ < \beta_M$ . For the T, R, O<sub>P</sub>, M<sub>C</sub> and Tr phases, the primitive and conventional cells coincide. The distortions are exaggerated for clarity. Ellipses represent the cross sections of optical indicatrix by the {100} pseudocubic planes. The axes of the ellipses indicate the vibration directions of the slow and fast rays, respectively, traveling perpendicular to those planes. A monoclinic ferroic phase can adopt three structural variants which are conventionally denoted as  $M_A$ ,  $M_B$  and  $M_C$ , respectively<sup>1</sup>. In the  $M_A$  and  $M_B$  phases (Fig. S1e) the mirror plane is parallel to {110}, while in the  $M_C$  phase (Fig. S1f) it is parallel to {100}. The  $M_A$  and  $M_B$  phases differ in the direction of spontaneous polarization which is along *<uuv>* with u < v and u > v, respectively. These phases cannot be distinguished by means of PLM.

The optical behaviour of crystals can be conveniently represented by an optical indicatrix<sup>2,3</sup> which is a sphere in the C phase, an ellipsoid of revolution in the (uniaxial) crystals of T and R systems and a triaxial ellipsoid in the (biaxial) crystals of O, M and Tr systems. The lengths of the ellipsoid semi-axes are given by the principal refractive indices, while the length differences determine the values of linear birefringence ( $\Delta n$ ). The position of optical indicatrix with respect to the crystallographic axes is known to be determined by the point group of a crystal. Therefore, if the characteristics of the indicatrix are found from PLM observations, the crystal system can be determined. Figure S1 shows schematically the indicatrix sections of a crystal in the different phases when observed in polarizing microscope along the <100> directions. Note that the lengths of unequal indicatrix axes and, thereby, the magnitude and sign of birefringence are not prescribed by symmetry (but by crystal chemistry), so the indicatrix sections are qualitatively presented. If the vibration directions of crossed polarizers coincide with the vibration directions of the crystal (i. e with the axes of the ellipses shown in Figure S1), the crystal is in extinction (i.e. completely dark under crossed polarizers). One can deduce from Figure S1 that if a crystal is observed along one of the <100> directions (the optical axis of the microscope is perpendicular to one of {100} planes), the extinction directions may be, depending on crystal symmetry, parallel or perpendicular to <100>, or form an angle of  $\delta \approx \alpha/2 \approx \beta/2 \approx 45^{\circ}$  with <100>. In the M and Tr phases other  $\delta$  values are allowed by symmetry. The possible values of  $\delta$  for <100> observation directions are listed in Table 1 and for other observation directions in Table S1.

Figure S1 shows only one variant of cubic lattice distortion for each ferroic phase. Several other variants (orientational strain states) are possible. They are distinguished by the components of the spontaneous strain tensor and can be characterized by the orientations of indicatrix axes. For example, in the T phase, the indicatrix principal axis (optic axis) can have three different directions being parallel to the [100], [010] and [001] axes of the parent C phase, respectively. In the R phase, four <111> directions of the optic axis are possible. In the O<sub>P</sub> and O<sub>S</sub> phases, the indicatrix is biaxial, the optic axes do not coincide with the principal axes of the indicatrix. There are six orientation states in the O<sub>P</sub> phase where all three indicatrix axes are parallel to one of the <001> directions. Six orientation states can also be permitted in the O<sub>S</sub> phase. In these states two indicatrix axes are directed along <110> and the third axis is parallel to <001>.

**Table S1.** Permissible extinction directions in ferroelastic domains and orientations of domain walls which can be observed by polarizing microscope on (110) and (111) crystal plates in the different ferroelastic phases: rhombohedral (R), tetragonal (T), orthorhombic ( $O_P$  and  $O_S$ ), monoclinic ( $M_A$ ,  $M_B$  and  $M_C$ ) and triclinic (Tr), after transformation from the cubic  $m\overline{3}m$  parent phase.  $\delta$  is the angle between the crossed polarizers and the [ $\overline{1}10$ ] direction at which the extinction is observed; the filled circle (•) indicates the permissible domains which are in extinction at any  $\delta$  angle; the crossed circle ( $\oplus$ ) indicates the possibility of regions without extinction at any  $\delta$  angle;  $\varphi$  is the permissible angle between the domain wall trace on the plate surface and the [ $\overline{1}10$ ] direction (walls which are *not* perpendicular to the surface are listed in brackets); angle  $\varphi_1$  (for S walls) may adopt any values, except for  $0^{\circ}$ ,  $90^{\circ}$  and  $\pm 45^{\circ}$ .

		(110)	(111)		
Phase	δ	φ	δ	φ	
Т	0°, 90°	90°, (±35°)	$0^{\circ}, 90^{\circ}, \pm 30^{\circ}, \pm 60^{\circ}, \oplus$	(0°), 90°, ±30°, (±60°)	
R	0°, 90°, ±35°, ±55°, ⊕	0°, 90°, (90°), (±35°), (±55°)	$0^{\circ}, 90^{\circ}, \pm 30^{\circ}, \pm 60^{\circ}, \oplus, \bullet$	(0°), 90°, ±30°, (±60°)	
O <sub>P</sub>	0°, 90°	90°, (±35°)	$0^{\circ}, 90^{\circ}, \pm 30^{\circ}, \pm 60^{\circ}, \oplus$	(0°), 90°, ±30°, (±60°)	
Os	0°, 90°, ±35°, ±55°, ⊕	$0^{\circ}, (0^{\circ}), 90^{\circ}, (90^{\circ}),$ (±35°), (±55°), ± $\varphi_1$	$0^{\circ}, 90^{\circ}, \pm 30^{\circ}, \pm 60^{\circ}, \oplus$	(0°), 90°, ±30°, (±60°), (±30°± $\varphi_1$ ), (90°± $\varphi_1$ )	

Coexistence of different orientation states in the same crystal results in the formation of twins of special type known as ferroelastic domains. To minimize the elastic energy the twin boundaries (domain walls) must be planar, and their orientation must satisfy the mechanical compatibility conditions. The permissible directions of ferroelastic domain walls have been calculated and reported for each phase<sup>4,5</sup>. In the T, R and O<sub>P</sub> phases, all walls must be parallel to one of the {001} or {110} planes. In other phases, additional orientations are possible which are not prominent crystallographic planes with fixed indices and are determined by the ratio between the components of the second-rank spontaneous strain tensor. The walls with such orientations are known as S walls. Deviations from theoretically prescribed walls orientations are associated with enhanced elastic energy. Therefore, such deviations, if observed in real crystals, are usually small.

The directions in which the permissible walls are observed on the surfaces of crystals of different orientations with respect to the crystallographic axes are summarized in Table 1 and in Table S1. The

possible angles  $\varphi$  between the wall traces on the surface and the [100] or [ $\overline{1}10$ ] direction are given, and if the wall is inclined to the surface, it is given in brackets.

In the ferroelectric phases, antiparallel (or 180°) domains can exist, besides ferroelastic domains. Ferroelectric 180° domains have the same orientation of optical indicatrix and, thereby, the same extinction positions. However, 180° domain walls can sometimes be visible under the polarizing microscope<sup>6,7</sup> in the form of lines of arbitrary shape (not necessarily straight lines). Note that we have never observed such a kind of walls in the studied MAPbCl<sub>3</sub> crystals.

In some low-temperature phases of  $MAPbX_3$  crystals a superstructure has been found with doubling of lattice parameters along one or three crystallographic directions. Such a superstructure cannot be verified using PLM.

#### S2. Optical behaviour of MAPbCl<sub>3</sub> crystals in the α phase

In the  $\alpha$  phase of all studied (100), (110) and (111) plates, we observe complete extinction at any orientation of crossed polarizers, suggesting that the crystal is isotropic. Fig. S2 gives an example.



Figure S2 Photograph of a (001) MAPbCl<sub>3</sub> crystal plate in the  $\alpha$  phase between crossed polarizers. This is the same crystal as shown in Fig. 2e, f of the main text, but oriented so as to form an arbitrary angle  $\delta = 20^{\circ}$ . A first-order red plate is superimposed. The colour of the crystal is the same (magenta) as the surrounding isotropic medium, which means that the crystal is in complete extinction. The temperature, the directions of crystallographic axes and polarizers are indicated.

#### S3. Domain structure of MAPbCl<sub>3</sub> crystals in the β phase.

Figure S3 shows typical PLM images of a comparatively large crystal polished prior to observation. Complete extinction is observed in many regions of the crystal when the crossed polarizers

are at the angle of  $\delta = 45^{\circ}$  to the <100> crystallographic directions (Fig. S3b). However, in some regions the extinction is incomplete, and they remain bright at any  $\delta$ . This is clearly seen in the photograph of Fig. S3c which is taken with a superimposed first-order red plate. Areas of complete extinction have the same (zero) retardation as the non-birefringent background around the crystal and, accordingly, they must have the same (magenta) colour. Any slight and barely visible deviation from the complete extinction in Fig. S3b results in a noticeable change of colour in Fig. S3c. Note that some small areas of the crystal remain dark at any orientation of polarizers, with or without first order red plate. These are opaque inclusions, not regions in extinction. The observed behaviour is incompatible with the T, OP, MC and Tr phases in which a complete extinction should be observed at  $\delta = 0^{\circ}/90^{\circ}$  or  $\delta \neq \pm 45^{\circ}$  (see Table 1). The extinction angle of  $\delta = 45^{\circ}$  is allowed in both the R and O<sub>s</sub> phases, but only the O<sub>s</sub> phase is compatible with the fact that some parts of the crystal do not reveal extinction either at  $\delta = 45^{\circ}$  or  $\delta = 0^{\circ}$ . In these parts two or more domains are located one under the other across the thickness of the crystal plate, so that the light ray passes through all of them. If the vibration directions in some of these orthorhombic domains are oriented at  $\delta = 0^{\circ}$ , while they are at  $\delta = 45^{\circ}$  in some others, the total extinction is absent. On the (001) plates of the T, O<sub>P</sub> or R phases, the vibration directions in each domain are parallel or perpendicular to the vibration direction of all other domains, and complete extinction should be observed in all parts of the crystal simultaneously.

The domain overlapping can also explain the existence of randomly distributed areas of different colours in Fig. S3. The overlapped domains are birefringent objects superimposed in addition or subtraction positions depending on the orientation of the domains. These domains give rise to positive or negative contribution to the total optical retardations, respectively, and if their relative thickness is different in different parts of the crystal plate, different total retardation appears and, accordingly, different interference colours, including black, should be observed.





Figure S3 Photographs of a (001) oriented CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> crystal plate in the  $\beta$  phase between crossed polarizers. a, the angle between the direction of polarizers and [100],  $\delta = 0$ . c,d,  $\delta = 45^{\circ}$ . Photograph in panel c is taken with superimposed first-order red plate to distinguish non-transparent (black) and birefringent (coloured) regions. A large crystal was polished to obtain the plate thickness of t = 0.2 mm. The temperature, the directions of crystallographic axes, the directions of polarizers and the angle  $\delta$  are indicated.

The domain structure of  $\beta$  phase on the (110) crystal plate is shown in Fig. S4a. Besides the domain walls forming angles of  $\varphi \approx 35^{\circ}$  and 90° with the [ $\overline{1}10$ ] crystallographic direction which are allowed in all phases listed in Table S1, one can clearly see the walls with  $\varphi \approx 55^{\circ}$  and the walls parallel to [ $\overline{1}10$ ] which are not permissible for the T and O<sub>P</sub> phases. In these two phases the whole crystal should be in extinction at the considered position of polarizers, but in fact only some domains are in extinction. Some other domains extinct at  $\delta = \pm 35^{\circ}$  and  $\delta = \pm 55^{\circ}$ . Such behaviour is consistent with the O<sub>S</sub> symmetry.



Figure S4 Examples of domain structure of CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> crystals in the  $\beta$  phase observed between crossed polarizers. **a**, (110) plate polished to the thickness of  $t \approx 0.2$  mm. The inset is an enlarged view demonstrating the domain walls at an angle of  $\varphi \approx 55^{\circ}$  to [ $\bar{1}10$ ]. **b**, **c**, (111) plate polished to the thickness of  $t \approx 0.2$  mm after different cooling cycles through a phase transition. A first-order red plate is superimposed in **c**. The temperature, crystallographic directions and polarizers directions are indicated.

The domains we observe in the  $\beta$  phase in large crystals with polished surfaces and a thickness in a micrometre scale are typically comparatively small (see Figs 2a, and S4a,c). Much larger domains, like the domain stripe in Figure S4b with a thickness of ~ 0.5 mm, appear rarely. To explain these facts, we note that a temperature-induced phase transition typically proceeds via the formation of nuclei of the new phase and their growth. In an ideal crystal the nuclei may appear in any part of the sample and may have

any orientation states allowed by the symmetry. When different nuclei merge, the domain walls separating them are formed. In a real crystal the nuclei appear first around crystal defects which may facilitate the nucleation process. A lot of such defects appear at the crystal surface after polishing, leading to the formations of multiple domains and a fine domain structure. In the crystals with as-grown surfaces such as those shown in Figs. 2b,c, which are expected to contain a comparatively small number of surface defects, comparatively large domains are often formed.



Figure S5 Examples of domain structure observed on a CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> crystal in the  $\gamma$  phase between crossed polarizers. a-c, (111) plate polished to the thickness of  $t \approx 0.2$  mm. The temperature, crystallographic directions and polarizers directions are indicated.

#### S4. Domain structure of MAPbCl<sub>3</sub> crystals in the γ phase.

In contrast to the  $\beta$  phase, the domains in the  $\gamma$  phase are usually large. Single-domain state is observed on (001) and (110)-oriented plates in most cases, while (111)-plates can be single- or polydomain after different cooling/heating cycles through a phase transition. Figures S5a-c show the domain structure of a (111) plate in the  $\gamma$  phase. Three large domains with the size of ~ 1 mm occupy almost the whole crystal. They appear in extinction at the positions of polarizers separated by the angle of  $\approx 30^{\circ}$ , as Fig. S5 demonstrates [small deviations from the expected 30-degree angle are due to a small deviation of the plate from the exact (111) orientation]. According to Table S1, this behaviour can be found in crystals of any system. The domain walls are observed directed at angles  $\varphi \approx 0^{\circ}$ ,  $\pm 30^{\circ}$  and  $60^{\circ}$ , which also can exist in any system. The possible reason why the domains of the  $\gamma$  phase are typically large is that, in contrast to O<sub>S</sub>, some orientation states of the O<sub>P</sub> symmetry are mechanically incompatible<sup>4,5</sup>. Therefore, if two nuclei with incompatible orientations approach one another during the domain growth process at the  $\beta$ - $\gamma$  phase transition, one of them continues to grow and the other one should shrink and disappear in order to avoid the formation of an impermissible wall. As such, large domains appear at the end of phase transition.

#### S5. Measurements of optical birefringence.

Linear optical birefringence in biaxial crystals is characterized by three principal values:  $\Delta n_1 = n_3$ -  $n_2$ ,  $\Delta n_2 = n_2 - n_1$  and  $\Delta n_3 = n_3 - n_1$ , where  $n_1$ ,  $n_2$  and  $n_3$  are the refractive indices<sup>3</sup>. The temperature dependences of birefringence measured on (001) plates of MAPbCl<sub>3</sub> are shown in Fig. 1c and the values near the phase transitions and at the lowest studied temperature of 80 K are presented in Table S2. In the  $\gamma$  phase the principal axes of indicatrix coincide with the crystallographic axes [100], [010] and [001] (see Fig. S1c), so we measure the principal values of birefringence. They should be related by the expression  $\Delta n_1 + \Delta n_2 = \Delta n_3$ , which is really satisfied (compare the last two columns in Table S2), confirming the correctness of our measurements. In the  $\beta$  phase (Fig. S1d), only one of the indicatrix axes coincides with <100>, namely the axis parallel to the monoclinic *b* axis of the primitive perovskite cell. We measure the corresponding birefringence  $\Delta n_1 \approx 0.008$  in domains with extinction at  $\delta = \pm 45^\circ$  (such as the lower domain in Figs. 2b-d). The effective birefringence ( $\Delta n_{eff}$ ) measured in domains with  $\delta = 0^\circ/90^\circ$  (the upper domain in Figs. 2b-d) should have an intermediate value between  $\Delta n_2$  and  $\Delta n_3$ . To measure directly  $\Delta n_2$  and  $\Delta n_3$  by a compensator, (110) plates are needed. Such plates have not been found among as-grown crystals, while on (110) plates prepared by cutting and by polishing, fine domain structure has been always observed and domains large enough for birefringence measurements could not be found.

#### S6. Phase transition temperatures.

Figure S6 presents the variations of the temperatures of phase transitions from  $\alpha$  to  $\beta$  and from  $\beta$  to  $\gamma$  phase as a function of applied electric field, measured in CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> crystal upon cooling and heating. It demonstrates that the transition temperatures are independent of electric field.

Phase	<i>T</i> (K)	$\Delta n_1$	$\Delta n_2$	$\Delta n_{\rm eff}$	$\Delta n_3$	$\Delta n_1 + \Delta n_2$
β	178	$0.0075 \pm 0.0005$		$0.00099 \pm 0.00011$		
	172	$0.0079 \\ \pm 0.0005$		$0.0014 \pm 0.00012$		
γ	171	$0.0423 \pm 0.0005$	$0.0515 \pm 0.0010$		$0.0959 \pm 0.0014$	0.0938
	80	$0.0364 \pm 0.0009$	$0.07770 \pm 0.00015$		$\begin{array}{c} 0.113 \\ \pm \ 0.005 \end{array}$	0.114

**Table S2.** Linear birefringence,  $\Delta n$ , measured on (100) plates of CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> crystals at selected temperatures.



Figure S6 Dependence of the temperatures of phase transitions from  $\alpha$  to  $\beta$  and from  $\beta$  to  $\gamma$  phase on the applied electric field measured in CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> crystal upon cooling and heating.

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