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## Introduction

The discovery of superior optoelectronic properties of organicinorganic lead halide perovskites1-3 has opened new prospects for low-cost, high-performance photonic devices. These materials have great potential for numerous devices such as lightemitting diodes, photodetectors, and solar cells. Particularly impressive is a quick rise of power conversion efficiency of single-junction solar cells based on perovskite absorbers that currently exceeds 25%.4 Although the optical and electronic parameters of hybrid perovskites are excellent, their practical application is still hampered by long-term stability problems related to the resistance to atmospheric conditions such as moisture, temperature and UV illumination.5-7 In the search for better materials the organic cation was replaced with cesium, Cs<sup>+</sup>, in order to obtain the inorganic CsPbBr<sub>3</sub> perovskite structure of improved stability and photovoltaic properties comparable to those of analogous hybrid MAPbBr<sub>3</sub> (MA =

# Time-dependent transformation routes of perovskites CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub> under high pressure<sup>+</sup>

Marek Szafrański, 🝺 \* a Andrzej Katrusiak 🗐 b and Kenny Ståhl<sup>c</sup>

All-inorganic halide perovskites are prospective materials for diverse applications in photovoltaic and optoelectronic devices. Their high performance is associated with good operational stability, which is the key problem of hybrid organic–inorganic perovskites. However, for these materials only fragmentary information is available on the mechanical robustness and response to external stress, fundamentally important for strain engineering in multilayers, pressure-assisted technologies, and flexible panels applications. Here we show that all-inorganic perovskites  $CsPbX_3$  (where X = Cl, Br) undergo various types of pressure-induced transformations, including reversible phase transitions, irreversible chemical routes depend on the mode of the applied stress and are related to the kinetics of transitions to the most stable phases. The slow-kinetics transformations in a moderate pressure range of technological importance, between 0.5 and 1.5 GPa, can require days or even weeks, depending on the sample quality and external stimuli. The pressure-induced narrowing and widening of energy gaps has been explained by the mechanism combining Pb–X bond lengths and PbX<sub>6</sub> octahedra tilts with the electronic structure of the crystals.

[CH<sub>3</sub>NH<sub>3</sub>]<sup>+</sup>).<sup>8,9</sup> This finding renewed a wide interest in allinorganic halide perovskites, which currently are considered not only for photovoltaic applications, but also for lightemitting diodes,<sup>10,11</sup> multicolor displays,<sup>12</sup> lasers,<sup>13</sup> and highenergy detectors.<sup>14</sup>

Recently, a growing interest is observed in the strain engineering aimed at enhancing the performance of the perovskitebased optoelectronic devices.15-17 This approach requires the understanding of relationships between the strain-induced crystal structure modifications and the associated properties. One of the best tools to effectively study such relationships in controlled conditions is hydrostatic pressure, capable of precisely manipulating the crystal structure and tuning the electronic parameters of the crystals. Moreover, the pressureassisted techniques for fabrication perovskite wafers or thick films on substrates18,19 can generate significant changes in their structure and properties. Therefore, the knowledge about the structural response to the external stress is of primary importance. The high-pressure studies of inorganic metal halide perovskites were reported by several groups,<sup>20-28</sup> but it is characteristic that all diffraction experiments were performed for powdered samples only, which are not ideally suited for accurate structural determinations for highly pseudo-symmetric materials, nor for spectroscopic studies and visual microscopic observations. Presently, we have undertaken this study based on the single-crystal X-ray diffraction experiments, supported by microscopic observations, and single-crystal

<sup>&</sup>lt;sup>a</sup>Faculty of Physics, Adam Mickiewicz University, Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland. E-mail: masza@amu.edu.pl

<sup>&</sup>lt;sup>b</sup>Faculty of Chemistry, Adam Mickiewicz University, Universytetu Poznańskiego 8, 61-614 Poznań, Poland

<sup>&</sup>lt;sup>c</sup>Chemistry Department, Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark

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## **Results and discussion**

# X-ray diffraction experiments, dielectric measurements and microscopic observations of CsPbBr<sub>3</sub> under pressure

At atmospheric pressure above room temperature CsPbBr<sub>3</sub> undergoes two successive phase transitions:<sup>29,30</sup> the prototypic perovskite phase I of cubic space group (s. g.) Pm3m at 403 K transforms to phase II of tetragonal s.g. P4/mbn, and at 361 K it transforms further to phase III of orthorhombic s.g. Pmna. Both these critical temperatures increase when the crystal is compressed,<sup>20</sup> and therefore none of these transitions is expected to occur in high-pressure experiments in this study, performed at room temperature. The hydrostatic compression of a single-crystal phase III of CsPbBr<sub>3</sub> resulted in monotonic changes in the lattice parameters up to about 1.3 GPa, as shown in Fig. 1a. At still higher pressure a phase transition damaged the single-crystals used for the X-ray diffraction measurements. It is worth noting that already above 0.5 GPa the lattice strain generated micro cracks and other defects, which could be seen through the optical microscope. This strain resulted in a clear broadening or splitting of Bragg reflections and hence the structural parameters derived from the SCXRD data collected in this pressure region were determined with a lower accuracy, as indicated by increased standard deviations in Fig. 1b. However, the most intriguing was the slow transformation of the crystals left under the pressure between 0.5-1.3 GPa, illustrated by



Fig. 2 Microscopic observations of a single crystal of 3D-CsPbBr<sub>3</sub> phase III compressed in isopropanol at 0.10, 0.44 and 0.60 GPa. A ruby chip for pressure calibration lies at the left edge of the DAC chamber.

a series of crystal photos in Fig. 2. The transformation was manifested by a formation of strongly defected areas which expanded to all the crystal sample over time. The new form in the sample is clearly distinguished by its white color from the 3D-CsPbBr<sub>3</sub> orange form. It should be noted that time required for this process varied between different crystals samples, but it could be accelerated by heating the high-pressure cell to 330– 350 K. The similar slow-kinetics transformations were observed in our earlier high-pressure experiments on CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub>,<sup>31</sup> but those transitions were fully reversible. The transformed CsPbBr<sub>3</sub> samples remained colorless after the pressure release, and no reverse transformation to the orange phase III was observed even for months.



Fig. 1 Compression of the unit-cell volume and lattice parameters of 3D-CsPbBr<sub>3</sub> phase III (a), and pressure dependence of structural parameters (b and c) measured by SCXRD. The average Pb–Br distance was calculated for the three independent bonds (Fig. S1†). The inset shows the Pb–Br–Pb angles connected to the tilts of the PbBr<sub>6</sub> octahedra.

#### Paper

Owing to the irreversible character of the transformation of CsPbBr<sub>3</sub> to the white form, the sample could be recovered from the DAC and its high-resolution PXRD data was recorded. It turned out that the PXRD data consists of two phases that could be indexed separately and for each of them the crystal structure has been determined. The Rietveld refinement (Fig. 3a and S2, Table S1†) has shown that the sample contains both the white form of 1D-CsPbBr<sub>3</sub>,<sup>32</sup> of orthorhombic s. g. *Pmnb*, Z = 4, a = 4.5948(2), b = 9.6985(6), c = 16.7763(10) Å, V = 747.60(13) Å<sup>3</sup>, and 2D-CsPb<sub>2</sub>Br<sub>5</sub>,<sup>33</sup> of tetragonal s. g. *I4/mcm*, Z = 4, a = 8.4930(6), c = 15.2072(7) Å, V = 1096,92(21) Å<sup>3</sup>. Thus, the moderate pressure of 0.5–1.5 GPa destabilizes the perovskite structure of orange 3D-CsPbBr<sub>3</sub> phase III and in hydrostatic

conditions assured by isopropanol it transforms to white 1D-CsPbBr<sub>3</sub> and to 2D-CsPb<sub>2</sub>Br<sub>5</sub> (see Fig. 3b). The latter compound is formed according to the chemical reaction: 2CsPbBr<sub>3</sub>  $\rightarrow$  CsPb<sub>2</sub>Br<sub>5</sub> + CsBr. The byproduct CsBr was not detected, as it dissolved in isopropanol (possibly with a small amount of water) and this solution leaked out after opening the DAC chamber. Consequently, it was absent in the analyzed part of the sample.

In order to better characterize the slow transformation of CsPbBr<sub>3</sub>, we have used another technique with another type of pressure-transmitting medium. The polar isopropanol was replaced with gaseous helium and the electric permittivity of the polycrystalline sample was used as a probe of structural



Fig. 3 The orange phase III of CsPbBr<sub>3</sub> transformed into white 1D-CsPbBr<sub>3</sub> and 2D-CsPb<sub>2</sub>Br<sub>5</sub> at 0.60 GPa in isopropanol (a and b), and the 3D-1D transition observed in a pellet (shown in the inset) under pressure of gaseous He (c and d). The real part of electric permittivity  $\varepsilon'$  under different pressures measured on heating (red lines) and cooling (blue), at the probing electric field frequency of 100 kHz. The white phases were mechanically extracted and identified by PXRD using Rietveld refinement.

changes. The results of dielectric measurements (Fig. 3c) show that increasing pressure suppresses the dielectric response of CsPbBr<sub>3</sub>, which matches the general tendency observed for other materials. However, most remarkable is the comparison of the heating and cooling runs. They are identical at 0.27 GPa, somewhat different at 0.47 GPa, but at 0.70 GPa the electric permittivity spectacularly drops in the cooling run, reflecting the dramatic changes in the crystal structure. After releasing pressure and removing a part of one electrode, the white islands were revealed in the originally fully orange pellet (see the inset in Fig. 3d). The subsequent PXRD analysis showed that this is the pure white 1D-CsPbBr<sub>3</sub>, with no traces of 2D-CsPb<sub>2</sub>Br<sub>5</sub> (Fig. 3d and S3, Table S1<sup>†</sup>). This experiment confirmed the instability of the 3D perovskite structure of CsPbBr3 in the moderate pressure and temperature range. Noteworthy, at ambient pressure an inverse situation takes place: the white form 1D-CsPbBr<sub>3</sub> can be crystallized together with the orange form 3D-CsPbBr<sub>3</sub> from the solution of specific stoichiometry,<sup>32</sup> but it transforms irreversibly to the orange isomer at 424 K.<sup>34</sup> Thus, we can conclude that at atmospheric pressure the free energy of 3D-CsPbBr3 is only somewhat lower compared with 1D-CsPbBr<sub>3</sub>, but these minima are separated by an energy barrier. Under pressure the energy barrier clearly lowers and the relation between the minima reverses in favor of 1D form.

The time-dependent PXRD experiments performed under 0.77 GPa, using the DAC filled with aprotic Galden as the hydrostatic liquid, evidenced that 3D-CsPbBr<sub>3</sub> transforms into 1D-CsPbBr<sub>3</sub>, similarly as in gaseous helium (Fig. S4, Table S1†). A similar transformation was observed recently in the pellets pressed in oil.<sup>35</sup>

Our microscopic observations showed that when the single crystals of orange CsPbBr<sub>3</sub> phase III are compressed quickly, without longer intervals, the white phase is not formed and around 1.5 GPa the crystals reversibly transform to a new light-yellow phase IV. The transition is associated with numerous cracks and other defects, as illustrated in Fig. 4a for the crystal

compressed in the DAC (see also Fig. S6<sup>†</sup>). These observations were fully confirmed by XRPD experiments where pressure was changed with time intervals shorter than 1 h (Fig. 4b). The PXRD has shown that in the pulverized sample the transition onset occurs between 1.3 and 1.54 GPa. Moreover, the substantially increased background in the diffraction pattern measured at 1.54 GPa marks an increase of the crystal structure disorder, while the positions and intensities of reflections suggest a coexistence of phases III and IV. Pure phase IV is represented in Fig. 4b by the diffraction pattern collected at 2.12 GPa. This pattern shows a partial loss of the long-range order of the crystal, but a few broad reflections indicate that the average residual crystal structure approximates that of phase III. With these features, phase IV can be described as a partly amorphous version of phase III. The transition to phase IV is fully reversible, as testified by the diffraction pattern collected after the pressure release to 0.05 GPa (Fig. 4b).

#### Absorption edge of compressed CsPbBr<sub>3</sub>

The absorption edge of CsPbBr<sub>3</sub> was measured on a singlecrystal plate approximately 2.5 µm thick, during the compression and decompression cycles. The representative spectra are shown in Fig. 5a and b. The determined pressure dependence  $E_{g}(p)$ , plotted in Fig. 5c, shows that the bandgap initially narrows linearly, but above circa 1.0 GPa the pressure effect saturates and about 1.5 GPa the  $E_{g}$  value becomes nearly constant. It contrasts to the previously reported<sup>24</sup> gradual blue shift of  $E_{g}$  starting at 1 GPa and continued to 2 GPa (see the green points in Fig. 5c; these data were obtained from the experiment where the silicon oil, hydrostatic to about 0.5 GPa only, was applied as a pressure medium). The turning point at 1 GPa was interpreted as resulting from the isostructural phase transition,<sup>24</sup> but we have not observed such a transition at 1.0 GPa. The isostructural phase transition must be discontinuous and associated with a jump-wise volume change, whereas the evidently continuous changes in the lattice parameters were



Fig. 4 Single crystal of orange 3D-CsPbBr<sub>3</sub> quickly compressed in isopropanol in a DAC (a), and PXRD patterns for the powder quickly compressed and after releasing the pressure (b). Isopropanol was used as the hydrostatic liquid.



**Fig. 5** Selected absorption spectra of a single-crystal plate of 3D-CsPbBr<sub>3</sub> (a and b) and the energy gap (c) determined from the absorption edge measured in the compression (blue) and decompression (red) runs, compared with the literature data<sup>24</sup> (green). The insets show the crystal just below the transition at 1.44 GPa and in the phase transition region at 1.58 GPa, where the coexistence of phases III (orange) and IV (slightly yellowish) is clearly visible due to the strong piezochromic effect. The spectra (a and b) are shifted vertically to avoid the overlapping.

observed in the considered pressure range.<sup>24</sup> Also, no characteristic features of isostructural phase transitions can be found in our structural data around 1.0 GPa (Fig. 1) nor in all range up to 1.5 GPa.

The nonlinear  $E_{g}(p)$  can be rationalized by the crystal structure response to hydrostatic pressure and by the related changes in the structural parameters. The calculations of the electronic structure of CsPbBr3 have shown that electronic states responsible for the absorption edge mainly involve orbitals Pb 6s, 6p and Br 4p, whereas the contribution of Cs cations is secondary. Therefore, similarly as in hybrid lead halides,36 the shortening of Pb-Br distance is associated with a stronger overlapping of the crucial atomic orbitals (Pb 6s and Br 4p), which results in the band gap narrowing, whereas the Pb-Br-Pb bending reduces this overlapping and leads to the band gap widening. Both these two types of structural transformations absorbing the crystal strain under pressure and their competing effects on the bandgap are present in CsPbBr<sub>3</sub>. To about 0.8 GPa the contraction of the Pb-Br bonds predominates and hence the red shift of the absorption edge. Similar effect was observed in the low-pressure range for MAPbBr3 and for other hybrid organic-inorganic perovskite photovoltaics.31,36 Under higher pressure the compression of Pb-Br bonds is reduced (see Fig. 1b) and consequently the  $E_{g}(p)$  dependence becomes flattened. Thus, for 3D-CsPbBr<sub>3</sub> phase III, this is not its phase transition, but the nonlinear change in the pressure dependence of the Pb-Br distance, which is responsible for the anomalous energy gap behavior between 1 and 1.5 GPa.

The microscopic distortion of the compressed CsPbBr<sub>3</sub> phase III, described above as the Pb-Br bonds shortening and the Pb-Br-Pb angles bending, can be rationalized in terms of the structural features of this crystal, illustrated in Fig. 6 and S7.<sup>†</sup> The tilts of PbBr<sub>6</sub> octahedra (measured by the Pb-Br-Pb angles) are expected to require less energy to change for accommodating the compressed volume, compared to the covalent Pb-Br bonds shortening, which surprisingly is quite significant in the initial stages of the compression (Fig. 1). However, there is less space on the convex side of the Pb-Br-Pb angles, compared to their concave side, as clearly seen from the Br-Cs distances indicated in Fig. 6. Owing to this surrounding of the Br anions, the crystal volume compression is accommodated by the simultaneous squeezing of Pb-Br bonds and the increased tilts of PbBr<sub>6</sub> octahedra. But the PbBr<sub>6</sub> reorientations toward the sharpening of Pb-Br-Pb angles, expected from the mechanical point of view and also favoured by the electrostatic attraction to the closer Cs<sup>+</sup> cations, are opposed by the repulsion due to the Br-Cs distances shortening to below the sum of ionic radii of Br<sup>-</sup> and Cs<sup>+</sup> (equal to 3.61 Å according to Goldschmidt and 3.64 Å according to Pauling). Hence the considerable shortening of bonds Pb-Br, connected with the initial  $E_{g}(p)$  reduction in phase III.

The quickly compressed orange 3D-CsPbBr<sub>3</sub> phase III at around 1.5 GPa transforms to slightly yellowish phase IV. This transition is associated with a strong piezochromic effect illustrated in Fig. 5c. In the transition region phases III and IV coexist within 0.2–0.3 GPa both during the compression and decompression cycles. In the absorption spectra the coexistence



Fig. 6 Crystal structure of CsPbBr<sub>3</sub> phase III at ambient conditions, viewed along [y], with the voids (shown in gold) calculated for the probing radius 0.8 Å and step 0.1 Å The shortest Br–Cs distances are indicated.

of phases III and IV is reflected as two absorption edges, as it is shown in Fig. 5a at 1.58 GPa, and in Fig. 5b at 1.44 and 1.17 GPa. The results presented in Fig. 5 indicate a first-order nature of the transition with a characteristic sudden change of the absorption edge and an apparent pressure hysteresis between the compression and decompression cycles. The large blue shift of the absorption edge and the bandgap widening suggest that the structure profoundly changes. At the same time a part of the diffraction peaks characteristic of phase III is also preserved in phase IV in the diffraction pattern collected at 2.12 GPa (Fig. 4b), which might indicate an isostructural phase transition. Such a transition was the main consideration for explaining the anomalous changes in the optical properties of 3D-CsPbBr<sub>3</sub>,<sup>23,24</sup> but this approach seems to be oversimplified. As seen in Fig. 4b, the Bragg reflections significantly broaden and the strong diffused scattering appears in the PXRD patterns in the phase transition region, and became very pronounced for the pure phase IV at 2.12 GPa. This indicates that the crystal structure of phase IV is strongly disordered, which can be interpreted as the beginning of amorphization. The process can proceed through the local symmetry breaking and distortions in the framework built of the corner-sharing PbBr<sub>6</sub> octahedra. As a result, the Pb-Br distances and Pb-Br-Pb angles are, starting from the transition point, stochastically distributed with different values in the distorted structure. Therefore, the electronic structure of CsPbBr<sub>3</sub> cannot be faithfully modelled for the average structural parameters and such calculations clearly failed.<sup>23,24</sup> The calculations predicted a continuous evolution of  $E_{o}$  at the transition to phase IV, while the experiment performed in hydrostatic conditions shows evidently the jump-wise blue shift of the absorption edge (Fig. 5), corroborating the sudden changes of structural parameters and the abrupt modification of electronic bands of the crystal. The compression of phase IV leads to the continuous blue shift of the edge and to the linear increase of  $E_{g}$ . It is remarkable that the pressure reduction results in some hysteresis in the values of the bandgap in phase IV, as illustrated in Fig. 5c. This pressure memory effect disappears after the reverse transition to phase III, which leads to the perfect agreement between the  $E_{g}$  values determined during the compression and decompression cycles. These results confirm that the transition between phases III and IV is fully reversible.

#### Pressure dependence of structural parameters in CsPbCl<sub>3</sub>

At ambient pressure CsPbCl<sub>3</sub> undergoes three successive phase transitions in a narrow temperature range of about 10 K. The prototypic cubic phase I of s. g. *Pm3m* transforms at 320 K to the tetragonal phase II, s. g. *P4/mbm*, and further at 315 and 311 K



Fig. 7 Compression of structural parameters of CsPbCl<sub>3</sub>: unit-cell volume and lattice parameters of CsPbCl<sub>3</sub> (a), the average Pb–Cl length of three independent bonds (b), and Pb–Cl–Pb angles (c). Where not indicated, the standard deviations are smaller than the plotted points.



Fig. 8 Time-dependent transformation of a single crystal of CsPbCl<sub>3</sub> compressed in the DAC (a), as well as PXRD patterns of CsPbCl<sub>3</sub> slowly transforming between phases IV and V at 0.65 GPa (b), and of CsPbCl<sub>3</sub> quickly compressed to phase VI (c), as described in the text.

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to the orthorhombic phases III (s. g. Cmcm) and IV (s. g. Pnma), respectively. These transitions occur above the room temperature and their T<sub>c</sub> values raise with pressure.<sup>20</sup> All our highpressure experiments were performed at room temperature, *i.e.* below these phase transitions. The SCXRD studies (Fig. 7) were limited to about 0.65 GPa because of profound deterioration of the quality of samples under higher pressures. We observed single defects forming under pressure of c.a. 0.5 GPa, but sometimes even at lower pressure, depending on the crystal sample. The microscopic observation of the pressure- and timedependent erosion in a single crystal is illustrated in Fig. 8a. In the pressure range below 0.4 GPa the crystal was stable without any noticable formation of defects, at least within several days. The first single defects captured under optical microscope appeared at 0.48 GPa, but their size and distribution were hardly time-dependent. Only the pressure increase to 0.70 GPa resulted in a quick development of the pulverised portions. These observations indicate that the crystal undergoes a slow transformation associated with a large lattice strain. The rate of this transformation varied from sample to sample between hours to even weeks, suggesting a key role of defects formed at the crystallization stage.

To confirm the pressure-induced slow transformation of the CsPbCl<sub>3</sub> crystal structure, we performed two series of X-ray powder diffraction experiments applying two different modes of compression. In the first scenario, after the data collection in phase IV at 0.11 GPa, pressure was increased to 0.65 GPa, i.e. to the range of the crystal slow transformation. Under this pressure the changes in the diffraction pattern were monitored as a function of time during two weeks. The representative PXRD patterns in Fig. 8b show that just after the pressure increase to 0.65 GPa the sample remained in phase IV, but in the course of time substantial changes arose. The increased number of reflections, and particularly the low- $2\theta$  ones, indicate that the crystal transforms to a lower-symmetry phase V. This slowly formed phase V remains stable at still higher pressures, as evidenced by the PXRD measurements at 2.20 and 3.88 GPa (Fig. 8b). The pressure release to 0.07 GPa resulted in a reverse transition to phase IV, but a full restoration of the initial phase required some time as testified by a coexistence of phases IV and V just after the pressure release. Nevertheless, the slowkinetics transition in CsPbCl<sub>3</sub> is fully reversible as opposed to CsPbBr<sub>3</sub>.

In the second series of the high-pressure PXRD measurements, after the data collection for phase IV at 0.46 GPa, the pressure was increased immediately to 2.20 GPa. The results plotted in Fig. 8c reveal a transition of phase IV to another high-pressure phase VI, distinctly different than phase V. Both phases V and VI can exist in a similar pressure range, but their formation depends on the compression route. The sample remained in phase VI for a long time and at still higher pressure, which is consistent with the earlier PXRD study,<sup>27</sup> most likely performed in a quick compression mode, as most of synchrotron measurements. After we released pressure to 0.08 GPa phase IV was restored (Fig. 8c). Compared to phase IV, the PXRD patterns of phase VI contain less reflections, all of them strongly broadened, as well as clearly increased diffused

scattering. These features indicate a partial reduction of the crystal structure long-range order, and they are similar to those in 3D-CsPbBr<sub>3</sub> phase IV.

#### Pressure dependence of the absorption edge in CsPbCl<sub>3</sub>

The absorption spectra of CsPbCl<sub>3</sub> were measured for a thin single-crystal plate. The pressure was increased quickly to prevent the transition to phase V, which would hamper transmissive measurements. During the measurements in the compression and decompression cycles the crystal optical quality was controlled by using the microscope. The exemplary spectra are plotted in Fig. 9a. The compression of the crystal resulted in a gradual red shift of the absorption edge up to about 1.3 GPa, where the onset of the transition to phase VI takes place. This transition is associated with a large jump-wise blue shift of the edge. The spectrum recorded at 1.29 GPa shows a clear coexistence of phases IV and VI, manifested by two absorption edges corresponding to these phases. This coexistence was observed in the phase transition region within 0.2-0.3 GPa. The subsequent increase of pressure up to 4.13 GPa caused a continuous blue shift of the edge. According to the absorption edge behavior, the pressure dependence of the energy gap (Fig. 9b) shows a jump-wise change at the transition point, indicating a strong first-order character of the transition. This is contrary to the previously reported<sup>27</sup> continuous changes of the bandgap (green points in Fig. 9b) and of the position of the photoluminescence band. These significant discrepancies in the energy gap of 3D-CsPbCl<sub>3</sub> phase VI between our and the literature data can be due to anisotropic strain generated by silicone oil (hydrostatic to about 0.5 GPa only) used in the previous experiments.<sup>27</sup> The linear decrease of  $E_{\rm g}$  as a function of pressure up to the transition point well correlates with the linear pressure dependence of the average Pb-Cl distance (Fig. 7b). It testifies that in the compressed 3D-CsPbCl<sub>3</sub> phase IV the Pb-Cl bonds shortening is a dominant structural change absorbing the pressure-generated strain and determining the electronic bands responsible for the absorption edge.

The energy gap values determined during the decompression of  $CsPbCl_3$  crystal are substantially larger than those during the compression (see Fig. 9b). This pressure-memory effect is similar to that in  $CsPbBr_3$ . Although in  $CsPbCl_3$  this effect disappears after the reverse transition to phase IV, the features of absorption spectra recorded at 0.83 and 0.48 GPa clearly indicate that only a part of the crystal sample transformed back to phase IV, while the other part remained in partly amorphous phase VI. Some traces of the high-pressure phase were also seen just after the pressure release, and only after *c.a.* 0.5 h the complete restoration of the initial spectrum, characteristic of phase IV, was recorded.

The understanding of changes observed in the diffraction patterns and in the absorption spectra of CsPbCl<sub>3</sub>, induced by the transition at 1.3 GPa, requires a deeper analysis. It seems that the postulated isostructural phase transition is insufficient to explain these changes, especially in the light of the disputable evidence for step-wise volume change,<sup>25</sup> necessary for such type of transition. The crucial are the amorphization symptoms,



**Fig. 9** Absorption edge of CsPbCl<sub>3</sub> under pressure: (a) selected absorption spectra of a single-crystal plate of 3D-CsPbCl<sub>3</sub> recorded during its compression (bottom) and decompression (top), shifted vertically to avoid their overlapping. (b) The pressure dependence of the energy gap compared with the literature data.<sup>27</sup>

detected in the powder-diffraction experiments (Fig. 8c), which indicate a local structure collapse, resulting in a distribution of the Pb–Cl lengths and Pb–Cl–Pb angles. Such distortions in the framework of PbCl<sub>6</sub> octahedra leads to the broadened diffraction peaks situated at similar positions as in phase IV, and to the increase in the background scattering. But most importantly, the abrupt collapse of the crystal structure profoundly modifies the electronic bands of the material and its optical properties.

## Conclusions

Our systematic study shows that under pressure perovskites CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> are prone to time-dependent structural transformations, which proceed in various time scales. No such pronounced kinetic effects were observed for these crystals as a function of temperature, although they undergo a series of phase transitions at ambient pressure. Both CsPbCl<sub>3</sub> and CsPbBr3 undergo pressure-induced transitions that differ in character, depending on the time scale and method of the applied external stimuli. The slow-kinetics transformations shed new light on the stress-related response and stability of these all-inorganic perovskite structures. Our study shows the importance of genuinely hydrostatic conditions for the clarity and correctness of the discussion on the structural and optical properties of these materials. The hydrostatic results can drastically differ from the high-pressure experiments performed in non-hydrostatic conditions, systematically affected by the pressure gradients and regions under different anisotropic stress in the sample, which confuse the conclusions assuming the homogenous stress and uniform sample. The nonhydrostatic effects can in turn lead to heuristic rules or to advanced modelling and simulations based on the averaged crystal structures strained in a different way than the samples for which the physical properties were recorded. There are many such reports in prominent journals, which confuse the transparent description of the mechanisms of strain-energy gap relations in the important field of perovskites for photovoltaic and optoelectronic applications. Our present report only signals these problems for two all-inorganic perovskites. The obtained results show that the long-time kinetics transformations revealed in CsPbCl3 and CsPbBr3 have much in common with the previously described transformations in analogous hybrid perovskites [CH<sub>3</sub>NH<sub>3</sub>]PbX<sub>3</sub>.<sup>31</sup> Surely, more careful research on the structure and properties of perovskite photovoltaic materials is needed.

## Methods

### Synthesis and crystals growth

Crystals CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub> were grown by a low-temperature method from the aqueous solutions, as described previously.<sup>14,29</sup> Cesium bromide and chloride were prepared through reaction between Cs<sub>2</sub>CO<sub>3</sub> (Aldrich, 99%) and HBr (Acros Organics, 48% water solution) or HCl (POCH, 35% water solution, specially pure), respectively, while PbBr<sub>2</sub> and PbCl<sub>2</sub> were synthesized in the reaction between Pb(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O (Aldrich, 99.999%) and the appropriate acid. The precursor solutions were prepared by dissolving stoichiometric amounts of CsBr and PbBr<sub>2</sub> or CsCl and PbCl<sub>2</sub> in hot strongly acidified water. The solutions were saturated and left to crystallize during slow cooling and water evaporation at room temperature. The temperature of the crystals nucleation was controlled to start below 315 K for  $CsPbCl_3$  and below 360 K for  $CsPbBr_3$ , in order to avoid the crystals twinning resulting from the ferroelastic phase transitions occurring in these compounds at higher temperatures.<sup>30,37</sup>

#### High-pressure single-crystal and powder X-ray diffraction

The single-crystal X-ray diffraction (SCXRD) and powder X-ray diffraction (PXRD) high-pressure experiments have been performed with a Merrill-Bassett diamond anvil cell (DAC)38 modified by mounting the diamond anvils (with 0.8 mm culets) directly on steel supporting discs with conical windows. The gaskets were made of 0.1-0.3 mm thick tungsten foil with a spark-eroded hole 0.3-0.4 mm in diameter. The carefully selected single crystals of CsPbBr3 or CsPbCl3 were glued to the culet of one anvil. For powder-diffraction experiments the crystals were pulverized just before loading to the pressure cell. A ruby chip glued inside the pressure chamber served for the pressure calibration by the fluorescence method.<sup>39</sup> Isopropanol and Galden were alternatively used as the hydrostatic fluids. All high-pressure X-ray diffraction experiments were performed using an Oxford Diffraction Gemini A Ultra diffractometer operating with graphite-monochromated MoKa radiation. For the high-pressure cell centering the gasket-shadowing method<sup>40</sup> was applied. The CrysAlisPro software<sup>41</sup> was used for the data collection and processing. The structures were solved and refined using SHELX software.42 Crystallographic information files (CIFs) for CsPbCl<sub>3</sub> (2060421-2060427) and CsPbBr<sub>3</sub> (2060567-2060576) have been deposited with the Inorganic Crystal Structure Database.

The PXRD analyses of the samples recovered from the highpressure cells were carried out on a high-resolution Bruker D8 diffractometer equipped with a Johansson monochromator selecting the characteristic  $\lambda(CuK\alpha_1) = 1.54059$  Å line. The sample was gently smeared over about 4 mm<sup>2</sup> of the central surface of a single-crystal silicon plate, oriented to eliminate the background. In this way high-quality PXRD patterns were recorded even for very small amount of the sample.

#### Dielectric measurements under pressure

High-pressure dielectric studies were performed on the pellets of compressed polycrystalline samples. Gold electrodes were deposited on the flat surfaces of the pellets by the sputtering method using a Scancoat SIX (BOC Edwards). Additionally, the electrodes were covered with a silver paste to attach the wires. The sample was mounted in a beryllium–copper high-pressure cell filled with gaseous helium. The pressure was generated by a gas compressor U11 (Unipress) and calibrated by means of a manganin gauge with an accuracy of  $\pm 3$  MPa. The temperature was controlled inside the cell by a copper–constantan thermocouple. Measurements of electric permittivity were carried out with a Hewlett-Packard 4192A impedance analyzer at a rate of temperature changes 0.5 K min<sup>-1</sup>.

#### **Optical absorption spectra**

The optical absorption spectra were measured using a Jasco MSV-5100 microspectrometer in the 300–600 nm range. The

measurements were performed on single-crystal plates 2–3  $\mu$ m thick, placed in the DAC equipped with type IIa diamond anvils. The pressure chamber was filled with isopropanol. The absorbance was measured using the incident beam diameter of 30  $\mu$ m, the continuous scan speed of 200 nm min<sup>-1</sup>, and the spectral bandwidth 5 nm. Direct bandgap Tauc plots<sup>43</sup> were applied for the energy gap ( $E_g$ ) determination.

## Conflicts of interest

There are no conflicts to declare.

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