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# 1. Introduction

Recently, hybrid organic–inorganic perovskites (HOIPs) and related materials have attracted great attention in view of the diverse physical properties they can show, such as magnetism,<sup>1</sup> ferroelectricity,<sup>2</sup> multiferroism,<sup>3,4</sup> light harvesting,<sup>5</sup> *etc.* Additionally, the fact that in some HOIPs, such properties can be tuned by external stimuli (such as temperature, pressure, light, and electric and magnetic fields)<sup>6–9</sup> has triggered a vast amount of studies about

# Hybrid lead halide $[(CH_3)_2NH_2]PbX_3$ (X = Cl<sup>-</sup> and Br<sup>-</sup>) hexagonal perovskites with multiple functional properties<sup>+</sup>

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We have been able to prepare two new lead halides with the formula DMAPbX<sub>3</sub> (where DMA is dimethylammonium and X is Cl<sup>-</sup> or Br<sup>-</sup>), which display a 4H-hexagonal perovskite polytype, an unusual crystal structure in hybrid organic-inorganic perovskites. Both compounds experience a first-order phase transition, the chloride at ~320 K and the bromide at ~250 K, which involves two cooperative processes: an off-center shift of the lead cations and an order-disorder process of the DMA cations. Additionally, a sharp dielectric transition is associated with this structural transition in both hybrids. Both compounds are semiconductors with band gap values of 3.5 eV (X: Cl<sup>-</sup>) and 3.0 eV (X: Br<sup>-</sup>). Also, the LT-phase of the Br<sup>-</sup> compound displays a broad red light photoluminescence (PL) emission (620 nm) and PLE excitation with the maximum at a soft UV wavelength (360 nm). This broadband emission and large Stokes-shifted PL seem to be related to a self-trapped exciton mechanism. Therefore, the uncommon 4H-hexagonal perovskite is a promising crystal structure for understanding and designing new hybrid materials with broad photoluminescent emission and dielectric properties.

their potential applications in switchable dielectric devices, sensors, cooling devices, solar cells, *etc.*<sup>10,11</sup>

From the structural point of view, HOIPs have a general formula ABX<sub>3</sub> with a perovskite-type structure, in which the A<sup>+</sup> and/or X<sup>-</sup> ions are replaced by organic cations and/or organic linkers, respectively.<sup>12</sup> Several X anions have been used to obtain HOIPs, such as monoatomic halogen anions (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>), diatomic cyanide anion  $(CN^{-})^{13-15}$  and multiatomic ones, such as formate  $(HCOO^{-})$ , <sup>16-20</sup> thiocyanide  $(SCN^{-})$ , <sup>21</sup> azide  $(N_3^{-})$ , <sup>22,23</sup> dicyanamide [N(CN)2<sup>2-]24,25</sup> and dicyanometallates [M(CN)2<sup>n-].26</sup> As for the A-cations, they are typically alkylammonium (NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub><sup>+</sup>) or alkylphosphonium (PR1R2R3R4+) cations.27,28 The presence of organic components in these compounds introduces additional functionalities and structural flexibility, which cannot be achieved in purely inorganic perovskites, opening up enormous possibilities for finding exciting new (multi)functional and (multi)stimuliresponsive materials.<sup>29</sup> Also, their diverse structural and compositional variability offers substantial opportunities for tuning and modulating their physical properties by facile chemical modification.30

In this context, hybrid halide perovskites with the formula [AmH]PbX<sub>3</sub> (AmH = methylammonium:  $CH_3NH_3^+$  (MA), and formamidinium:  $HC(NH_2)^+$  (FA); and X =  $Cl^-$ ,  $Br^-$  and  $I^-$ ) are a rapidly developing class of HOIPs, owing to the emergence of



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<sup>†</sup> Electronic supplementary information (ESI) available: PXRD patterns obtained at room temperature, thermogravimetric curves, additional crystallographic figures and tables. CCDC 1855518–1855520. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9tc03543e

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perovskite solar cells (PSCs),<sup>31,32</sup> since unprecedented and intriguing photoconductivity was discovered in the methylammonium lead triiodide perovskite MAPbI<sub>3</sub>.<sup>5</sup> PSCs are one of the most promising solar cells with power conversion efficiencies (PCEs) over 24%,<sup>33</sup> a value that surpasses other mature and emerging photovoltaic technologies.

Going beyond photovoltaic applications, one emerging application field for HOIPs is as white light-emitting diodes (WLEDs) for solid-state lighting,<sup>34,35</sup> where single-component white-light emitters are highly in demand as they have an easily controlled emission, better color-rendering capability, and better reproducibility, compared to the multicomponent phosphors.<sup>35</sup>

The basis for this application relies on the idea of spatially confined charges, suppressing the exciton dissociation and enhancing the radiative recombination to yield a large emission efficiency, which in turn can be achieved, for example, by playing with the structural dimensionality in crystalline systems.<sup>36</sup> Thus, most of the white light-emitting HOIP materials reported to date are in fact layered  $2D^{37-42}$  or 1D-perovskites<sup>36</sup> of hybrid lead bromide or chloride. These single materials emit broadband white light with a continuous emission spanning from 400 to 700 nm. This makes those HOIPs and related materials interesting as broadband phosphors, for applications in artificial illumination or the manufacture of displays, among others.

Along the same lines, we have recently reported two new 2D dimethylammonium lead halides with general formula  $DMA_7Pb_4X_{15}$  (X = Cl<sup>-</sup>, Br<sup>-</sup>),<sup>38</sup> which also exhibit broadband photoluminescent emission and a dielectric transition. Interestingly, these hybrids have an unprecedented 2D-structure formed by layers of distorted [PbX<sub>6</sub>] octahedra, which share corners and faces, and contain intercalated DMA cations. The presence of dielectric transitions, associated with the structural phase transitions, helped us in understanding the behaviour of these systems, in which we have related the observed emission and the structural distortions of the [PbX<sub>6</sub>] octahedra induced by the large size of the DMA cations.

Also, we have recently reported that the dimethylammonium lead triiodide DMAPbI<sub>3</sub>, a 1D-hexagonal perovskite with 2H-structure,<sup>39</sup> shows a first-order phase transition at ~250 K, from the space-group  $P6_3/mmc$  (HT-phase) to the space-group  $P2_1/c$  (LT-phase). This compound also shows a large value of dielectric constant and a dielectric anomaly associated with the structural transition, and some structural distortions of the [PbX<sub>6</sub>] octahedra in the LT-phase.

Taking these facts into account, we have looked for other novel lead halide materials with uncommon crystal structures that could exhibit interesting functional properties.

In this work, we focus our studies on the dimethylammonium lead halides DMAPbX<sub>3</sub> with  $X = Cl^-$  and  $Br^-$ . From the structural point of view, only the room temperature crystal structure of DMAPbBr<sub>3</sub> has been reported till now.<sup>40</sup> It displays a 4H-hexagonal perovskite polytype, characterized by an anionic substructure consisting of dimeric units of face-sharing [PbBr<sub>6</sub>] octahedra, which in turn share the free corners to form a three-dimensional network,<sup>41</sup> and with the DMA cations showing orientational disorder. Thermally induced structural changes in this  $Br^-$  hybrid, and similar behaviour in the new corresponding  $Cl^-$  hybrid, could reasonably be expected.

As will be shown below, we have successfully synthesized the two DMAPbX<sub>3</sub> (X = Cl<sup>-</sup> and Br<sup>-</sup>) hybrids as single crystals and as polycrystalline materials, and we have elucidated the crystal structures of both compounds at different temperatures, deepening the structural characterization of the Br<sup>-</sup> compound at low temperature and reporting for the first time the crystal structure of the Cl<sup>-</sup> compound. Also, we have carefully studied the evolution of the structure, and dielectric and photoluminescence properties of these compounds as a function of temperature. In addition, we have calculated the electronic band structure of these compounds using density functional theory (DFT). We expect this study to shed light on the understanding of structure–property relationships in hybrid halides with this relatively little explored and peculiar 4H-hexagonal perovskite structure.

# 2. Experimental section

## 2.1. Materials

All starting materials were purchased from Sigma-Aldrich, of analytical grade and used without further purification treatment:  $(CH_3)_2NH_2Cl$  (DMACl, 99%),  $(CH_3)_2NH$  solution (40 wt% in H<sub>2</sub>O), PbCl<sub>2</sub> (99%), PbBr<sub>2</sub> (99%), HCl solution (37 wt% in H<sub>2</sub>O) and HBr solution (48 wt% in H<sub>2</sub>O).

## 2.2. Synthesis of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Br (DMABr)

Dimethylamine  $(CH_3)_2NH$  solution in a slight excess was reacted with hydrobromic acid (HBr) in an ice bath. The crystallization of dimethylammonium bromide (DMABr) was achieved using a rotary evaporator. The white powder obtained was recrystallized several times in absolute diethyl ether, and finally dried in a vacuum line overnight.

## 2.3. Synthesis of $(CH_3)_2NH_2PbX_3$ (DMAPbX<sub>3</sub>) (X = Cl<sup>-</sup>, Br<sup>-</sup>)

Single-crystals of both DMAPbX<sub>3</sub> compounds were obtained by crystallization from an *N*,*N*-dimethylformamide (DMF) solution. For this purpose, stoichiometric amounts of PbX<sub>2</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>) (4 mmol) and of DMAX (X = Cl<sup>-</sup>, Br<sup>-</sup>) (4 mmol) were dissolved by adding 5 ml of DMF. The obtained solutions were filtered through 0.45  $\mu$ m PTFE filters to minimize nucleation sites. Colourless needle-shaped single crystals of DMAPbX<sub>3</sub> were obtained upon slow evaporation of the solvent at room temperature after several days.

Additionally, polycrystalline powders of the DMAPbX<sub>3</sub> compounds were easily obtained at room temperature by a simple solid-state method of mechanosynthesis. For that purpose, equimolar amounts of PbX<sub>2</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>) and DMAX (X = Cl<sup>-</sup>, Br<sup>-</sup>) were placed in an agate mortar and carefully ground with a pestle for 30 minutes.

# 2.4. Thermal analysis

Thermogravimetric analysis (TGA) was carried out using TGA-DTA Thermal Analysis SDT2960 equipment. For each experiment, approximately 27 mg of the ground single crystals was heated at a rate of 5 K min<sup>-1</sup> from 300 K to 1200 K, using a corundum crucible, under a flow of dry nitrogen. Differential scanning calorimetry (DSC) analyses were carried out using a TA Instruments MDSC Q-2000 equipped with a liquid nitrogen cooling system, by heating and cooling the samples during several cycles at 10 K min<sup>-1</sup> up to 380 K under a nitrogen atmosphere.

# 2.5. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns of the obtained powders, and of the ground single-crystals, were collected using a Siemens D-5000 diffractometer using CuK $\alpha$  radiation at room temperature.

# 2.6. Single crystal X-ray diffraction

Single-crystal X-ray diffraction (SCXRD) experiments were carried out at temperatures well above and below the observed DSC transitions. For that purpose, single-crystal data sets of each sample were collected at 320 K and 100 K using a Bruker X8 Kappa X-ray diffractometer equipped with an APEXII CCD detector and using monochromatic MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Suitable crystals were chosen and mounted on a MiTeGen Micro-Mount<sup>™</sup> using Paratone<sup>®</sup> N (Hampton Research), except for data collected at high temperature, where the crystal was attached at the end of a capillary glass fiber using Araldite Rapid bicomponent (Ceys). To carry out these experiments, the temperature of the crystal was changed at different rates surrounding the sample with a cold stream of nitrogen gas from an Oxford Cryosystem 700 cooler. The data integration and reduction were performed using the APEX3 v2018.1-0 (Bruker AXS, 2018) software suite. The intensities collected were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods on the basis of symmetryequivalent data using TWINABS 2012/1 of the suite software. The structures were solved by the novel dual-space algorithm implemented in the SHELXT2014<sup>43</sup> program and were refined by the leastsquares method on SHELXL2017/1.44 The presence of multiple lattices was clear from visual inspection of diffraction images in all data collected, therefore all datasets were indexed using CELL\_NOW 2008/4 obtaining the solutions that interpret most of the diffraction peaks with  $I/\sigma(I) > 6$  found in the images measured. The integrations of the reflections were performed with SAINT 8.38A taking into account the orientation matrices of all the twin domains found simultaneously. All the software used to treat the twinned data is included in the APEX3 suite.

To refine the structures, anisotropic thermal factors were employed for the non-H atoms. For T = 320 K, the atoms of the whole DMA cation could not be found in the Fourier map due to the heavily disordered arrangement of this cation. The contribution of the disordered DMA cation in the compound DMAPbCl<sub>3</sub> at T = 320 K to the structure factors was taken into account by back Fourier transformation using the SQUEEZE procedure implemented in PLATON.<sup>45</sup>

Meanwhile, for T = 100 K, the hydrogen atoms of the  $\text{NH}_2^+$  group of the DMA cations were found in the Fourier map and the rest of the hydrogen atoms of the DMA were introduced at idealized positions. All hydrogen atoms were restrained using the riding model implemented in SHELXL2017/1.

Detailed experimental crystallographic data for DMAPbCl<sub>3</sub> (T = 100 and 320 K) and DMAPbBr<sub>3</sub> (T = 100 K) are included in

the ESI,† Table S1. CCDC 1855518–1855520† contain the supplementary crystallographic data for this paper.

## 2.7. Dielectric properties

The complex dielectric permittivity ( $\varepsilon_r = \varepsilon_r' - i\varepsilon_r''$ ) of the coldpress pelletized samples was measured as a function of frequency and temperature with a parallel-plate capacitor coupled to a Solartron1260A Impedance/Gain-Phase Analyzer, capable of measuring in the frequency range from 1 Hz up to 1 MHz using an amplitude of 1 V. The capacitor was mounted in a Janis SVT200T cryostat refrigerated with liquid nitrogen and with a Lakeshore 332 incorporated to control the temperature from 100 K up to 350 K. The data were collected on heating, and before carrying out the measurement, the pellets were maintained at each temperature for two minutes, so as to allow them to reach thermal equilibrium. Pelletized samples, with an area of approximately 133 mm<sup>2</sup> and a thickness of approximately 1 mm, were prepared by cold-pressing to fit into the capacitor. Gold was previously sputtered on the surfaces of the pelletized samples to ensure a good electrical contact. All the dielectric measurements were carried out in a nitrogen atmosphere, performing several cycles of vacuum and nitrogen gas to ensure a sample environment free of water.

## 2.8. Ultraviolet-visible (UV-vis) spectroscopy

Optical diffuse-reflectance measurements of ground single crystals were performed at room temperature using a Jasco V-730 UV-visible double-beam spectrophotometer with a single mono-chromator, operating from 200 to 900 nm. BaSO<sub>4</sub> was used as a non-absorbing reflectance reference. The generated reflectance-*versus*-wavelength data were used to estimate the band-gap of the materials by converting reflectance to absorbance data according to the Kubelka–Munk equation:<sup>46</sup>  $F(R) = \alpha = (1 - R)^2/2R$ , where *R* is the reflectance data and  $\alpha$  are the absorption coefficients.

Emission spectra were measured on a Horiba FluoroMax Plus-P spectrofluorometer equipped with a 150 W ozone-free xenon arc lamp and an R928P photon-counting emission detector, as well as a photodiode reference detector for monitoring lamp output. Samples were excited using a 150 W xenon arc lamp at 300 nm and then the emission was measured from 380 nm to 800 nm.

The chromaticity coordinates were calculated using the ColorCalculator by OSRAM Sylvania, Inc.<sup>47</sup> and plotted using the 1931 color space chromaticity diagram.

Temperature-dependent luminescence measurements were performed with a cryo-stage, Linkam THMS-LNP95 cooling system.

#### 2.9. Electronic structure calculations

The first-principles calculations were performed in the DFT framework as implemented in the Siesta package<sup>48</sup> (v. 4.1-b4) with the GGA-based PBE functional to describe the exchange–correlation term<sup>49</sup> and taking into account spin–orbit coupling (SOC). Calculations have been carried out with the experimentally determined crystal structures freezing lead and halide atom positions. The DMA<sup>+</sup> cation, which is neither involved in conduction nor in valence bands, is simulated adding a background

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of compensating positive charge density to make the simulated  $[PbX_3]^-$  system neutral. Core electrons are built up using ATOM (ATM 4.2.7) software with relativistic Troullier–Martins norm-conserving pseudo-potentials<sup>50</sup> including nonlinear core corrections. 3s2 3p5, 4s2 4p5 and 6s2 6p2 were used as valence electrons for Cl, Br, and Pb, respectively. Pseudo-potentials were tested for transferability using single atom all-electron comparisons, and band electronic calculations for PbCl<sub>2</sub> and PbBr<sub>2</sub> structures were carried out and compared with bands reported elsewhere<sup>51</sup> showing a good agreement with PW calculations. The valence wave function was developed over a double- $\zeta$  polarized (DZP) basis set of finite-range numerical pseudoatomic orbitals. An energy cutoff of 200 Ry for the real-space mesh size was used as well as a  $6 \times 6 \times 6$  Monkhorst–Pack grid sampling the Brillouin zone.

# 3. Results and discussion

# 3.1. Synthesis and basic characterization

By using an easy mechanosynthesis route under mild conditions (at ambient temperature), which is totally reproducible, we have prepared the two DMAPbX<sub>3</sub> (X = Cl<sup>-</sup> and Br<sup>-</sup>) hybrids as polycrystalline materials. Also, by a wet route involving crystallization, we have obtained single crystals of both compounds. As confirmed by PXRD, the obtained sample powders are single-phase materials. In both cases, their purity was confirmed by comparison of their experimental PXRD patterns with the profile obtained from their single-crystal structure at room temperature (Fig. S1 of ESI<sup>+</sup>).

According to the TGA results (Fig. S2 of ESI<sup>†</sup>), these DMAPbX<sub>3</sub> compounds are stable up to  $T \sim 450$  K (when X = Cl<sup>-</sup>) and  $T \sim 470$  K (when X = Br<sup>-</sup>). Both hybrids decompose at higher temperatures in two steps: they experience a first weight loss (~23.83% at  $T \sim 450$ –460 K for DMAPbCl<sub>3</sub>, ~25.49% at  $T \sim 450$ –640 K for DMAPbBr<sub>3</sub>), which corresponds to the loss of the DMA cations and one (out of the three) X anion being released predominantly as their acid-base gas conjugate HX + (CH<sub>3</sub>)<sub>2</sub>NH;<sup>52-54</sup> and a second weight loss (~76.17% at  $T \sim 760$ –1100 K for DMAPbCl<sub>3</sub>, ~74.51% at  $T \sim 710$ –870 K for DMAPbBr<sub>3</sub>) related to the complete volatilization of the remaining inorganic PbX<sub>2</sub> residue.

## 3.2. Differential scanning calorimetry (DSC)

DSC experiments revealed that both compounds experience a reversible phase transition near room temperature (just below RT in the case of the Br<sup>-</sup> compound, and just above RT in the Cl<sup>-</sup> one, see Fig. 1): as shown in the results, each of them displays an endothermic peak on heating (DMAPbCl<sub>3</sub> at  $T_t \sim 315$  K and DMAPbBr<sub>3</sub> at  $T_t \sim 253$  K), whose associated exothermic peak appears on cooling at slightly lower temperatures (at  $T_t \sim 312$  K and at  $T_t \sim 251$  K, respectively).

The sharp shapes of the endothermic/exothermic peaks indicate the first-order character of the phase transition. The changes in the enthalpy  $\Delta H$  (J mol<sup>-1</sup>) and the entropy  $\Delta S$  (J mol<sup>-1</sup> K<sup>-1</sup>) were determined from the area under the heat flow/temperature curves. The results yield for the phase transition of DMAPbCl<sub>3</sub>,  $\Delta H \sim 3719$  (*endo*)–3690 (*exo*) J mol<sup>-1</sup> and  $\Delta S \sim 11.8$ 

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Fig. 1 DSC results as a function of temperature, obtained by heating and cooling the samples (a) DMAPbBr<sub>3</sub> and (b) DMAPbCl<sub>3</sub> at a rate of 10 K min<sup>-1</sup>.

(*endo*)–11.8 (*exo*) J mol<sup>-1</sup> K<sup>-1</sup>, and for the phase transition of DMAPbBr<sub>3</sub>,  $\Delta H \sim 2181$  (*endo*)–2461 (*exo*) J mol<sup>-1</sup> and  $\Delta S \sim 8.6$  (*endo*)–9.8 (*exo*) J mol<sup>-1</sup> K<sup>-1</sup>.

Taking into account that  $\Delta S = R \ln(N)$  for an order–disorder transition, where *R* is the gas constant and *N* is the ratio of the number of configurations in the disordered and ordered system, values of  $N \sim 4$  and  $N \sim 3$  are calculated for the chloride and bromide compounds, respectively. Those values are similar to that observed in the related lead iodide DMAPbI<sub>3</sub>,<sup>39</sup> and also to that observed in the related manganese formate [DMA][Mn-(HCOO)<sub>3</sub>],<sup>42</sup> another very well-known example of a hybrid perovskite that also contains the DMA cation in the A position. In both hybrids, the phase transition is related to a thermally activated order–disorder process of the DMA cation. This makes us think that there may be a similar mechanism in these compounds.

# 3.3. Crystal structures obtained by single-crystal X-ray diffraction

Single-crystal X-ray diffraction experiments were carried out at temperatures well above and below the observed DSC transition  $(T_t)$ , namely at 320 K and 100 K.

First of all, the SCXRD studies reveal that both compounds present different crystal structures above and below the phase transition temperature, which will be hereafter labelled as HT-polymorph ( $T > T_t$ ) and LT-polymorph ( $T < T_t$ ) for

convenience. Furthermore, they show that this solid-to-solid HT–LT structural phase transition is completely reversible, even if the crystals of the two compounds get twinned on cooling.

As we anticipated in the Introduction section, the singlecrystal structure of the LT-phase of the  $Br^-$  hybrid, and the structures of both the LT- and HT-polymorphs of the  $Cl^-$  hybrid are reported for the first time in this work.

In this context, the HT-polymorph of the Cl<sup>-</sup> compound shows a hexagonal symmetry with the space group  $P6_3/mmc$ , equal to the HT-phase Br<sup>-</sup> compound case already described in the literature.<sup>40</sup> In parallel, the LT-polymorphs of both compounds are orthorhombic and crystallize in the non-centrosymmetric space group  $P2_12_12_1$  (see Table S1 (ESI†) and Fig. 2).

In all cases, the HT and LT structures of both compounds are based on the 4H-hexagonal perovskite polytype, which consists of  $[Pb_2X_9]$  dimers of face-sharing  $[PbX_6]$  octahedra linked to each



**Fig. 2** Crystal structure of the LT-phase of the [DMA]PbX<sub>3</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>) hybrids viewed along two different directions: (a) along *a*-axis and (b) along *c*-axis. The DMA cations are cooperatively ordered and the Pb<sup>2+</sup> cations show a cooperative off-center shift in the [PbX<sub>6</sub>] octahedra.

other by corner-sharing, forming a 3D framework, and with the DMA cations acting as countercations. The framework forms hexagonal channels that run unobstructed along the c axis and are occupied by the DMA cations. However, there are significant structural differences between the HT- and LT-polymorphs.

Starting with the HT-phase, the first feature that is worth noting is that in these structures, each  $Pb^{2+}$  cation sits at the center of an almost regular octahedral environment, even if three of the six X ions are bonded to three Pb ions as part of corner-sharing octahedra and the other three X ions are only bonded to one Pb ion, thus forming face-sharing octahedra.

For example, all Pb–Br bond lengths are similar to 2.99 Å in the HT bromide compound<sup>40</sup> (see Tables S2 and S3 of ESI†). Meanwhile, there is a small difference in these two sets of bond distances for the HT chloride compound, with values around 2.85 Å (face-sharing) and 2.88 Å (corner-sharing). The distortion from a completely regular octahedral coordination is also evidenced in the values of the X–Pb–X angles, which deviate significantly from the ideal values of 90° and 180°. The second fact that should be highlighted is that in these HT-phases, the DMA cations show orientational disorder with nitrogen and carbon atoms apparently located in different feasible positions. In fact, in the chlorine hybrid, this disorder is so high that the positions of the C and N atoms could not be determined by X-ray diffraction.

On the other hand, in the LT-phase, the Pb<sup>2+</sup> cations sit in a very highly distorted octahedral environment as six different Pb–X distances are detected, ranging from ~2.69 Å to ~3.16 Å in the Cl<sup>-</sup> compound, and from ~2.84 Å to ~3.26 Å in the Br<sup>-</sup> compound (see Tables S2, S3 and Fig. S3 of the ESI†). Moreover, the Pb<sup>2+</sup> cations are cooperatively off-center shifted towards one of the corners of such octahedra (see Fig. S3 of the ESI†). Such a displacement could be caused by the presence of their 6s<sup>2</sup> electrons ("lone pair"), which are chemically inactive but can be sterically active, resulting in an asymmetry of the metal coordination and a distorted crystal structure. Note, as shown below in the calculations section, a comparison of the LT and HT phase PDOSs for the Pb centers shows the higher 6s<sup>2</sup> orbital character of the valence band for the LT phase.

Another remarkable feature of the LT phases is the ordering of the DMA cations, which is cooperative and antiparallel inside the unit cell.

We note that such a structural phase transition, involving the two mentioned main elements, is similar to that previously observed in DMAPbI<sub>3</sub>,<sup>39</sup> even if this I<sup>-</sup> compound form a 2H-hexagonal perovskite with a 1D framework while the here studied DMAPbX<sub>3</sub> members with X = Br<sup>-</sup> and Cl<sup>-</sup> display a 4H-hexagonal perovskite polytype with a 3D framework. In fact, the 4H-hexagonal framework displayed by the here described Cl<sup>-</sup> and Br<sup>-</sup> compounds is intermediate between that exhibited by the 2H-hexagonal polytype and the cubic perovskite: in the 2H-hexagonal perovskite, the 1D framework displays exclusively face-sharing connectivity between each [PbX<sub>6</sub>] octahedron and two nearest neighbours; in the cubic perovskite, the 3D framework is formed by octahedra linked exclusively by cornersharing with six nearest neighbours; meanwhile, in the here described 4H-hexagonal perovskite structure, all octahedra are linked to four nearest neighbours (one by face-sharing and three by corner-sharing).

Furthermore, the four  $Pb^{2+}-Pb^{2+}$  distances are very different in the 4H polytype with one shorter distance between the facesharing  $Pb^{2+}$  cations and three larger distances between the corner-sharing  $Pb^{2+}$  cations (see Fig. S4 of the ESI†). Meanwhile, the 4H polytype shows diverse connectivity with the characteristics of both the 2H-hexagonal polytype and cubic perovskite. This diverse connectivity has a significant impact on the electronic properties of the obtained materials, as will be shown in the next subsections.

## 3.4. Dielectric properties

Dielectric measurements allow us to understand the mechanism of the transition between the ordered LT-phase and the disordered HT-phase of the DMAPbX<sub>3</sub> (X = Cl<sup>-</sup> and Br<sup>-</sup>) hybrids better. Fig. 3 shows the temperature dependence of the real part of the complex dielectric permittivity (the so-called dielectric constant,  $\varepsilon_r'$ ) in the temperature range of 200–350 K. As can be seen, both halides display a sharp dielectric transition at ~321 K, in the case of the DMAPbCl<sub>3</sub> compound, and at ~252 K, in the case of DMAPbBr<sub>3</sub>. As expected, those dielectric anomalies match very well with the temperature of the phase transition detected by DSC (~312–315 K and ~251–253 K for the Cl<sup>-</sup> and Br<sup>-</sup> hybrid, respectively).



Fig. 3 Temperature dependence of the dielectric constant ( $\epsilon_r$ ), measured at different frequencies (16–100 kHz), for (a) DMAPbCl<sub>3</sub> and (b) DMAPbBr<sub>3</sub>.

In order to rationalize the observed dielectric response, we had a careful look at the structures of both hybrids and we can identify two cooperative antiferrodistortive processes that could be involved in the structural and dielectric transition:

(I) An off-center shift of the  $Pb^{2+}$  cations in the LT polymorphs. This distortion induces the appearance of electric dipoles, and the [PbX<sub>6</sub>] octahedra become polar. Taking into account that those octahedra are arranged in [Pb<sub>2</sub>X<sub>9</sub>] dimers, as shown in Fig. S3 of the ESI,† and that the unit cell comprises four [Pb<sub>2</sub>X<sub>9</sub>] dimers, which are antiparallel to each other, the resulting net polarization in those entities becomes zero.

(II) An order-disorder process of the DMA cations, which are polar species, and whose associated dipole moments display an antiparallel arrangement in the LT-phase, while they get averaged in the disordered HT-phase.

It is also worth noting that the dielectric constant of the Cl<sup>-</sup> compound displays a certain frequency dependence in the HT phase. This feature reminds us of DMAPbI<sub>3</sub> and MAPbI<sub>3-x</sub>Cl<sub>x</sub> compounds, which exhibit a strong frequency dependence and even giant values of the dielectric of  $\varepsilon_r$  at room temperature and at low measuring frequencies<sup>55</sup> due to the appearance of ionic conductivity and the activation of extrinsic contributions. To clarify this point in the case of the Cl<sup>-</sup> compound, we have analysed its impedance complex plane plots at different temperatures below and above the dielectric transition (Fig. S5 of ESI<sup>+</sup>). These plots indicate that this compound exhibits an insulator response (impedance around or higher than MΩ) below T < T325 K and a certain conductivity (impedance around  $k\Omega$ ) about T > 325 K. Therefore, the observed frequency dependence of  $\varepsilon_r'$  in the Cl<sup>-</sup> hybrid is due to a certain conductivity in the HT phase. In any case, it should be indicated that the conductivity of DMAPbCl<sub>3</sub> is lower than that previously observed for the DMAPbI<sub>3</sub> compound.<sup>39</sup>

Finally, it is important to note the similarity between the dielectric transitions displayed by the here presented compounds and those observed in the hybrid organic–inorganic perovskites  $DMAPbI_3^{39}$  and  $MAPbX_3$  (X = Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>),<sup>56</sup> whose origin has been related to order–disorder processes of the polar DMA and MA cations.<sup>57</sup> In all these systems, there are reorientations of the electrical dipoles associated with the organic cations with respect to the inorganic framework in the HT phase, while the cations and their associated dipoles are ordered and basically frozen in the LT phase, although the molecules still retain a certain state of motion (such as twisting, bending, *etc.*) until very low-temperature (below 100 K).<sup>58–60</sup>

Taking into account the crystal structure characteristics of the LT and HT phases of the here studied DMAPbX<sub>3</sub> compounds (X = Cl<sup>-</sup> and Br<sup>-</sup>), we suggest that a similar mechanism is responsible for the dielectric transition they experience associated with their structural phase transition. Therefore, these 4H-hexagonal perovskites join the emergent families of halide perovskites with dielectric phase transitions, such as 2H-hexagonal perovskites<sup>38,61-63</sup> and 2D layered perovskites.<sup>64-66</sup>

## 3.5. UV-visible spectroscopy

In order to check the optoelectronic properties of both compounds, we have evaluated their light absorbance at room temperature and



Fig. 4 Absorption spectra of the DMAPbX<sub>3</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>) hybrids at room temperature.

their photoluminescence (PL) spectra at several temperatures. Fig. 4 shows the absorption spectra of both compounds at room temperature. As can be seen, high-energy absorptions with peaks at around 300 nm and 360 nm are observed for the Cl<sup>-</sup> and Br<sup>-</sup> hybrids, respectively. The absorbance cut-off wavelengths are ~350 nm for the Cl<sup>-</sup> and ~425 nm for the Br<sup>-</sup> compound. The corresponding optical band gaps were calculated using the Kubelka–Munk equation, obtaining values of 3.5 eV (Cl) and 3.0 eV (Br).

Additionally, both spectra have a shoulder near the absorption edge, which suggests the presence of tightly bound excitons. This type of exciton has been reported in 2D hybrid perovskites where the low dielectric constant of the organic layer and 2D structure of the inorganic layers enhance the attraction between the electron and hole in an exciton.

It is worth noting that the values of the optical band gap of the DMAPbX<sub>3</sub> compounds, which crystallize in the 4H-polytype, are intermediate between those of the 2H-polytypes and the cubic perovskites, as summarized in Table 1. Therefore, these results reveal once again the strong influence of the crystal structure and its dimensionality on the electronic properties of the materials. In this context, we would like to recall the wellknown relationship between the electronic bandwidth (*W*) and the number of nearest neighbours (*z*): the bandwidth is directly proportional to z ( $W \propto z$ ). In 2H- and 4H-perovskites, *z* is 2 and 4, respectively, meanwhile, in the case of the cubic perovskites, the value of *z* is 6, yielding wider electronic bands, thus resulting in a reduction of the band gap.

 $\label{eq:table_transform} \begin{array}{ll} \mbox{Table 1} & \mbox{Optical band gaps (in eV) of the DMAPbX_3 hybrids studied in this} \\ \mbox{work, compared with other APbX_3 hybrids reported in the literature} \end{array}$ 

	Band gap (eV)			
	$\mathbf{X} = \mathbf{Cl}^{-}$	$X = Br^{-}$	z	Packing
TMAPbX <sub>3</sub> <sup>41</sup>		3.45	2	2H-polytype
$(CH_3)_3 SPbX_3^{67}$	3.78	3.68	4	4H-polytype (Cl)
			2	2H-polytype (Br)
DMAPbX <sub>3</sub>	3.5	3.0	4	4H-polytype
MAPbX <sub>3</sub> <sup>68</sup>	2.97	2.23	6	Cubic
FAPbX <sub>3</sub>	$3.01^{69}$	$2.17^{70}$	6	Cubic
CsPbX <sub>3</sub> <sup>68</sup>	2.91	2.27	6	Cubic

On the other hand, the solid steady-state photoluminescence (PL) spectra were measured at different temperatures (Fig. S6 of the ESI<sup>†</sup>). We have observed that the HT and LT phase of the Cl compound and the HT phase of the Br<sup>-</sup> compound do not exhibit PL emission. However, the LT phase of the Br- compound displays a broad PL emission with a maximum around 620 nm (2 eV) and the PLE spectra show a peak at 370 nm (3.35 eV), see Fig. 5. These different PL properties can be reasonably understood from the point of view that high temperatures maximize interactions between excitons and phonons resulting in non-radiative quenching paths. On the other hand, the high electronegativity difference of the pair Pb-Cl, the last responsible for the structure of electronic bands in the material, does not facilitate the necessary conditions for the production of electronhole pairs to generate trapped excitons with radiative emission equivalent to the observed PL in the LT phase of the Pb-Br compound.

Also, it is worth highlighting that both excitation and emission maxima show a large Stokes shift of approximately 250 nm (1.35 eV).

Such features remind us of those reported for the related 2D sulfonium-based hybrid  $(tms)_4Pb_3Br_{10}$  [tms = trimethylsulfonium;  $(CH_3)_3S^{+}$ ],<sup>71</sup> a compound with a different structure arrangement but that also displays a Pb–Br framework containing face-sharing and corner-sharing Pb–Br octahedra. For this  $(tms)_4Pb_3Br_{10}$  compound, a self-trapped exciton mechanism has been proposed to explain the origin of the observed PL properties.<sup>71</sup>

In view of the similarities, we suggest that a similar mechanism could explain the observed PL response of the DMAPbBr<sub>3</sub> compound, where the large Stokes shift would be provoked by a large structural distortion associated with self-trapped excitons.

It is worth noting that if exciton self-trapping is indeed an intrinsic property of both DMAPbBr<sub>3</sub> and  $(tms)_4Pb_3Br_{10}$ , this characteristic could be related to the different connectivities of the [Pb–Br<sub>6</sub>] octahedra in these compounds, which gives rise to slabs of face-sharing octahedra whose extension gets interrupted by the presence of corner-shared [PbBr<sub>6</sub>] octahedra. In fact, face-sharing connectivity favours electronic localization and shortens the Pb–Pb distances in comparison to the Pb–Pb distances in



Fig. 5 Normalized photoluminescence spectrum (red line) and photoluminescence excitation spectrum (black line) for DMAPbBr\_3 at T = 100 K.

corner-shared PbBr<sub>6</sub> octahedra. These shorter distances that provoke an interaction between the lead cations is very sensitive to any change in the electronic configuration of these cations. Therefore, the diverse connectivity seems to favour both the presence of self-trapped excitons and the localized distortions.

## 3.6. Electronic band structure calculations

DFT calculations were carried to estimate the electronic band structure of both HT and LT polymorphs depending on halide X. According to the results, both LT- and HT-polymorphs are direct band gap semiconductors at the  $\Gamma$  point, although the LT structures exhibited a slightly indirect character. Both Cl<sup>-</sup> and Br<sup>-</sup> based LT structures have a gap slightly shifted away, placing the valence band maximum (VBM) in the  $\Gamma$  to *Z k*-point interval and the conduction band minimum (CBM) in the  $\Gamma$  to *Y k*-point interval, see Fig. 6. This shifting of the bandgap from a high-symmetry point of the Brillouin zone has been ascribed to the signature of the Rashba effect in relation to the giant spin–orbit coupling of the Pb atom, as noted before for similar systems.<sup>72</sup> The calculated band gaps including SOC are shown in Table 2.

DFT calculated band gaps give a typical significant underestimation (40–60%) compared to the experimental band gaps.

Table 2 Experimental and theoretical bandgaps of the LT and HT compounds

Structure	Halide	Theoretical (eV)	Experimental (eV)
НТ	Br	1.7	3.0
LT	Br	2.0	
HT	Cl	2.2	
LT	Cl	2.6	3.5

However, computed band gaps capture the main trends. The calculated band gaps for the  $Br^-$  compound are ~0.5 eV smaller than those for the  $Cl^-$  compound, a result which is comparable to the experimental band gap difference.

Also, the observed band gap difference between the Cl<sup>-</sup> and Br<sup>-</sup> compounds is in agreement with those reported for related compounds.<sup>73</sup> It follows the theoretical and experimental tendency that indicates that the band gap decreases as the effective electronegativity difference between the metal cations and anions in the compound decreases, as in the case of the here shown Cl<sup>-</sup> and Br<sup>-</sup> compounds.

Despite the different HT phase (hexagonal) or LT phase (orthorhombic) structures, the electronic bands present similar features, the most relevant being differences placed around the  $\Gamma$  point, see Fig. 6.



**Fig. 6** DFT calculations of electronic band structures following the conventional path<sup>74</sup> *ГXSYFZURTZ*|*YT*|*UX*|*SR* and *FMKFALHA*|*LM*|*KH* exploring the main *k*-points in the reduced Brillouin Zone for the hexagonal and orthorhombic structure, respectively. Hexagonal (a) HT-APbBr3, (b) HT-APbCl<sub>3</sub> and orthorhombic (c) LT-APbBr<sub>3</sub>, (d) LT-APbCl<sub>3</sub>, using the PBE functional with SOC.

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Around the  $\Gamma$  point in the CBM for the LT structures, the bands are double split in the *Y*–*Z* interval, probably due to the loss of symmetry elements going from a hexagonal to orthorhombic structure on lowering temperature. Another remarkable difference is that electronic band flat dispersion intervals are observed in the LT structures following the  $\Gamma$  or *Z* closed path and these flat dispersions are absent compared to the equivalent closed  $\Gamma$  or A cycle in the HT structures.

The projected density of states (PDOS) of the electronic bands shows for all structures the typical Pb 6s hybridation with the p-type orbital from the halide atom in the VB; meanwhile, the CB is mainly constituted by Pb 6p and p-type orbitals from the halides, see inset of the PDOS in Fig. 6. This is confirmation of our approach dealing only with the inorganic framework (Pb and halide atoms) and simplifying discrete organic cations by one background of compensating positive charge density for calculations of the band states in hybrid halide perovskites.

# 4. Conclusions

We have prepared two lead halides with general formula  $DMAPbX_3$  (X = Cl<sup>-</sup> and Br<sup>-</sup>) by using an easy route under mild conditions at room temperature and with excellent reproducibility. The crystal structure of the LT phase of the bromide hybrid and both LT and HT structures of the chloride hybrid are reported for the first time in this work. The two polymorphs of both compounds display a 4H-hexagonal perovskite polytype, an unusual crystal structure in hybrid perovskites, which consists of  $[Pb_2X_9]$  dimers of face-sharing  $[PbX_6]$  octahedra linked to each other by corner-sharing, forming a 3D framework, and with the DMA cations acting as countercations. The framework forms hexagonal channels that run unobstructed along the c axis and are occupied by the DMA cations.

These compounds experience a first-order structural phase transition at ~320 K (Cl<sup>-</sup> compound) and ~250 K (Br<sup>-</sup> compound), which involves two cooperative antiferrodistortive processes: an off-center shift of the Pb<sup>2+</sup> cations in the LT-structure and an order-disorder process of the DMA cations. The polar DMA cations display an antiparallel arrangement in the LT-phase, which gets averaged in the disordered HT-phase, being responsible for the observed dielectric anomaly clearly associated with the structural phase transition.

Both compounds are semiconductors with experimental band gap values of 3.5 eV (Cl) and 3.0 eV (Br). Their electronic band structures, obtained by DFT calculations, show that frontier orbitals are related to the inorganic framework: the VB is mainly constituted by the hybridation of the np orbitals from the halide atoms with the Pb 6s orbital, while the CB is mainly constituted by Pb 6p and p-type orbitals from the halides.

The LT phase of the  $Br^-$  compound displays a broad red light PL emission and PLE excitation with the maximum at a soft UV wavelength. This broadband emission and large Stokes-shifted PL seem to be related to a self-trapped exciton mechanism.

Moreover, the 4H-perovskite bandwidth *W* is lower than that of the related cubic perovskites; this is due to the lower number of nearest neighbours, 4 in the 4H-perovskites *versus* 6 in the cubic-ones, yielding narrower electronic bands and relatively larger band gaps. Therefore, the uncommon 4H-hexagonal perovskite can be considered to be another interesting element with intermediate features in the versatile family of new hybrid materials exhibiting broad photoluminescent emission and dielectric properties.

# Conflicts of interest

There are no conflicts to declare.

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