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Phase Transition, Dielectric Properties, and Ionic Transport in the [(CH₃)₂NH₂]PbI₃ Organic–Inorganic Hybrid with 2H-Hexagonal Perovskite Structure

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Supporting Information

ABSTRACT: In this work, we focus on $[(CH_3)_2NH_2]PbI_3$, a member of the [AmineH]PbI₃ series of hybrid organic—inorganic compounds, reporting a very easy mechanosynthesis route for its preparation at room temperature. We report that this $[(CH_3)_2NH_2]$ -PbI₃ compound with 2H-perovskite structure experiences a first-order transition at ≈ 250 K from hexagonal symmetry $P6_3/mmc$ (HT phase) to monoclinic symmetry $P2_1/c$ (LT phase), which involves two cooperative processes: an off-center shift of the Pb²⁺ cations and an order—disorder process of the N atoms of the DMA cations. Very interestingly, this compound shows a dielectric anomaly associated with the structural phase transition. Additionally, this compound displays very large values of the appearance of a certain conductivity



and the activation of extrinsic contributions, as demonstrated by impedance spectroscopy. The large optical band gap displayed by this material ($E_g = 2.59 \text{ eV}$) rules out the possibility that the observed conductivity can be electronic and points to ionic conductivity, as confirmed by density functional theory calculations that indicate that the lowest activation energy of 0.68 eV corresponds to the iodine anions, and suggests the most favorable diffusion paths for these anions. The obtained results thus indicate that $[(CH_3)_2NH_2]PbI_3$ is an electronic insulator and an ionic conductor, where the electronic conductivity is disfavored because of the low dimensionality of the $[(CH_3)_2NH_2]PbI_3$ structure.

■ INTRODUCTION

ABX₃ compounds with perovskite structure have been intensively and extensively studied over the past several decades because of their structural richness and amazing variety of interesting properties, such as piezoelectricity, ferroelectricity,¹ ferromagnetism,² magnetoresistance,³ superconductivity,⁴ multiferroicity,⁵ etc. Traditionally, the studies of perovskite compounds have been focused on ceramic materials,⁶ mainly on transition metal oxides of the general formula ABX₃ (A = alkali, alkaline earth, or lanthanide cation, B = transition metal cation, and X = O).

Interestingly, in the past few years, significant effort has been devoted to the development of new members of the versatile families of the so-called perovskite-, chiral-, and niccolite-like organic–inorganic hybrids,⁷ where the A- and/or X-site inorganic moieties of the conventional perovskites have been replaced by organic building blocks.^{8–12} The multiple combinations available together with the possibility of extending well-established concepts (tolerance factor, structure–property relationship, etc.) and tuning strategies of inorganic perovskites to this new family of compounds open up enormous possibilities for finding exciting new (multi)functional and (multi)stimulus responsive materials.^{12–15}

This is the case for the families with the general formula $[amineH][M(X)_3]$ (amineH = midsized protonated amines, M

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= divalent transition metal cations, and X = a polyatomic ligand such as HCOO⁻, N₃⁻, or CN⁻), which have already revealed very remarkable properties such as noteworthy cooperative magnetic, electric, or elastic order.¹⁶ Moreover, the metal formates [amineH][M(HCOO)₃] [M²⁺ = Mn²⁺, Fe²⁺, Co²⁺, or Ni²⁺; amineH = dimethylammonium (DMA)] have been found to exhibit type I multiferroicity,¹⁷ and methylammonium (MA) Co-formate, [CH₃NH₃][Co(HCOO)₃], coupled between magnetic and electric order, opening the large, flexible, multifunctional, and designable family of hybrid perovskites to magnetically induced multiferroic behavior.¹⁸

Another family of perovskite hybrids that is attracting a great deal of attention is that of lead halides with the formula $[AmH]PbX_3$ (X = Cl, Br, or I) because unprecedented and intriguing photoconductivity was discovered in the methylammonium lead triiodide perovskite, [CH3NH3]PbI3 (MAPbI₃).¹⁹ In this context, the solar energy conversion efficiency for a device based on this compound has already reached 21.6%,²⁰ a value that surpasses those of dye-sensitized, quantum dot, organic, and amorphous silicon solar cells, and other emerging PV technologies, making this compound a very promising material for low-cost and high-efficiency photovoltaic applications. Despite the recent substantial progress, perovskite solar cells based on MAPbI₃ have to overcome several inconveniences to be commercially viable (such as the toxicity of lead, the bad long-term stability of this compound,²¹ its high sensitivity to humidity, etc.), so that materials beyond MAPbI₃ are currently being addressed.²²

In this work, and in the search for new materials and properties in hybrid compounds with ABX_3 stoichiometry, we have focused on the dimethylammonium lead triiodide compound, $[(CH_3)_2NH_2]PbI_3$, DMAPbI₃. This hybrid, which belongs to the [AmH]PbI₃ series, has been recently prepared and studied²³ in the search for alternatives to MAPbI₃.

This DMA compound has nevertheless revealed important differences with respect to the MA-iodide.

(i) It does not show a three-dimensional (3D) perovskite structure as is the case of MAPbI₃.²² Instead, it crystallizes in a 2H-hexagonal polytype consisting of infinite chains of face-sharing [PbI₆] octahedra separated by chains of DMA cations,²³ the structure that results from an all-hexagonal stacking of the closely packed AX₃ layers instead of the cubic sequence of the former.²⁴

This difference can be rationalized on the basis of Goldschmidt's tolerance factor,²⁵ which has been recently extended to organic–inorganic perovskites by Kieslich et al.,²⁶ that in total parallel with the case of inorganic perovskites, ABO₃ can be used as a guiding tool for hybrid perovskite structures. In this context, tolerance factors (TFs) with values of 0.9–1 favor almost cubic perovskite structures; meanwhile, a lower TF of 0.80–0.89 gives rise to distorted perovskite structures (rhombohedral, tetragonal, etc.). On the other hand, a TF of >1 leads to hexagonal structures in which layers of face-sharing octahedra are introduced into the structure.

This is the case for this compound, where the presence of a larger cation in the A position, DMA instead of the smaller MA, results in a TF of >1.

(ii) The DMAPbI₃ compound shows an optical band gap (E_g) of 2.39 eV,²³ which is not suitable for photovoltaic applications.

In any case, this $DMAPbI_3$ compound has attracted our attention from a different point of view, as the presence of the DMA cations—which are polar and carry an associated dipole

moment—can give rise to interesting behaviors and properties as demonstrated in the case of the related metal formates $[DMA][M(HCOO)_3]$ with perovskite structure.^{17,27–29} For example, in those formates, the DMA cations experience thermally induced order—disorder processes, inducing structural phase transitions,³⁰ dielectric transitions, and cooperative electric order.^{29,30}

On this basis and the experience we have acquired studying those metal formates, our goal in this work is to explore whether DMAPbI₃ also presents such features. This study, which will ultimately seek to establish composition–structure– property relationships of interest, in principle, for dielectric materials could also provide useful information for improving our understanding of the origin of the exceptional properties of the analogue photovoltaic MAPbI₃ compound.

To perform this work, we have prepared this compound using a very easy route, which is different from that described previously,²³ that we present here. We have determined in its structural characteristics from low temperatures to room temperature by means of single-crystal X-ray diffraction and studied its electrical properties by means of dielectric measurements, impedance spectroscopy, and density functional theory (DFT) calculations.

EXPERIMENTAL SECTION

Synthesis. We have developed a new method for synthesizing DMAPbI₃, which is different and much easier than the one previously described for the synthesis of this compound.²³

This method implies, as first step, the synthesis of $[(CH_3)_2NH_2]I$ (DMAI). This compound is subsequently reacted with lead iodide by means of a mechanosynthesis process performed at room temperature, leading to the production of the desired compound.

All starting reagents, the $(CH_3)_2NH$ solution (40 wt % in H_2O), PbI₂ (99%), and the HI solution (57 wt % in H_2O) were of analytical grade from Sigma-Aldrich and used without further treatment.

First Step: Synthesis of $[(CH_3)_2NH_2]I$ (DMAI). The dimethylamine $(CH_3)_2NH$ solution in a slight excess was reacted with hydriodic acid (HI) in an ice bath. The crystallization of dimethylammonium iodide was achieved using a rotary evaporator. The obtained white microcrystals were washed with absolute diethyl ether several times and finally dried in a vacuum line overnight.

Second Step: Synthesis of $[(CH_3)_2NH_2]PbI_3$ (DMAPbI_3). The DMAPbI_3 compound, as a powder sample, was prepared by means of a mechanosynthesis method performed at room temperature. For this purpose, equimolar amounts of PbI_2 and DMAI were placed in an agate mortar and ground carefully for 15 min with a pestle until a visually homogeneous yellow powder was obtained.

Additionally, single crystals of DMAPbI₃ were also prepared. For this purpose, the previously obtained yellow powder of DMAPbI₃ was dissolved in tetrahydrofuran and yellow needle-shaped single crystals were obtained upon slow evaporation of the solvent at room temperature.

Scanning Electron Microscopy. The morphology of the asobtained samples was studied by means of scanning electron microscopy (SEM), in a JEOL 6400 microscope.

Thermal Analysis. Thermogravimetric analyses (TGAs) of the obtained polycrystalline powder were performed in TGA-DTA Thermal Analysis SDT2960 equipment. For these experiments, approximately 27 mg of sample was heated at a rate of 5 K/min from 300 to 1200 K using corundum crucibles under a flow of dry nitrogen.

Differential scanning calorimetric (DSC) analyses were performed in a TA Instruments MDSC Q-2000 instrument equipped with a liquid nitrogen cooling system by heating and cooling the sample for several cycles at a rate of 10 K/min up to 380 K under a nitrogen atmosphere.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) patterns from the obtained polycrystalline powder were recorded in a

Siemens D-5000 diffractometer using Cu K α radiation at room temperature. They were also compared with the profiles obtained from the single-crystal structure at room temperature, which were generated by Mercury version 3.5.1.³¹

Single-Crystal X-ray Diffraction. Two suitable single crystals were selected from the sample to collect diffraction data at two different temperatures, namely, 293 and 100 K, in a Bruker Kappa diffractometer equipped with an APEX II CCD detector using monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Crystals were mounted on a MiTeGen MicroMount using Paratone (Chevron Corp.). To perform these experiments, the first crystal was measured at room temperature and the second one cooled at different rates using a cold stream of nitrogen gas from an Oxford Cryostream 700 cooler. Collection, integration, and reduction of data were performed using the APEX2 V2015.9-0 (Bruker AXS, 2015) suite of software, which includes the programs reported below. The intensity integration was performed with SAINT 8.34A and corrected for Lorentz and polarization effects and also for absorption by multiscan methods on the basis of symmetry-equivalent data using either SADABS 2008/1 or TWINABS 2012/1 depending on the presence of twinning. A single lattice was found for the crystal collected at room temperature (space group $P6_3/mmc$). A second crystal was indexed measuring three runs of 80 images each at different decreasing temperatures (275, 250, 200, 150, and 100 K). A complete and highly redundant data set was collected at 100 K.

The structures were determined by the direct method using the SHELXT2014³² program and were refined by the least-squares method on SHELXL2014/7.³² The presence of multiple lattices was clear from visual inspection of diffraction images collected at low temperatures. The data set at 100 K was indexed using CELL_NOW 2008/4, producing three orientation matrices that interpret all the diffraction peaks. The integration of the reflections was performed taking into account the orientation matrices of the three twin domains simultaneously.

To refine the structures, anisotropic thermal factors were employed for the non-H atoms. For 293 K, the hydrogen atoms of the DMA cation could not be found in the Fourier map because of the disordered arrangement of this cation.

Meanwhile, for 100 K, the hydrogen atoms of the $\rm NH_2^+$ 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 refined using the riding model implemented in SHELXL2014/7.

Dielectric Properties and Impedance Spectroscopy. The complex dielectric permittivity ($\varepsilon_r = \varepsilon'_r - i\varepsilon''_r$) of the pelletized polycrystalline sample 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 10 μ Hz to 32 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 instrument incorporated to control the temperature from 100 to 350 K. The data were collected on heating and after having waited 2 min at each temperature.

Pelletized samples, made of cold-press polycrystalline powder, with an area of approximately 133 mm^2 and a thickness of approximately 0.7 mm were prepared to fit into the capacitor, and gold was sputtered on their surfaces to ensure a good electrical contact with the electrodes.

All the dielectric measurements were taken in a nitrogen atmosphere in which several cycles of vacuum and nitrogen gas were performed to ensure that the sample environment is free of water.

The impedance analysis software SMART (Solartron Analytical) was used for data acquisition and processing. Impedance complex plane plots were analyzed using the LEVM program, a particular software for complex nonlinear least-squares fitting.³³

Density Functional Theory Calculations. To investigate the minimum energy paths and the migration activation energy of ionic diffusion, DFT calculations were performed. The calculations were performed using the Vienna Ab initio Simulation Package (VASP).³⁴

Kohn–Sham equations were solved using the projector-augmentedwave (PAW) method³⁵ with the PBEsol exchange correlation functional³⁶ using the same procedure as in ref 37. Spin–orbit coupling (SOC) is not considered in these calculations. A 2 × 2 × 2 supercell (480 atoms) based on the low-temperature structure was modeled. A plane-wave cutoff energy of 600 eV, a k-point sampling at the γ point, and the PBEsol exchange correlation functional were employed. For the initial and final structure relaxation, forces were converged to <0.01 eV Å⁻¹.

Migration mediated by ion vacancies was examined using the nudged elastic band and constrained energy minimization methods;³⁴ in the latter, the migrating species is propagated along the direction of migration in a series of small steps with all unconstrained degrees of freedom relaxed at each step.

Ultraviolet–Visible (UV–vis) Spectroscopy. Optical diffusereflectance measurements of the obtained polycrystalline powder were performed at room temperature using a Jasco V-730 UV–visible double-beam spectrophotometer with a single monochromator, operating from 200 to 900 nm. BaSO₄ was used as a nonabsorbing reflectance reference. The generated reflectance versus wavelength data were used to estimate the band gap of the material by converting reflectance to absorbance data according to the Kubelka–Munk equation: $F(R) = \alpha = (1 - R)^2/2R$, where *R* is the reflectance and α values are the absorption coefficients.

RESULTS AND DISCUSSION

Synthesis and Basic Characterization. We report here a very easy and quick method for obtaining DMAPbI₃ by means of a mechanically activated solid state reaction that takes place at room temperature.

This method is much simpler than that previously reported in the literature,²³ which requires heating and preparation under a nitrogen atmosphere.

The obtained polycrystalline powder sample was a singlephase material as confirmed by comparison between the experimental PXRD patterns and the profile obtained from the single-crystal structure at room temperature (Figure S1).

It is worth noting that, different from the related MAPbI₃ compound, the DMAPbI₃ iodide studied here is stable in air for several months at least at room temperature, as confirmed by PXRD (Figure S2).

The morphology of the obtained polycrystalline sample and the single crystals was characterized by SEM. This study showed that the polycrystalline powders consist of sintered particles with an average diameter of ~2 μ m (Figure 1a), while the single crystals have a needlelike morphology with a diameter of ~150 μ m and lengths of several millimeters (Figure 1b).

In addition, the TGA results show that this compound is stable up to ~623 K (Figure S3). Above that temperature, it decomposes in two steps: in the first one (weight loss of ~28.27%), it loses the DMA cations and one of the I⁻ anions



Figure 1. SEM micrographs of (a) the obtained polycrystalline powder and (b) single crystals of $[(CH_3)_2NH_2]PbI_3$.

(per formula unit); after the second one (weight loss of \sim 71.73%) above 873 K, the compound becomes fully volatized.

Differential Scanning Calorimetry (DSC). According to the DSC results, this compound experiences a reversible phase transition just below room temperature. As shown in Figure 2, an acute endothermic peak is seen around 257 K upon heating and the corresponding exothermic peak is observed around 250 K upon cooling.



Figure 2. DSC results as a function of temperature obtained by heating and cooling the $[(CH_3)_2NH_2]PbI_3$ sample at a rate of 10 K min⁻¹.

The observed thermal hysteresis indicates the first-order character of such a phase transition, which involves an enthalpy change (ΔH) of ~2374 J mol⁻¹ (heating) to 2324 J mol⁻¹ (cooling) and an entropy change (ΔS) of ~9.2 J mol⁻¹ K⁻¹ (heating) to 9.3 J mol⁻¹ K⁻¹ (cooling), as determined from the area under the heat flow/temperature curve and the peak temperature, T_{max} .

Taking into account the fact that for an order-disorder transition $\Delta S = R \ln(N)$, where *R* is the gas constant and *N* is the ratio of the number of configurations in the disordered and ordered system, we calculated a value for *N* of ~3. This value is similar to that observed in the hybrid organic-inorganic perovskite $[(CH_3)_2NH_2][Mn(HCOO)_3]^{29}$ which also contains the DMA cation in position A, with the nitrogen atoms evenly distributed in three different positions. In any case, it should be noted that this model is oversimplified and does not take into account a number of factors, such as lattice distortions or intermolecular interactions.

Crystal Structures Determined by Single-Crystal X-ray Diffraction. The single-crystal X-ray studies reveal that this compound presents two different crystal structures above and below the transition temperature, T_t . Above that temperature (HT phase), the sample shows hexagonal symmetry, in space group $P6_3/mmc$ as previously reported.²³ Nevertheless, below T_t (LT phase), the crystal structure changes to monoclinic $P2_1/c$ down to the lowest measuring temperature, 100 K.

The crystallographic data of these two polymorphs are summarized in Table 1 and Table S1.

It is interesting to note that both polymorphs display 2Hhexagonal perovskite crystal structures (Figures 3 and 4), a polytype that, as indicated above, consists of infinite chains of face-sharing [PbI₆] octahedra running along the *c*-axis of the unit cell separated by DMA cations.

This means that in both temperature intervals the DMA cation is relatively too large and the A-X bond remains too

Table 1. Selected Bond Lengths (angstroms) for $DMAPbI_3$ at 293 and 100 K

| 293 K | | 100 K | |
|-------|-----------|----------|-----------|
| Pb-I | 3.204 (1) | Pb1-I2 | 3.106 (2) |
| | | Pb1-I3 | 3.190 (2) |
| | | Pb1–I4 | 3.165 (2) |
| | | Pb1–I3i | 3.248 (2) |
| | | Pb1–I4i | 3.272 (2) |
| | | Pb1–I2ii | 3.340 (2) |



Figure 3. Crystal structure of the $[(CH_3)_2NH_2]PbI_3$ HT phase viewed along two different orientations, where the N atoms of the DMA cations are disordered in three crystallographic positions and the Pb²⁺ cations sit at the center of the octahedra.

long, compared to the size of Pb^{2+} and I^- , and the B-X bond length leading to t > 1 and a hexagonal stacking sequence.

It is also interesting to note that this solid to solid phase transformation of the HT phase into the LT phase is reversible, although the crystal becomes twinned when it is cooled below T_{t} .

HT Phase. The structural data for this phase obtained here, which are summarized in Table 1 and Table S1 and in Figure 3, are in full agreement with those previously reported in the literature.²³

In this structure, each Pb²⁺ cation is connected to its two Pb²⁺ nearest neighbors through six iodide bridges (Figure 3) in a regular octahedral environment where the Pb–I distance is ~3.20 Å (Table 1) and the Pb²⁺ cations sit at the center of the octahedra. Most interestingly, the DMA cations are disordered with nitrogen apparently located in three different possible positions (Figure 3), as in the case of the [(CH₃)₂NH₂][M-(HCOO)₃] compounds mentioned above (with M²⁺ = Mn²⁺, Co²⁺, Ni²⁺, or Fe²⁺).^{17,29}

LT Phase. In the case of the LT phase, which we report here for the first time, the Pb^{2+} cations are no longer in a regular octahedral environment as six different Pb–I distances are detected, ranging from ~3.11 to ~3.34 Å (with three shorter Pb–I bond lengths and three longer Pb–I bond lengths) (Table 1 and Figure 4). Very interestingly, the Pb²⁺ cations are



Figure 4. Crystal structure of the $[(CH_3)_2NH_2]PbI_3$ LT phase viewed along two different orientations, where the DMA cations are cooperatively ordered and the Pb^{2+} cations show a cooperative offcenter shift.

in fact cooperatively off-center shifted toward one face of such octahedra (Figure S4). Such displacement is probably caused by the presence of their $6s^2$ 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 as is this case here.

In this context, it is worth noting that the Pb^{2+} cations in the related MAPbI₃ compound do not show signs of the stereochemically active lone pair effect. The manifestation of this latter can be rationalized through specific orbital interactions between the 6s orbital of the Pb^{2+} cation and the 5p orbitals of the I⁻ anion. Typically, the extent of this orbital mixing is low, and the $[PbI_6]$ octahedra are only minimally distorted. Exceptionally, strong orbital mixing can take place and thus activate the lone pair effect.³⁸

Therefore, the orbital mixing is stronger in the $\rm DMAPbI_3$ than in the $\rm MAPbI_3$ compound.

As a result of this distortion in the DMA compound, the $[PbI_6]$ chains become polar in DMAPbI₃, even if they are arranged antiparallel to one other in the unit cell (see below).

Additionally, in this LT phase, the DMA cations are ordered with the N atoms sitting in a single crystallographic position (Figure 4). As for the possibility that the N atoms of the DMA cations interact with the [PbI₆] chains through H-bonds, these could be of two types in view of the structural data: through linear and stronger N–H…I interactions ($d_{\rm N-I} \sim 3.11$ Å) or through bifurcated and weaker H-bonds ($d_{\rm N-I} \sim 3.25$ Å, and $d_{\rm N-I} \sim 3.32$ Å) (see Figure S5). In any case, all such

interactions are going to be very weak as the distances are larger than those normally considered for N–H…I bonds (around 2.7 Å) and also those recently reported for black formamidinium lead halide (N–H…I, 2.75–3.00 Å).³⁹

Another interesting point is the ordering of the DMA cations inside the unit cell, which is cooperative and shows an antiparallel arrangement of the polar DMA cations.

Therefore, the HT to LT phase transition experienced by this $DMAPbI_3$ compound involves two cooperative processes: an off-center shift of the Pb^{2+} cations and an order–disorder process of the polar DMA cations. This leads to a LT phase, which shows an antiferrodistortive arrangement of both the $[PbI_6]$ chains and the DMA cations.

Dielectric Properties and Impedance Spectroscopy Analysis. Figure 5 shows the temperature dependence of the



Figure 5. Temperature dependence of the dielectric constant (ε'_r) of [(CH₃)₂NH₂]PbI₃ measured at different frequencies (10–10⁵ Hz). The inset shows the frequency dependence of the dielectric constant (ε'_r) measured at different temperatures.

real part of the complex dielectric permittivity (the so-called dielectric constant, ε'_r) of DMAPbI₃ in the temperature range of 100–325 K. As one can see, two different behaviors are observed as a function of temperature. At <225 K, the dielectric constant shows a low value ($\varepsilon'_r \approx 10$), which is almost independent of temperature and frequency; meanwhile, at >225 K, ε'_r is strongly frequency dependent and increases markedly with temperature, reaching very large values at room temperature, especially at low measuring frequencies (for example, $\varepsilon'_r \approx 1000$ at 325 K for $\nu = 10$ Hz). Another interesting feature is the small kink that is observed around 260 K, close to the phase transition temperature, and detected in all the experiments performed at different measuring frequencies.

Taking into account the fact that the presence of extrinsic factors such electronic and/or ionic conductivity could result in the appearance of artifacts in the dielectric measurements, we have performed additional studies to explore further the dielectric behavior displayed by this compound. For this purpose, we have performed impedance complex plane (Z'' vs Z') analysis of the data obtained at different temperatures, as this is a very powerful tool for unraveling the dielectric response of materials.^{40,41}

Figure 6 shows typical impedance complex plane plots for this compound in the temperature interval of 100-225 K (Figure 6a) and above 225 K (Figure 6b). As one can see, in



Figure 6. Impedance complex plane plots and equivalent circuits obtained for $[(CH_3)_2NH_2]PbI_3$ at (a) 200 and (b) 300 K.

the lower-temperature interval (100–225 K), the corresponding impedance complex plane plots show a single large semiarc, which can be modeled by an equivalent circuit containing two elements connected in parallel, a resistance (R) and a capacitance (C), which is frequency independent. As this large semi-arc intercepts zero and the order of magnitude of its capacitance is on the order of picofarads per centimeter, it seems to be associated with the material bulk response. Taking into account the fact that this is the only contribution present at temperatures of \leq 225 K, in this temperature range the observed dielectric response is purely intrinsic.

On the other hand above 225 K, the impedance complex plane plots show two arcs: one larger in the low-frequency range together with a second smaller one in the high-frequency range. In this case, the large arc can be modeled by an equivalent circuit containing three elements connected in parallel: a resistance (R) and a capacitance (C), which are frequency independent, and a frequency-dependent distributed element (DE). The capacitance of the large arc is on the order of nanofarads per centimeter, typical of extrinsic contributions such as electrode effects, blocking electrodes, etc.

Meanwhile, the small arc can be modeled as a single *RC* connected in series with the circuit that describes the large arc. As this small arc intercepts zero for at 250 K, and its capacitance is lower than the values of the large arc, it seems to be associated with the material bulk response.

This means that in this higher-temperature interval the dielectric response of $DMAPbI_3$ contains both intrinsic and extrinsic contributions.

Another interesting observation is that while it is in the interval of 100–225 K this compound behaves as an insulator ($\sigma < 1$ nS/cm) and above 225 K it becomes semiconducting (i.e., $\sigma \sim 0.183 \ \mu$ S/cm for 300 K).

All these results indicate the activation of interfacial polarization effects in the DMAPbI₃ compound above 225 K, which would be related to the presence of a space charge layer at the grain boundaries and/or electrodes, and that would give rise to the very large dielectric constant values detected at room temperature.

With this knowledge in hand, another interesting question refers to the origin of a certain conductivity observed in this compound above 225 K, which in principle could be of electronic and/or ionic nature.⁴²

Nevertheless, the relatively large optical band gap shown by this compound ($E_{\rm g} \sim 2.59$ eV) (Figure S6), the value of which is in full agreement with that reported in ref 23, rules out the possibility that the observed conductivity can have an electronic origin and points more to the presence of ionic conductivity, an aspect that we have further investigated by means of DFT calculations and present in the next section.

Again with respect to the dielectric results, another interesting feature, briefly mentioned above, concerns the dielectric anomaly observed at 260 K, close to the structural phase transition T_v which is detected at all the measuring frequencies. We relate it to the cooperative antialignments of dipolar moments that take place in the LT phase and that disappear in the HT phase. As we have discussed in the previous section, the phase transition involves two cooperative antiferrodistortive processes: an off-center shift of the Pb²⁺ cations and an order—disorder process of the polar DMA cations.

In the first case, the displacement of the Pb^{2+} cation induces the appearance of electric dipoles whose arrangement along the $[PbI_6]$ chains is shown in Figure 7. As one can see, these dipoles are arranged antiparallel along the *b*-axis even if with a certain canting, so that a net dipole moment along the *c*-axis results. Nevertheless, as the unit cell comprises two chains that



Figure 7. Crystal structure of the $[(CH_3)_2NH_2]PbI_3$ LT phase where the blue arrows represent the electric dipoles of the DMA cations and the dark green arrows represent the electric dipoles induced by the offcenter shift of the Pb²⁺ cation.

are antiparallel to each other, the resulting net polarization turns out to be zero.

In addition, the order-disorder process of the polar DMA cations is also involved in the observed dielectric transition. We have to note that the polar DMA cations display an antiparallel arrangement in the LT phase (Figure 7), while these are averaged out in the disordered HT phase.

In this context, the order–disorder transition of the DMA cations resembles those observed in hybrid organic–inorganic perovskites $[(CH_3)_2NH_2][M(HCOO)_3]$ ($M^{2+} = Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, or Fe^{2+})^{17,29}$ and $[(CH_3)_2NH_2][Cd(N_3)_3]^{43}$ even if in this latter compound the DMA cations display a ferroelectric arrangement, instead of the antialignments of dipolar moments that we are reporting here for the DMAPbI₃ compound.

We should also mention that MAPbI₃ shows a similar dielectric transition related to a phase transition at 162 K.⁴⁴ In this compound, the low-temperature (<162 K) phase displays a 3D perovskite structure with orthorhombic symmetry (space group *Pnma*), where the MA cations are cooperatively ordered, while for the range of 162-330 K, MAPbI₃ displays a 3D perovskite structure with tetragonal symmetry (space group I4/ *mcm*), where the MA cations are disordered.⁴⁵ Nevertheless, in that case, the phase transition is related only to the orderdisorder process of MA cations as no distortion due to offcenter shifts of the Pb2+ cations has been reported. Another interesting remark is that in the case of the DMAPbI₃ compound studied here such structural and dielectric transitions take place at 260 K, a rather high temperature (~100 K higher) when compared to that of the MA analogue material.

DFT Calculations. To gain information about the possibility of ionic conductivity in the DMAPbI₃, we have performed DFT calculations to investigate the minimum energy paths and migration activation energy.

In this context, it is well established that the mobile ionic species in the solid state is associated with some type of vacancy or interstitial defects, the concentration of which is controlled by intrinsic Schottky and Frenkel defect reactions, non-stoichiometry, or doping.⁴ In materials with the ABX₃ perovskite-like structure, vacancy diffusion is the most common process and interstitial migration has not been observed in inorganic perovskite oxides or halides because of the lack of interstitial space in such closely packed structures.

In the case of DMAPbI₃, three vacancy diffusion mechanisms involving conventional hopping between neighboring positions were considered (Figure S7). These were (i) migration of I⁻ along one-dimensional chains of face-sharing [PbI₆] octahedra and also interchain migration (3D delocalization), (ii) migration of Pb²⁺ along one-dimensional chains of face-sharing [PbI₆] octahedra (one-dimensional delocalization), and (iii) migration of H⁺ into a neighbor DMA cation (3D delocalization). In this work, we have ruled out migration of the DMA cation because of its large size, but we suggest that the H⁺ cation can migrate because it is the smallest and because of the regular alignment of the DMA cation in the crystal structure. In this context, high proton conductivity has been reported in the porous coordination polymers⁴⁶ and metal– organic framework⁴⁶ with aligned imidazolium groups.

The obtained results give the lowest activation energy of 0.68 eV for the diffusion of iodide anions (Figure 8) and the highest activation energy of 2.35 eV for the H^+ of DMA cation. For the Pb^{2+} cations, the activation energy of 1.41 eV was obtained.



Figure 8. Energy profile of the iodide ion vacancy migration path in $[(CH_3)_2NH_2]PbI_3$ calculated via DFT with sketches about the location of the iodide ions and iodide vacancies (\Box) in scenarios A–C.

In comparison with that of the MAPbI₃ compound (Table 2), we note that the activation energy for the diffusion of the I⁻ anions is quite similar in both compounds, while the activation energy of Pb²⁺ cations is lower in the DMA than in the MA compound. We suggest that this could be related to the different crystal structures of both compounds, where the face-sharing [PbI₆] octahedra in the DMA compound favor the migration of the Pb²⁺ cations, while the corner-sharing [PbI₆] octahedra in the MA compound hinder cation migration.

Table 2. Calculated Activation Energies for Migration of I^- and Pb^{2+} in $DMAPbI_3$ and $MAPbI_3$

| | $E_{\rm a}$ (eV) for I ⁻ anion | $E_{\rm a}~({\rm eV})$ for ${\rm Pb}^{2+}$ cation |
|---------------------|---|---|
| DMAPbI ₃ | 0.68 | 1.41 |
| MAPbI ₃ | 0.58 (ref 37) | 2.31 (ref 37) |

CONCLUSIONS

We have prepared the DMAPbI₃ compound at room temperature using an easy route and mild conditions (mechanosynthesis route). Unlike the analogue MAPbI₃, the DMAPbI₃ 2H-perovskite is stable under ambient conditions for several months and starts decomposing above 623 K. From a structural point of view, DMAPbI₃ experiences a first-order transition at \approx 250 K from space group *P6*₃/*mmc* (HT phase) to space group *P2*₁/*c* (LT phase). This phase transition involves two cooperative processes: an off-center shift of the Pb²⁺ cations and an order–disorder process of the polar DMA cations.

Very interestingly, this compound shows a dielectric anomaly associated with the phase transition at 260 K. We attribute it to an antiparallel arrangement of both the polar $[PbI_6]$ chains and the polar DMA cations in the LT phase, which become apolar and disordered, respectively, in the HT phase. Additionally, this compound displays very large values of the dielectric constant at room temperature and low frequencies due to the appearance of a certain conductivity and the activation of extrinsic contributions, as demonstrated by impedance spectroscopy.

The large optical gap ($E_{\rm g} \sim 2.59$ eV) displayed by this material rules out the possibility that the observed conductivity

can be electronic and points to ionic conductivity, as confirmed by DFT calculations that have shown the minimum energy paths ($E_a = 0.68 \text{ eV}$) for the movement of the I⁻ anions.

Therefore, the replacement of the methylammonium cation with the larger dimethylammonium cation provokes important changes in the crystal, electronic structure, and properties, while the ionic conductivity of the I^- anion is maintained in both the MAPbI₃ and DMAPbI₃ compounds.

These findings allow us to gain more information about the key ingredients that give rise to the exceptional properties of the MAPbI₃ compound. For example, a 3D framework based on corner-sharing $[PbI_6]$ octahedra is essential to obtaining a semiconductor with optimal band gap and photoconductivity properties. In addition, a framework based on $[PbI_6]$ octahedra seems to favor the ionic mobility of the iodide anions, which is in turn responsible for the very large dielectric constant values displayed by the DMAPbI₃ compound at room temperature (and low frequencies).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b03095.

Thermogravimetric analysis, crystal structure details, UV–vis spectra, a Tauc plot, and vacancy diffusion mechanisms (PDF)

Crystallographic data for $[(CH_3)_2NH_2]PbI_3$ at room temperature (CIF)

Crystallographic data for $[(CH_3)_2NH_2]PbI_3$ at T = 100 K(CIF) (CIF)

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Notes

The authors declare no competing financial interest.

CCDC 1497286 and 1497287 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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