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Polar Nature of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ Perovskite-Like Hybrids

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S Supporting Information

ABSTRACT: High-quality single crystals of perovskite-like $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ hybrids have been synthesized, using a layered-solution crystal-growth technique. The large dielectric constant is strongly affected by the polar ordering of its constituents. Progressive dipolar ordering of the methylammonium cation upon cooling below 300 K gradually converts the hexagonal structure (space group $P6_3/mmc$) into a monoclinic phase ($C2/c$) at 160 K. A well-pronounced, ferroelectric phase transition at 143 K is governed by in-plane ordering of the bismuth lone pair that breaks inversion symmetry and results in a polar phase (space group $P2_1$). The dielectric constant is markedly higher in the $C2/c$ phase above this transition. Here, the bismuth lone pair is disordered in-plane, allowing the polarizability to be substantially enhanced. Density functional theory calculations estimate a large ferroelectric polarization of $7.94 \mu\text{C}/\text{cm}^2$ along the polar axis in the $P2_1$ phase. The calculated polarization has almost equal contributions of the methylammonium and Bi^{3+} lone pair, which are fairly decoupled.

INTRODUCTION

Organic/inorganic hybrid materials, and in particular $\text{CH}_3\text{NH}_3\text{PbI}_3$, have recently attracted growing attention as light-harvesting materials in solar cell devices because of their unique optical^{1,2} and excitonic^{3,4} properties and electrical⁵ and ionic conductivity.⁶ From extensive research spanning several decades, it is known that these hybrids are easy to synthesize. Because these hybrids consist of both organic and inorganic moieties that can both be tuned, substitution of either of the components yields a diverse class of structurally different materials with a wide range of functional properties.⁷ Where early interest in these hybrid materials focused on their magnetic properties,^{8,9} many other properties have since been studied, including the coexistence of ferromagnetic and ferroelectric ordering.^{10,11} Such materials could find applications in ferroelectric RAM and magnetic data storage¹² as well as have potential as electrically controlled magnetic sensors and spintronic devices for data storage.^{13,14} Recent advances have mainly focused on the photovoltaic properties and optoelectronic applications of organic/inorganic hybrids. Although a full understanding of how these materials function has not yet been achieved, it is known that efficient solar cells require an absorber material that exhibits three key attributes: excellent optical properties, charge separation, and charge transport. While various recent studies have focused on tuning of the

optical band gap,^{15–19} in this work we focus on the charge separation/transport properties. Such materials require a high dielectric constant to induce charge separation and a polar character to facilitate charge transport.²⁰ While the best-performing organic/inorganic hybrid solar cells are lead-based, substitution of lead is desired because of its toxicity.²¹ The feasibility of substituting tin for lead has been studied,^{22–24} but this has the major disadvantage that tin oxidizes easily. Tin-based devices are thus less stable than lead-based devices, and commercial applications are more difficult. Thus, a lead substitute is required that is less toxic, is stable, and has the potential for a high dielectric constant. Here we substitute bismuth for lead. Although bismuth is a heavy metal, it is considered to have a low toxic effect on the human body.^{25,26} Organic/inorganic hybrids based on trivalent bismuth are expected to exhibit semiconducting behavior and have band structures very similar to those of divalent lead-based hybrids. This is because Bi^{3+} ions are isoelectronic to Pb^{2+} , and the electronegativities and ionic radii of these elements are similar.^{27,28} Furthermore, oxide-based bismuth compounds

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Figure 1. Dielectric constant along the c axis of a single crystal $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$. (a) Dielectric constant and loss as a function of the temperature. The results are plotted for three different frequencies of 10^4 , 10^5 , and 10^6 Hz. (b) $\ln \tau$ as a function of $1/T$, demonstrating Arrhenius behavior at temperatures between 60 and 90 K.

are known to exhibit high dielectric constants.²⁹ Pioneering results by Park et al.³⁰ and Lyu et al.³¹ revealed the successful implementation of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ ^{30,31} and the fully inorganic $\text{Cs}_3\text{Bi}_2\text{I}_9$ ³⁰ in solar cell devices with efficiencies above 1%. Although the optical properties of these materials are inferior to those of the lead-based hybrids, a high dielectric constant provides an environment where defects are more effectively screened.⁷ Thus, in addition to photovoltaic devices, such high dielectric constant materials allow potential applications in other electronic devices, such as channel layers in thin-film transistors³² and gate insulators in field-effect transistors.³³ The single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ obtained in our study are stable under ambient conditions. We observe no degradation over the course of months, making these bismuth-based hybrids possible contenders for stable, lead-free electronic devices.

Our results show how trivalent bismuth alters the structure of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ from that of the divalent metal (M) hybrid perovskites $\text{CH}_3\text{NH}_3\text{MX}_3$ while maintaining striking structural similarities. Single-crystal X-ray diffraction (XRD) studies reveal that the room temperature structure is hexagonal with bismuth cations that are displaced in antipolar fashion. Gradual dipolar ordering of the methylammonium cation upon cooling yields a twinned monoclinic structure at 160 K. A well-pronounced ferroelectric phase transition at 143 K occurs, governed by in-plane ordering of the bismuth lone pair. This breaks the inversion symmetry and results in a highly twinned monoclinic polar low-temperature phase. Density functional theory (DFT) calculations show a remarkably high ferroelectric polarization of $7.94 \mu\text{C}/\text{cm}^2$ along the polar axis. The 143 K phase transition is also evidenced by differential scanning calorimetry and dielectric measurements. The dielectric constant is found to be significantly higher in the nonpolar phase. The in-plane disordering of the neighboring Bi^{3+} lone-pair electrons above 143 K significantly enhances the electric polarizability.

EXPERIMENTAL SECTION

Crystal Growth. Single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ were grown at room temperature using a modified version¹⁹ of the layered-solution approach, previously reported by Mitzi.³⁴ Here, methylamine and bismuth iodide are dissolved in separate solutions of different densities. Because of the density difference, a sharp interface is formed when the two components are brought together. As slow diffusion takes place at the interface, single crystals start to grow.

Procedure. The single crystals were synthesized by closely following the procedure described in our previous work.¹⁹ Here, 70 mg (0.12

mmol) of BiI_3 (Sigma-Aldrich; 99%) was dissolved in 3.0 mL of concentrated (57 wt %) aqueous hydriodic acid (Sigma-Aldrich; 99.95%). A total of 3.0 mL of absolute methanol (Lab-Scan; anhydrous, 99.8%) was placed on top of the orange-brown BiI_3/HI mixture, without mixing both solutions. A concentrated (33 wt %) methylamine solution in absolute alcohol (Sigma-Aldrich) was added in great excess by gently adding 15 droplets on top of the methanol layer. Small crystals were observed after 2 days and extracted after 6 days by washing three times with diethyl ether (Avantor). After drying under ambient conditions, all crystals were stored in a drybox. The high-quality crystals are intense red in color and shaped like hexagonal platelets, with the biggest crystals being around 1.7 mm across.

Dielectric Measurements. Dielectric measurements were performed using a commercial Quantum Design Physical Properties Measurement System and an Agilent E4980A Precision LCR Meter. The contacts were made by hand using 0.05-mm-diameter platinum wires connected to the crystals by silver epoxy. The contacts were made on opposite faces (ab planes) of the hexagonal platelets for measurement along the c direction. Geometrically less accurate measurements with contacts in the basal plane indicated that the anisotropy in the dielectric constant is small. The capacitance and dielectric loss were measured in the frequency range between 100 Hz and 1 MHz and the temperature range between 10 and 340 K.

DSC. DSC measurements were performed using a Netzsch DSC 204 F1 instrument with an LN2 cooling system. A platinum crucible with a pierced lid was used to measure a powder sample of 7.76 mg over a temperature range of -175 to -20 °C at a rate of 10 K/min under a 100 mL/min argon flow (99.999% purity).

Single-Crystal XRD. Single-crystal XRD measurements were performed using a Bruker D8 Venture diffractometer operating with $\text{Mo K}\alpha$ radiation and equipped with a Triumph monochromator and a Photon100 area detector. The crystals were mounted on a 0.3 mm nylon loop using cryo-oil. An Oxford Cryosystems Cryostream Plus was used for cooling the samples using a nitrogen flow. Data were processed using the Bruker Apex II software incorporating *CELL_NOW* to determine the twin domains in the monoclinic phases, and the structures were solved and refined using the *SHELX97* software.³⁵

DFT Calculations. DFT calculations were performed in order to estimate the ferroelectric polarization in $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$. The calculations were performed using the Vienna Ab initio Simulation Package³⁶ and projector augmented-wave potentials.³⁷ The energy cutoff was fixed to 500 eV and the k -point mesh to $5 \times 3 \times 2$. The Berry phase theory was used to evaluate the ferroelectric polarization.³⁸ The tools of the Bilbao Crystallographic Server³⁹ were used for symmetry analysis, such as *PseudoSymmetry*⁴⁰ and *Amplimodes* software.^{41,42}

Absorption Measurements. A fiber-optic light source (Highlight 2100, Olympus Europe) was used for the absorption measurement. The absorption spectrum of a single crystal was measured using a

Table 1. Crystallographic and Refinement Parameters of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ at 300, 160, and 100 K

$(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$				
fw (g/mol)		1656.30		
cryst size (mm^3)		$0.060 \times 0.080 \times 0.080$		
color		intense red		
wavelength (Mo $K\alpha$ radiation, Å)		0.71073		
$D(\text{calcd})$ (g/cm^3)		4.148		
$F(000)$		2800		
refinement method		full-matrix least squares on F^2 , anisotropic displacement parameters		
abs corrn		multiscan		
		300(2) K	160(2) K	100(2) K
cryst syst	hexagonal	monoclinic	monoclinic	
space group	$P6_3/mmc$ (No. 194)	$C2/c$ (No. 15)	$P2_1$ (No. 4)	
symmetry	centrosymmetric	centrosymmetric	noncentrosymmetric (polar)	
Z	2	4	4	
a (Å)	8.568(2)	8.4952(6)	8.4729(17)	
b (Å)	8.568(2)	14.7126(10)	14.663(3)	
c (Å)	21.757(7)	21.6855(14)	21.347 (4)	
α (deg)	90.0	90.0	90.0	
β (deg)	90.0	90.024(2)	90.08(3)	
γ (deg)	120.0	90.0	90.0	
volume ($\text{\AA}^3$)	1381.1(8)	2710.4(3)	2652.0(9)	
abs coeff (mm^{-1})	23.211	23.211	23.721	
min/max transmn factor	0.074/0.105	0.004/0.016	0.004/0.017	
θ range (deg)	2.75–31.02	2.77–25.31	2.76–25.91	
index ranges	$-12 < h < 12, -12 < k < 11, -31 < l < 31$	$-10 < h < 10, 0 < k < 17, 0 < l < 26$	$-10 < h < 10, -17 < k < 17, -25 < l < 25$	
data/restraints/param	857/0/15	4880/0/58	9891/0/87	
GOF on F^2	1.374	1.678	1.177	
no. of total reflns	66767	4880	9819	
no. of unique reflns	857	2491	8292	
no. of obsd reflns [$F_o > 4\sigma(F_o)$]	805	4758	7280	
$R1$ [$F_o > 4\sigma(F_o)$]	0.0515	0.0528	0.0680	
$R1$ (all data)	0.0554	0.0554	0.0921	
$wR2$ [$F_o > 4\sigma(F_o)$]	0.1184	0.1173	0.1901	
$wR2$ (all data)	0.1200	0.1198	0.2094	
largest peak and hole ($\text{e}/\text{\AA}^3$)	2.07 and -1.89	1.59 and -1.44	6.06 and -4.71	

fiber-optic spectrometer (USB2000, Ocean Optics). Briefly, the absorption was measured by differential transmission, which is defined as $-\log(T_s/T_r)$, where T_s and T_r are the light intensities with and without the crystal sample in front of the tip of the optic fiber, respectively.

RESULTS AND DISCUSSION

High-quality single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ were obtained by the layered-solution crystal-growth method. CHN elemental analysis showed the presence of 2.20 wt % C, 1.03 wt % H, and 2.81 wt % N in the structure. Combined with the Bi:I ratio and structure obtained by single-crystal XRD, this corresponds to a structural formula of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$.

In Figure 1a, we show the dielectric constant and loss along the c direction as a function of the temperature, measured on a $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ single crystal with a surface area of 0.45 mm^2 and a thickness of 0.12 mm. The dielectric constant is high, with a value of around 38 at room temperature. We observe a sharp drop in its value at 143 K by a factor of 2. The temperature dependence of the dielectric constant is independent of the frequency, evidencing a phase transition. This result is in good agreement with work by Jakubas et al.,⁴³ who assigned this transition to possible ferroelectric ordering. Below we will show that this assignment is correct and provide the structural displacements that are associated with the polar

ordering, as the change in the crystal structure at this phase transition has not previously been reported. Figure 1a also shows a dielectric loss peak at around 80 K, which shifts toward higher temperatures as the frequency is increased. This is consistent with activated behavior, but there is no crystallographic evidence that it corresponds with further structural changes. In Figure 1b, we fit $\ln \tau$ versus $1/T$ to the Arrhenius relation $\tau = \tau_0 \exp[E_a/kT]$, where τ_0 is the characteristic time constant of the relaxation, E_a the activation energy, and k the Boltzmann constant. The fit confirms thermally activated relaxation with an activation energy of 91 meV and τ_0 of $5 \times 10^{-12} \text{ s}$. We associate this behavior with polar defects,⁴⁴ which have only a small effect on the dielectric constant.

Our DSC data, shown in Figure S1, show a first-order phase transition at 143 K, which corresponds to the transition observed in Figure 1. In order to investigate the origin of the large change in the dielectric constant at this transition, we performed single-crystal XRD data on a small ($\sim 0.08 \text{ mm}$) single crystal. The arrows in Figure 1a indicate the temperatures at which we studied the crystal structure: at room temperature (300 K), just above the phase transition (160 K), and below the phase transition (100 K). The space groups and symmetries, as well as the refinement parameters, are given in Table 1. Thermal ellipsoid structure representations are given in Figure S2.

High-Temperature Phase: 300 K. The crystal structure is hexagonal with space group $P6_3/mmc$ (Figure 2). The

Figure 2. Crystal structure of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ at 300 K, space group $P6_3/mmc$: (a) ac -plane view of four unit cells; (b) ab -plane view of four unit cells (BiI_6 octahedra are shaded green); (c) $\text{Bi}_2\text{I}_9^{3-}$ dimer showing face-sharing of octahedra through linkage with three iodide ions. The bismuth cations are displaced off-center in the octahedra along the c axis, as indicated by arrows.

orientations of the methylammonium molecules are disordered, and their likely dynamic rotational motion prevents the exact determination of their positions. Therefore, the molecule is drawn in Figure 2 at the position where the highest electron density was found, likely corresponding to the center of mass. Furthermore, methylammonium is depicted as CH_3CH_3 because there is no preferential orientation of the molecule, making the carbon and nitrogen positions indistinguishable. Moreover, although the hydrogen atoms were added according to geometrical considerations using the “riding” model of the *SHELX* software,³⁵ the symmetry allows them to rotate freely around the vertical axis of the methylammonium cation. As a result, the hydrogen positions shown in Figure 2 should be considered only as illustrative.

The crystal structures of the formula $\text{R}_3\text{M}_2\text{X}_9$, with R being a small (in)organic cation, M a trivalent metal such as Sb^{3+} and Bi^{3+} , and X a halogen, were studied previously. These studies include the compounds $\text{R}_3\text{Sb}_2\text{Cl}_9$,^{45–48} $(\text{CH}_3\text{NH}_3)_3\text{Sb}_2\text{I}_9$,⁴⁹ $(\text{CH}_3\text{NH}_3)_3\text{Sb}_2\text{Br}_9$,^{50,51} $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{Br}_9$,^{51,52} and $[\text{C}(\text{NH}_2)_3]_3\text{Bi}_2\text{I}_9$.⁴⁸ The material that we discuss here, $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$, was synthesized and studied earlier by Jakubas et al.⁴³ Their XRD and pyroelectric studies suggested that this compound is isomorphous with $(\text{CH}_3\text{NH}_3)_3\text{Sb}_2\text{I}_9$ ⁴⁹ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ ⁵³ at room temperature, but no evidence was provided. This conjecture is confirmed by our single-crystal XRD data. The room temperature crystal structure is similar to the structure recently reported by Lyu et al.³¹ Our unit cell parameters are slightly larger but closely match those found by Jakubas et al.⁴³ Interestingly, $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ is related to the cubic RMX_3 hybrid perovskite structure and can be described as a hexagonal analogue. In the RMX_3 perovskite structure, the RX_3 sublattice forms a face-centered-cubic (fcc) close-packed

lattice and metal ions occupy half of the octahedral holes. The $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ structure is based on an alternative type of close packing in which the $(\text{CH}_3\text{NH}_3)_3\text{I}_9$ sublattice is stacked in the sequence ABACBC along the c direction, denoted as $(\text{hcc})_2$ using Jagodzinski–Wyckoff notation.⁵⁴ The Bi^{3+} cations occupy the octahedral sites formed by six iodide ions. Because the close-packed stacking of the sublattice is different in the fcc and hcc arrangements, the octahedral interstitial sites are connected in a different manner. The MX_6 octahedra in RMX_3 are linked by corner-sharing, while the BiI_6 octahedra in $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ are linked by face-sharing, as shown in Figure 2. Because of charge balance, the Bi^{3+} cations are found in only one-third of the octahedral holes. As a result, the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ structure consists of $\text{Bi}_2\text{I}_9^{3-}$ dimers that are face-shared through common coordination to three iodide ions. The formation of isolated $\text{Bi}_2\text{I}_9^{3-}$ dimers is frequently encountered in iodobismuthates.⁵⁵

Figure 2c shows that the bismuth ions are not positioned in the center of the octahedron formed by the six iodide ions. Because of its lone pair, the bismuth ion is displaced off-center along the c direction, as shown by the terminal Bi–I bonds of 2.9524(10) Å, which are significantly shorter than the bridging Bi–I bonds of 3.2384(10) Å. Thus, the bismuth ions move away from the shared octahedral face. This off-center displacement of the octahedrally coordinated metal ions has also been observed in isomorphous systems.^{48,53} However, the resulting electronic dipoles within each dimer point in opposite directions, giving a net zero dipole moment. Thus, the structure exhibits antipolar character.

High-Temperature Phase: 160 K. Cooling the crystal from 300 to 160 K results in crystal structure changes. As can be seen in Figure S3, extra peaks in reciprocal space appear gradually and become fully developed at 160 K. The new peaks violate the condition hhl , where $l = 2n$, which arises from the c -glide plane of the $P6_3/mmc$ structure. While it was possible to refine the inorganic sublattice with reasonable thermal displacement factors in several hexagonal space groups, the fit parameters were unexpectedly high in each case. We conclude that the hexagonal symmetry is not maintained. Moreover, several warning signs for twinning were present, including the K factor [$K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$], being systematically higher for reflections with low intensity. Taking into account possible group–subgroup relationships of space groups,⁵⁶ we investigated possible orthorhombic and monoclinic solutions and found that the best description of the crystal structure at 160 K is in the monoclinic space group $\text{C}2/c$. This structure can be obtained from the room temperature $P6_3/mmc$ structure by the following transformation: $a_m = a_h$, $b_m = a_h + 2b_h$, $c_m = c_h$. We note that the c glide in $P6_3/mmc$ is not the same as the c glide in $\text{C}2/c$. The transformation from hexagonal to monoclinic results in three twin domains, rotated by 120° because the a and b axes are interchangeable in the hexagonal phase. Furthermore, because our monoclinic unit cell was found to have $\beta \approx 90^\circ$, the diffraction pattern emulates that of an orthorhombic unit cell. This gives rise to a twin component generated by 2-fold rotation around the c axis. Because this is possible for each of the three 120° rotated twin domains, a total of six twin domains were found, connected by a 6-fold rotation around the c axis. Figure S4 illustrates how the monoclinic twin domains are related to the hexagonal phase. The essentially equal refined twin fractions of the six domains (0.15, 0.19, 0.15, 0.15, 0.20, and 0.16) strongly support this choice of structure model. Moreover, the fit parameters, as listed in Table 1, greatly improved for this multitwin structural refinement. We note that

the low-temperature crystal structure of fully inorganic $\text{Cs}_3\text{Bi}_2\text{I}_9$ was also found to exist in a twinned monoclinic $\text{C}2/c$ phase.⁵⁷ However, this is the first time that $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ has been identified in the monoclinic phase. Looking in more detail at the refined structure, we find that the driving force for the change from hexagonal to monoclinic symmetry is an induced orientation of the methylammonium cations. At 300 K, the methylammonium cations are fully disordered. At 160 K, the large refined thermal displacement factors for carbon and nitrogen indicate that the molecules retain a degree of dynamic rotation, but they obtain a preferential orientation along the b axis. Because methylammonium has a dipole moment, this preferential alignment induces distortion of the BiI_6 octahedra, as shown in Figure 3, and reduces the symmetry to monoclinic.

Figure 3. Methylammonium iodide planes of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ at 160 K, showing dipolar alignment: (a) ab -plane view of terminal iodide ions (i.e., bonded to one bismuth ion); (b) ab -plane view of bridging iodide ions (i.e., bonded to two bismuth ions). The two planes are stacked on top of each other along the c direction. The arrows indicate shifts of the iodide ions compared to the room temperature structure, creating local dipole moments aligned with those of the methylammonium cations. Linkages are drawn between the iodide ions only to indicate that they coordinate the same bismuth ion.

The refined I–I distances in Figure 3 show how the triangular faces of the BiI_6 octahedra become distorted in the monoclinic phase. Looking at Figure 3a, the I4–I6 distance shortens to create a more negatively charged region, while I5 moves away and creates a more positively charged region. The resulting electric dipoles align with the dipoles of the methylammonium cations. The ab plane in Figure 3b shows the same effect but with the dipole alignment in the opposite direction. The iodide anions in these two planes are crystallographically distinct, allowing a nonzero dipole moment within each $\text{Bi}_2\text{I}_9^{3-}$ dimer. However, the overall inversion symmetry of the structure results in the cancellation of dipole

moments between different $\text{Bi}_2\text{I}_9^{3-}$ dimers, and hence there is zero net polarization in the material. The iodide triangles within a layer are also tilted out-of-plane by $3.4\text{--}3.8^\circ$. Within the error margins of the atom positions, this can be considered as a rigid rotation of the $\text{Bi}_2\text{I}_9^{3-}$ dimers with respect to the c axis, allowed by the monoclinic symmetry, without having an impact on its properties. Thus, the crystal structure slowly evolves from a hexagonal $\text{P}6_3/\text{mmc}$ phase at 300 K to a monoclinic $\text{C}2/c$ phase at 160 K by alignment of the methylammonium cations along the b direction. Notably, Jakubas et al.⁴³ observe a second-order phase transition at 223 K. The preferential alignment of the methylammonium cation develops over such a broad temperature range that no heat effects were observed in our DSC data. The monoclinic $\text{C}2/c$ phase retains its centrosymmetry and high dielectric constant.

Low-Temperature Phase: 100 K. We determined the low-temperature phase to be monoclinic with space group $\text{P}2_1$. Figure S5 shows reciprocal lattice planes in which extra peaks appear that violate both the hkl , where $h + k = 2n$, condition for C -centering and the $h0l$, where $l = 2n$, condition for the c glide of the monoclinic $\text{C}2/c$ phase. Because $\text{P}2_1$ is noncentrosymmetric (polar), 12 twin domains are possible. Figure S6 shows the allowed peak positions for the three monoclinic domains rotated by 120° , which accounts for all of the peaks. With $\beta \approx 90^\circ$ again, the same six domains as those in $\text{C}2/c$ are allowed. Adding an inversion twin to each domain results in a total of 12 twin domains. Thus, the phase transition at 143 K represents the breaking of the inversion symmetry. The DSC data show a first-order phase transition, and thus group–subgroup relationships between the two space groups do not necessarily hold. Nevertheless, $\text{P}2_1$ is a subgroup of $\text{C}2/c$.⁵⁶

Looking more closely at the refined crystal structure, the bismuth ions are still positioned off-center along the c direction in the BiI_6 octahedra at 100 K. In $\text{P}6_3/\text{mmc}$, off-centering in the ab plane is not possible, but monoclinic symmetry allows it. In the $\text{C}2/c$ phase, it is relatively small; the bismuth ions are displaced at an angle of 5.6° with respect to the c axis. This corresponds to a displacement of 2.1 pm projected on the ab plane. A striking difference between the $\text{C}2/c$ and $\text{P}2_1$ phases is that the bismuth ions are significantly more displaced off-center in the ab plane in the $\text{P}2_1$ phase. In the $\text{C}2/c$ unit cell, all bismuth ions are crystallographically equivalent, while in the $\text{P}2_1$ unit cell, there are four inequivalent bismuth ions. These four ions are displaced at angles of 27.5° , 21.6° , 19.2° , and 8.7° with respect to the c axis. The displacements, when projected onto the ab plane, are 9.8, 6.4, 6.7, and 4.5 pm, respectively. Thus, despite the fact that the bismuth ions are crystallographically independent, all four are displaced more off-center in the ab plane at an average angle of 19.3° with respect to the c axis. In fact, their displacements in the ab plane are, on average, 3.3 times larger in the low-temperature phase. Figure 4 shows the in-plane shifts of the four crystallographically distinct bismuth ions in the four different ab planes.

Because the bismuth shifts are driven by the presence of the Bi^{3+} lone pair, this implies that the phase transition at 143 K is caused by in-plane ordering of the lone pairs, which is thus the origin of the polar nature of the material. We find that while the antipolar nature along the c axis is maintained, the phase transition is associated with a polar displacement along the b axis and an antipolar displacement along the a axis. This is of central importance for photovoltaic properties because polar regions can create internal junctions that enable charge separation.⁵⁸ These junctions can create electric fields across

Figure 4. *ab*-plane projections of crystallographically distinct BiI_6 octahedra showing the bismuth displacements. The images are in order of stacking along the *c* direction. The red arrows only indicate the direction of the bismuth displacement and not the size of the displacement. The organic cations are omitted for clarity.

the polar domains and separate the photogenerated excitons into free charges. Moreover, they assist the transport of the free charges to reduce recombination,^{20,59} which is one of the defining factors for efficient solar cells. For 180° domains, the polar regions can align in three different configurations: the polarization direction can align parallel, head-to-head, and tail-to-tail. The parallel alignment creates a neutral domain wall, whereas the head-to-head and tail-to-tail configurations create charged domain walls.⁶⁰ At head-to-head domain walls, the adjacent bound charge layers induce a buildup of positive charges and hence a divergence in the electrostatic potential. This can be compensated for by conduction of electrons along the domain wall. On the other hand, at tail-to-tail domain walls, the buildup of negative charges allows for hole conduction to occur along the domain wall.⁶¹ Thus, the different alignments of the polar regions in the material allow for selective electron and hole conduction and therefore facilitate charge separation. Methylammonium has a large built-in polarization, and the asymmetry of the organic cation can facilitate the absence of an inversion center in the structure.⁵⁸ Moreover, the lone pair of bismuth can be a driving force for structural distortion. Thus, the polar nature of organic/inorganic hybrid materials is directly influenced by their structures, and our results show how the polar nature of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ has a great impact on its dielectric properties. We show that $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ has a polar phase below the phase transition at 143 K. However, Figure 1 shows that the dielectric constant remains large, well above the transition temperature in the centrosymmetric phase. This large dielectric constant will be favorable for charge separation in applications that operate under ambient conditions, whereas charge transport would benefit from a polar phase at room temperature. Future research to increase the transition temperature of such materials would be of great interest.

Now, we evaluate the ferroelectric polarization using the Berry phase theory. Starting from the low-symmetry structure with space group $P2_1$, we consider the centrosymmetric 160 K structure with space group $C2/c$ to be the reference structure, where partial disorder of the CH_3NH_3^+ groups was neglected and replaced by a centrosymmetrically ordered arrangement of all of the organic cations in the unit cell. This allows us to have a one-to-one mapping between the $P2_1$ and $C2/c$ structures. In Figure 5, we show the evolution of polarization from the $C2/c$ to $P2_1$ structure, as a function of the normalized amplitude (λ) of atomic displacements. The total polarization arising from all

Figure 5. Total polarization (black circles) and partial contributions arising from the CH_3NH_3^+ cations (blue down-triangles) and from the $\text{Bi}_2\text{I}_9^{3-}$ framework (red up-triangles). The partial contributions are calculated while keeping the other contribution in the centrosymmetric 160 K positions. For the inorganic contributions, this means that the organic cations are considered to be antiferrodistortively arranged. The CH_3NH_3^+ and $\text{Bi}_2\text{I}_9^{3-}$ contributions represent 55% and 45% of the total polarization, respectively.

of the correlated atomic displacements sums up to $7.94 \mu\text{C}/\text{cm}^2$ along the *b* axis. The estimated value is not small, even when compared to standard inorganic ferroelectric materials such as BaTiO_3 , whose polarization is around $27 \mu\text{C}/\text{cm}^2$.⁶² In order to obtain further insight, we performed a functional polarization analysis; i.e., we disentangled the contributions coming from the CH_3NH_3^+ organic cations and the $\text{Bi}_2\text{I}_9^{3-}$ framework, abbreviated as $P(\text{CH}_3\text{NH}_3^+)$ and $P(\text{Bi}_2\text{I}_9^{3-})$, respectively. This can be done by recalculating the polarization but considering the $\text{Bi}_2\text{I}_9^{3-}$ and CH_3NH_3^+ functional groups in their respective centrosymmetric positions, while displacing all of the other atoms. In Figure 5, we show the two contributions arising from $P(\text{CH}_3\text{NH}_3^+)$ and $P(\text{Bi}_2\text{I}_9^{3-})$, which are equal to 4.51 and $3.67 \mu\text{C}/\text{cm}^2$, respectively. We first note that the two contributions sum up linearly, i.e., reproducing the total polarization arising from all of the correlated atomic displacements. This suggests that the two subsystems are fairly decoupled or weakly interacting through hydrogen bonds. Furthermore, both contributions are comparable in size. $P(\text{CH}_3\text{NH}_3^+)$ can be interpreted as originating from the dipole

of the CH_3NH_3^+ cations, slightly tilted out of the b axis, as can be seen in Figure 6.

Figure 6. Comparison between the centrosymmetric (left) and polar (right) structures. The inversion center is located at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the centrosymmetric structure. The tilting of the CH_3NH_3^+ cations and the induced distortions into the $\text{Bi}_2\text{I}_9^{3-}$ framework remove this inversion center, and a polarization along the b axis arises.

In Figure 6, we compare the centrosymmetric reference phase with respect to the lower-symmetry polar structure. The centrosymmetric structure has an inversion center located at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The CH_3NH_3^+ cations at $z = \frac{1}{2}$ and $\frac{3}{4}$ are aligned parallel to the b axis, while in the polar structure, all CH_3NH_3^+ cations are tilted with respect to the b axis, giving rise to an uncompensated dipole moment. Furthermore, the induced distortions of the $\text{Bi}_2\text{I}_9^{3-}$ framework are clearly visible in Figure 6.

The higher dielectric constant in the room temperature phase is a consequence of the ferrielectric nature of the material below 143 K. The phase transition is induced by in-plane ordering of the bismuth lone pairs. Bringing the lone pair into a specified orientation reduces its motional freedom. This reduces the polarizability, which is directly related to its dielectric response. In order to obtain charge separation in electronic devices, the Coulomb interaction between the electron–hole pair should be reduced. A higher dielectric constant of the material reduces the binding energy. While our results show that $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ has a high dielectric constant at room temperature and can be an air-stable lead-free substitute for lead-based electronic devices, device performances in solar cells are mainly limited by its optical properties. Figure S7 shows the absorption spectrum of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$, measured on a single crystal. The spectrum shows a band gap of 2.0 eV, which is slightly smaller than previously reported values of around 2.1 eV^{30,31} for thin films. Similar studies on $\text{CH}_3\text{NH}_3\text{PbI}_3$ also show a more red absorption in single crystals compared to thin films.⁶³ Furthermore, the absence of emission suggests that the band gap of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ is indirect in nature, in agreement with the DFT studies performed by Lyu et al.³¹ This may explain that the solar cell efficiencies are below 1%.³⁰ Nevertheless, we show that the decoupled ordering of the bismuth lone pair and the methylammonium dipole gives access to different functionalities associated with both polar and nonpolar states.

CONCLUSIONS

We have synthesized high-quality single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$. Dielectric measurements along the c direction show a well-pronounced phase transition at 143 K, in agreement with the literature.⁴³ At 300 K, the crystal structure is antipolar in nature, adopting the hexagonal space group $P6_3/$

mmc . This is a hexagonal analogue of the cubic RMX_3 perovskite structure. Gradual dipolar ordering of the methylammonium cations upon cooling induces distortions in the BiI_6 octahedra. This results in a monoclinic phase with space group $C2/c$ at 160 K, containing six twin domains related by a 6-fold rotation around the c axis. Below the first-order phase transition at 143 K, we find a monoclinic phase with the polar space group $P2_1$ that contains 12 twin domains. DFT calculations show a remarkably high ferroelectric polarization of $7.94 \mu\text{C}/\text{cm}^2$ along the polar axis. Notably, the dielectric constant is significantly larger in the centrosymmetric phase. Our data show that the phase transition at 143 K is governed by in-plane ordering of the bismuth lone pair. The antipolar ordering along the c axis is maintained below the transition temperature, while a polar component along the b axis and an antipolar component along the a axis arise and give rise to the observed ferrielectric ordering.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01699.

DSC data, thermal ellipsoid figures, reciprocal lattice planes, and absorption data (PDF)

Crystallographic information files of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ at 100, 160, and 300 K (CIF)

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Notes

The authors declare no competing financial interest.

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