



Article Polymorphism and Red Photoluminescence Emission from 5s² Electron Pairs of Sb(III) in a New One-Dimensional Organic–Inorganic Hybrid Based on Methylhydrazine: MHy₂SbI₅

Magdalena Rowińska ¹, Dagmara Stefańska ¹, Tamara J. Bednarchuk ¹, Jan K. Zaręba ², Ryszard Jakubas ³ and Anna Gagor ^{1,*}

- ¹ Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland; t.bednarchuk@intibs.pl (T.J.B.)
- ² Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
- ³ Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland
- * Correspondence: a.gagor@intibs.pl

Abstract: We explore the crystal structure and luminescent properties of a new 1D organic–inorganic hybrid, MHy₂SbI₅, based on methylhydrazine. The compound reveals the red photoluminescence (PL) originating from the 5s² electron pairs of Sb(III) as well as complex structural behavior. MHy₂SbI₅ crystalizes in two polymorphic forms (I and II) with distinct thermal properties and structural characteristics. Polymorph I adopts the acentric *P*2₁2₁2₁ chiral space group confirmed by SHG, and, despite a thermally activated disorder of MHy, does not show any phase transitions, while polymorph II undergoes reversible low-temperature phase transition and high-temperature reconstructive transformation to polymorph I. The crystal structures of both forms consist of 1D perovskite zig-zag chains of corner-sharing SbI₆ octahedra. The intriguing phase transition behavior of II is associated with the unstable arrangement of the [SbI₅]^{2–} $_{\infty}$ chains in the structure. The energy band gap (E_g) values, estimated based on the UV-Vis absorption spectra, indicate that both polymorphs have band gaps, with E_g values of 2.01 eV for polymorph I and 2.12 eV for polymorph II.

Keywords: methylhydrazine; red PL; organic-inorganic perovskite; phase transition; antimony iodide

1. Introduction

In recent years, there has been a significant surge of interest in organic–inorganic materials with the perovskite structure, driven particularly by the excellent photovoltaic parameters of methylammonium lead iodide (MAPI). The solar cells based on this organic–inorganic semiconductor have undergone a revolutionary transformation, increasing the efficiency of performance up to 25% within a short period [1,2]. This advancement was attributed to extensive chemical engineering through chemical substitutions, in both the molecular and inorganic parts, particularly involving halogen site mixing and co-doping with other organic cations [3–5]. In addition to their use in photovoltaics, other organic–inorganic perovskite analogues have found widespread applications in various optoelectronic devices, such as light-emitting diodes (LEDs) [6–9], photodetectors [10], and dielectric switchers [11,12]. Some of them exhibit a highly efficient multiphoton-excited photoluminescence (PL) up-conversion that makes them suitable for many important applications such as in vivo imaging or photodynamic therapy [13].

Recent reports show that lead halide perovskites and their 2D derivatives can be successfully obtained with methylhydrazinium cation (MHy) [14–17]. However, due to the larger effective ionic radius compared to other perovskites such as methylammonium (MA) or formamidinium (FA) and a large dipole moment (3.24D compared to 2.26D in MA



Citation: Rowińska, M.; Stefańska, D.; Bednarchuk, T.J.; Zaręba, J.K.; Jakubas, R.; Gagor, A. Polymorphism and Red Photoluminescence Emission from 5s² Electron Pairs of Sb(III) in a New One-Dimensional Organic–Inorganic Hybrid Based on Methylhydrazine: MHy2SbI5. *Molecules* **2024**, *29*, 455. https://doi.org/10.3390/ molecules29020455

Academic Editors: Xiaoying Huang and Kezhao Du

Received: 29 December 2023 Revised: 11 January 2024 Accepted: 12 January 2024 Published: 17 January 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and 0.22D in FA), the properties of MHy-based perovskites differ significantly from their analogs. Both MHyPbBr₃ and MHyPbCl₃ crystallize in polar $P2_1$ symmetry, and the crystal structure is built of exceptionally distorted PbX₆ octahedra. Both materials show strong second-harmonic generation activity, one-photon photoluminescence and two-photon upconversion photoluminescence. MHy also acts as a spacer in 2D (layered) perovskites, where it prompts room-temperature ferroelectric and low-temperature polar long-range order in MHy₂PbBr₄ and MHy₂PbCl₄, respectively. Thus, MHy-molecular ions have high potential for symmetry breaking, which in addition to photovoltaic and light-emitting properties should also lead to attractive nonlinear optical (NLO), piezo-, pyro- and ferroelectric properties. It is worth mentioning that the smallest separation distance between the $[PbI_4]^{2-\infty}$ layers in MHy₂PbI₄ exhibited an exceptionally small bandgap (2.20 eV) and significantly reduced the dielectric confinement. Recently, MHy was employed as a perovskite in the construction of a polar multilayer hybrid perovskite, (IBA)₂MHy₂Pb₃Br₁₀ [18].

This brief survey demonstrates that MHy-based 3D and 2D perovskites exhibit intriguing properties that are quite different from properties of known analogs crystallizing with small polar amines. We thus aim to extend studies on other MHy-inorganic compounds, as they are still not recognized well. It is noteworthy that the first methylhydrazinium lead halide (MHy₂PbI₄) was reported in 2019 [17]. Since then, MHy has proven its ability for creating strong hydrogen bonds with halide acceptors that lead to distortions of the inorganic framework and play a major role in polar ordering.

A significant drawback hindering the large-scale commercialization of lead halides is the presence of lead in their structure. Simultaneously, intensive research efforts are underway to explore alternatives that do not contain lead and have a smaller negative impact on the environment [19–21]. One way is the substitution for lead by other elements including Ge(II), Cu(II), Sb(III) or Bi(III), which lead to structures of lower dimensionality. They can adopt either a zero-dimensional (0D) structure containing isolated octahedra [22], $(M_2X_9)^{3-}$ dimer units [23] or 1D chains [24–29]. Among these, there is particular interest in bismuth and antimony iodide-based compounds, primarily due to the potential semiconducting properties of the inorganic skeleton and the diverse range of structures exhibited by these systems, especially those characterized by acentric phases [30–35].

The presence of a lone $5s^2$ electron pair in the electronic configuration of Sb(III) and a lone $6s^2$ electron pair in Bi(III) can induce pronounced structural distortions, giving rise to electronic states that reside high in the valence band, shaping the electronic properties of these hybrids [36,37]. A lot of reports show that structural distortions and the dimensionality of the inorganic part are closely related to the photoluminescence of organic–inorganic halides. Weak deformations result in narrow PL bands and small Stokes shifts. Large structural distortions imply red-shifted and broad PL bands and large Stokes shifts. On the other hand, existing literature data on the key optoelectronic (exciton-binding energies, charge-carrier mobilities) and PL properties of organic–inorganic halides clearly indicate the importance of dynamics of the organic spacers in these systems [29,30].

The stereo-active effects in light-emitting 0D 5s² lone pair materials have been summarized in [38]. The luminescent properties of Sb(III)-based halides have been reported mostly for materials with 0D [SbCl₅]²⁻ square pyramidal units isolated by large organic cations [39–41], but also for octahedral or polynuclear octahedral units [42,43]. However, less active lone pairs in MX₆ octahedra also exhibit the tendency towards off-center displacements and dynamic distortions. Luminescent MI₆ and MBr₆ octahedra have mainly been found for Sn(II) halides [44]. RT PL has also been reported for [Sb₂I₉]³⁻ dimers in Cs₃Sb₂I₉, but with rather weak emission intensity [45].

In contrast to 0D discrete polyhedral units, the luminescent properties of 1D polymeric halides remain poorly understood, even though some of them exhibit efficient emissions [46]. This work constitutes another contribution to fill this gap. We delve into the connections between structure and properties that govern the performance of onedimensional, emissive $5s^2$ MHy-based antimony(III) iodides with extended 1D zig-zag chains of corner-sharing SbI₆ octahedra. Hybrids with the general formula R₂SbI₅ have already garnered significant attention from scientists as potential functional materials. This is owing to their outstanding properties, which include a strong second harmonic generation (SHG) response [32,47,48], ferroelectricity [48,49], a small bandgap with strong absorption ability [31,33,34,48–52], switchable dielectric properties [53] and excellent thermal stability [31]. Herein, we show the crystal structure and temperature behavior of two new polymorphic forms, temperature dependent structural phase transitions, thermal characteristics as well as luminescent properties.

2. Results

2.1. Thermal Properties of MHy₂SbI₅

The single crystals of MHy₂SbI₅ crystallize in two polymorphic forms, orthorhombic I and monoclinic II. Polymorph I is stable and does not undergo temperature-induced phase transitions, while polymorph II undergoes a reversible phase transition, manifested by endothermic/exothermic peaks at 222 K/227 K during the cooling/heating runs on the differential scanning calorimetry curves (DSC). The phase transition is of a first-order character with a thermal hysteresis of 5 K and a discontinues volume change of approximately 60 Å³. Figure 1 depicts DSC runs along with the volume change measured during cooling for both polymorphs. Above 370 K, polymorph II undergoes a reconstructive phase transition, transforming into polymorph I. The low-temperature phase transition in polymorph II is also confirmed by an anomaly in the electric permittivity. Figure S1a,b in the Supplementary Information File (SI) displays the temperature dependence of the real ε' (a) and imaginary ε'' (b) parts of the dielectric permittivity at various frequencies. The weak anomaly around 230 K (on heating) corresponds to the phase transition observed in the DSC. The abrupt changes in lattice parameters (Figure S1c,d) confirm a first order character of this transformation.



Figure 1. DCS curves (blue-cooling, red-heating) and the volume changes with cooling for polymorph **I** (**a**,**b**) and polymorph **II** (**c**,**d**). In (**b**,**d**) the lines are the guides for the eyes.

Both polymorphic forms have the same organic–inorganic one-dimensional (1D) perovskite structure built of $[SbI_5]^{2-}_{\infty}$ zig-zag chains of corner-sharing SbI₆ octahedra. Polymorph I crystallizes in orthorhombic, acentric $P2_12_12_1$ symmetry, as confirmed by the second-harmonic generation (SHG); refer to Figure S2 in SI. It may seem that this is another example of a structure in which the presence of MHy enforces an acentric arrangement of atoms. However, upon comparing the data on structures with the A₂SbI₅ stoichiometry it can be observed that the majority of them crystallize in non-centrosymmetric or polar space groups [26,51,52]. Hence, the absence of a center of symmetry in polymorph I should be attributed to the unique properties of this specific stoichiometry.

Polymorph **II** adopts a centrosymmetric, monoclinic structure with the $P2_1/n$ space group, and its unit cell is a $2c_{ortho}$ superstructure of polymorph **I**. Detailed information regarding the basic structural parameters of both crystals, data collection and refinement results obtained by single-crystal X-ray diffraction are presented in Table 1.

Table 1.	Crystal da	ta, collectior	n and refinen	nent results	for M	1Hy ₂ SbI ₅ .
----------	------------	----------------	---------------	--------------	-------	-------------------------------------

Crystal Data	Polymorph I		Polymorph II		
Chemical Formula	(CN ₂ H ₇) ₂ [SbI ₅]				
Molecular weight (Formula mass/g·mol ⁻¹)	836.31	836.31	836.31	836.31	
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_1/n$	$P2_{1}2_{1}2_{1}$	
Temperature (K)	100	295	290	365	
a [Å]	8.901 (3)	8.835 (3)	8.648 (3)	8.737 (3)	
b [Å]	10.291 (4)	10.550 (4)	37.271 (9)	10.689 (4)	
<i>c</i> [Å]	18.004 (5)	18.395 (5)	10.668 (4)	18.754 (5)	
$V[Å^3]$	1649.2 (10)	1714.6 (10)	3437.7 (19)	1751.4 (10)	
β [0]			91.32 (3)		
Z	4	4	8	4	
Data collection					
No of management in doman dant abcomund	12,731,	15,315,	57,907,	15,653,	
$[I > 2\pi(I)]$ reflections	3129,	3244,	8809,	3325,	
[1 > 20(1)] reflections	3018	2913	5784	1711	
R_{int}	0.027	0.025	0.035	0.057	
Refinement					
$\mathbf{R}[F^2 > 2\sigma(F^2)],$	0.032	0.028	0.035	0.048	
$wR(F^2)$, S	0.079, 1.08	0.064, 1.05	0.087, 1.05	0.157, 1.02	
Δ ρmax, Δ ρmin (e Å ⁻³)	2.39, -1.52	0.82, -0.77	0.99, -0.86	0.92, -0.85	
Turin milin mut	Refined as an				
I win rennement	inversion twin				
Absolute structure parameter	0.38 (14)	0.43 (13)		0.34 (12)	

In polymorph **I**, the asymmetric unit consists of two disordered protonated methylhydrazinium cations and the SbI_5^{2-} anion (Figure S3), which forms a one-dimensional zig-zag chain through corner-sharing SbI_6^{3-} octahedra. In polymorph **II**, the asymmetric unit comprises four protonated MHy cations and two inorganic SbI_5^{2-} anions (Figure S4). Two MHy cations are disordered over two positions, with occupancies of 0.75/0.25 and 0.62/0.38, while the third one is disordered over three positions.

In organic–inorganic hybrids, the order–disorder processes of the molecular part are usually the main driving forces for the phase transitions and structural distortions of inorganic substructures. In MHy₂SbI₅, in **I**, the ordering of MHy with temperature lowering does not bring about any important changes in the skeleton. The volume of the unit cell experiences normal, positive thermal expansion; the distortion parameters for the octahedra (calculated in Vesta [54]) change only slightly. The bond length distortion is very similar, with 0.045 at 295 K and 0.042 at 100 K, whereas the angle variance increases slightly after cooling from 2.8 deg.² to 4.4 deg.². Both MHy cations are ordered at 100 K and interact

through the N–H…N hydrogen bond with a N…N distance of 3.08(2) Å, and weak N–H…I hydrogen bonds with the iodine acceptors, with a minimum N…I distance of 3.51(2) Å.

In contrast to polymorph I, polymorph II undergoes transformations during both cooling and heating. At low temperatures, around 225 K, a phase transition occurs, associated with a lowering of symmetry, manifested by a complex diffraction pattern characteristic of pseudo-merohedral twining. It likely involves a symmetry reduction to the triclinic system and thus, due to the overlap of diffraction peaks, we were unable to determine the crystal structure of this phase. Moreover, upon heating to a temperature of ~370 K, a reconstructive phase transition occurs in which polymorph II transforms into an orthorhombic non-centrosymmetric form with a reduced unit cell, characteristic of polymorph I. The single-crystal diffraction data collected at 365 K, after cooling the crystal from 370 K, and the SHG signal which appears at high temperatures after $P2_1/n \rightarrow P2_12_12_1$ transition (shown Figure S2 in SI) constitute direct evidence of this transformation. This intriguing behavior of II arises from the arrangement of $[SbI_5]^{2-}_{\infty}$ chains in the crystal structure.

Both crystal structures essentially differ in the distribution of the 1D chains in the space. In the thermally stable polymorph I, the chains align in a herringbone-like configuration, ensuring optimal distances between neighboring chains. At room temperature, the shortest distances between chains are of 8.42 Å. In polymorph II, the arrangement of chains is different; there are two distinct alignments of chains, herringbone and nearly parallel. In the parallel configuration, the shortest distances between planes are equal to 7.74 Å, which stays at the origin of the structural instability of this form. Such a short distance between the chains is the shortest observed in the family of A_2SbI_5 . Figure 2 illustrates the arrangements of the crystal structure in both polymorphic forms and Sb–I distances.



(a) Polymorph I, orthorhombic $P2_12_12_1$ (b) Polymorph II, monoclinic $P2_1/n$

Figure 2. The crystal structure of orthorhombic polymorph I with acentric $P2_12_12_1$ symmetry and monoclinic, centrosymmetric $P2_1/n$ polymorph II: (**a**,**b**) the packing of the inorganic part along a_{ortho} , where herringbone and parallel motifs are highlighted by arrows; (**c**,**d**) $[\text{SbI}_5]^{2-}$ chains of corner-sharing octahedra in both I and II, with dissimilar structural motifs marked in blue; (**e**,**f**) the Sb–I bond lengths in both forms, with independent atoms drawn with front ellipsoids.

The arrangement of chains in the structure and associated with the packing disorder of MHy cations seem to be the crucial differences between both polymorphic forms. The geometry of the chains in both I and II does not differ significantly from each other. Figures S5 and S6 in SI show the details of $[SbI_5]^{2-}$ chains for both polymorphs. The local symmetry of antimony ions is the lowest possible, C_1 , both in I and II. In I there is one inequivalent Sb(1) position, whereas in II there are two independent Sb(1) and Sb(2) atomic sites. The Sb-I distances at room temperature in I are distributed within 2.87–3.24 Å, whereas in II they are within 2.86–3.27 Å; the Sb–I–Sb angles between neighboring octahedra are equal to 174 deg. in I, whereas they range from 170 to 171 in II.

2.3. Luminescence Properties

The room temperature absorption spectra of both orthorhombic polymorph I and monoclinic polymorph II of 1D MHy₂SbI₅ cover the entire UV-Vis range up to 650 nm (Figure S7). Based on the reflectance spectrum, the energy band gap (E_g) can be estimated using the Kubelka–Munk relation, also called remission function [55]:

$$F(R) = \frac{(1-R)^2}{2R}$$
(1)

where *R* is reflectance. However, the modification proposed by Tauc allows the determination of E_g through the graphical examination of the function [56]:

$$\left[F(R \cdot hv)\right]^n = B\left(hv - E_g\right) \tag{2}$$

where *h* is the Planck constant, *v* denotes the photon's frequency, and *B* is a constant. The value of the *n* factor depends on the type of electron transition and equals 1/2 or 2 for direct and indirect transition band gaps, respectively [57,58] (Figures S8 and S9). Assuming that both polymorphs have a direct band gap, as indicated by many examples in the literature [38,59], the band gap values are comparable and equal 2.01 eV for orthorhombic polymorph I and 2.12 eV for the monoclinic polymorph II. The obtained values are also in good agreement with the E_g of the low-dimensional hybrid halides based on Sb(III) [38,45,59–61].

The emission spectra recorded at 80 K are presented in Figure 3a. Both polymorphs exhibit broad emission spectra ranging from 625 nm to 1000 nm, associated with the active lone pair of $5s^2$ of Sb(III) ions (Figure 3c). Upon excitation by the 375 nm line, the electron is transferred to the ${}^{3}P_{2}$ excited state of Sb(III) ions. Due to the small energy separation between ${}^{3}P_{J}$ states, energy can be easily transferred to these levels. As a result, a broad luminescence band with FWHM of 0.34 eV and a large Stokes shift of around 1.57 eV is visible. Similar types of emission have been reported recently for other low-dimensional halides with antimony ions [38,45,59]. The shape as well as the position of the band maximum (713 nm) do not change with the crystal structure. Both MHy₂SbI₅ samples have red emission with x, y coordinates of 0.688 and 0.309 (Figure 3b).

The lack of dependence of PL emission on the crystal structure confirms the slight differences in the antimony ion environment in both polymorphs described in the previous chapter. The octahedral distortion parameters collected in Table 2 show only minor changes in the coordination sphere of antimony in both polymorphs and their temperature-activated modifications. It is worth noting that direct antimony coordination is crucial from the perspective of energy transfer in these compounds. The activity of the 5s² lone electron pair in the octahedral environment of antimony ions manifests in the off-center displacement of Sb ions from the symmetry center. In both compounds, the shifts are small, around 0.17 Å in I and 0.13 Å in II at room temperature. The large displacement parameters in both antimony and iodide positions suggest dynamic changes in the geometry around the antimony ion and thus dynamic changes of the stereo-activity of 5s². With temperature lowering, the off-center displacement of Sb is smaller compared to room temperature (equal

to 0.09 in I at 100K), which means that instability and dynamic changes associated with thermally activated atom vibrations impact the ability to effectively transfer energy, which, in turn, affects light emission in the PL process.

Table 2. Octahedral distortion parameters in both I and II calculated in Vesta [54].

	Polymorph I		Polymorph II	
Temperature	100 K	295 K	290 K	365 K
Average bond length (Å)	3.024	3.039	3.041	3.050
Polyhedral volume (Å ³)	36.81	37.39	37.42	37.75
Distortion index (bond length)	0.041	0.045	0.047	0.052
Bond angle variance (deg. ²)	4.38	2.78	6.61	6.41



Figure 3. (a) Comparison of the emission spectra of MHy_2SbI_5 samples recorded at 80 K, (b) CIE diagram showing *x*, *y* coordinates, and (c) simple energy level diagram of Sb(III) ions.

The temperature-dependent emission spectra of investigated samples were recorded every 5 K (Figure 4). As shown, the intensity of the emission significantly decreases with temperature, but the shape, as well as the band position, do not change (Figure S10). The emission is not very stable, and the temperature quenching $T_{0.5}$ is 96 K and 99 K for MHy₂SbI₅ polymorphs I and II, respectively. The energy activation for thermal quenching calculated using the Boltzmann function equals 79 meV and 60 meV for polymorphs I and II, respectively (Figures S11 and S12).



Figure 4. Temperature-dependent emission spectra and intensity contour maps of (**a**) MHy₂SbI₅, $P2_12_12_1$, polymorph I and (**b**) MHy₂SbI₅, $P2_1/n$, polymorph II.

3. Conclusions

In this study, we investigate the properties of a new 1D organic–inorganic hybrid compound, MHy₂SbI₅, with a focus on its crystal structure and luminescent behavior. This hybrid material crystallizes in two polymorphic forms (I and II), exhibiting distinct thermal and structural characteristics. Polymorph I adopts an acentric $P2_12_12_1$ chiral space group and remains stable without temperature-induced phase transitions. In contrast, polymorph II undergoes a reversible low-temperature phase transition and a high-temperature reconstructive transformation to polymorph I. Both crystal structures consist of 1D perovskite zig-zag chains of corner-sharing SbI₆ octahedra. The structural differences between them are attributed to the spatial arrangement of $[SbI_5]^{2-}_{\infty}$ chains in the crystal structure.

The luminescent properties of both polymorphs are characterized by a red photoluminescence (PL) originating from the $5s^2$ electron pairs of Sb(III) ions. The emission spectra recorded at 80 K show broad emission bands ranging from 625 nm to 1000 nm. The energy band gap (Eg) values, estimated based on the UV-Vis absorption spectra, indicate that both polymorphs have direct band gaps, with Eg values of 2.01 eV and 2.12 eV for polymorph I and II, respectively. Interestingly, the lack of dependence of PL emission on the crystal structure suggests only slight differences in the antimony(III) ion environment in both polymorphs. The octahedral distortion parameters show minor changes in the coordination sphere of antimony(III) in both polymorphs and their temperature-activated modifications.

In summary, the study provides insights into the structural and luminescent characteristics of the new organic–inorganic MHy₂SbI₅ with a 1D polymeric arrangement of antimony iodide complex ions, filling a gap in PL research in this class of materials and contributing to the understanding of structure-property relations in lead-free 1D perovskites.

4. Experimental Details

4.1. Synthesis

All materials needed for the synthesis of [NH₂-NH₂-CH₃]₂SbI₅ (MHIA-I) and [NH₂-NH₂-CH₃]₂SbI₅ (MHIA-II) were purchased from commercial sources (Sigma-Aldrich and

Merck (HI)) and used without further purification: [NH₂-NH₂-CH₃] (98%), SbI3 (>99.998%), HI (57%). The crystals were grown by a slow evaporation of a concentrated HI solution containing the 2:1 ratio of [NH₂-NH₂-CH₃] and SbI₃. The salts obtained were twice recrystallized from a methanol solution and their composition was verified by an elemental analysis: MHIA-I (C: 2.80 (theor. 2.82%), N: 6.52% (theor. 6.59%), H: 1.72% (theor. 1.66%) and MHIA-II (C: 2.73 (theor. 2.82%), N: 6.55% (theor. 6.59%), H: 1.70% (theor. 1.66%). The single crystals suitable for X-ray measurements were grown from an aqueous solution at a constant room temperature. Interestingly, modifications I and II of the MHy₂SbI₅ derivative were found to crystallize simultaneously from the methanol solution. Both polymorphs are dark red (burgundy) in color and crystallize in the form of well-shaped rhombohedrons. In addition to single-crystal X-ray diffraction measurements, absorption and emission measurements were conducted on single crystals verified by diffraction and subsequently powdered. A similar methodology was chosen for DSC and BDS measurements; however, due to the larger amount of material needed for the experiment, the possibility of mixing both phases must be considered.

4.2. Single-Crystal X-Ray Diffraction

Single-crystal X-ray diffraction measurements were obtained using the Oxford Diffraction Xcalibur four-circle diffractometer, which operates with an Atlas CCD detector and graphite-monochromated Mo K α radiation. The absorption correction was performed using the multiscan method in CrysAlis PRO 1.171.39.46 (Rigaku Oxford Diffraction, 2018). The solution and refinement of the crystal structure were carried out in Olex2 1.5 [62]. SHELXT [63]; SHELXL [64]. The diffraction from two polymorphic forms was collected at 100 K, 295 K (orthorhombic, polymorph I) and 290 K, 365 K for monoclinic, polymorph II. All structures were deposited in the CCDC database, with 2322356, 2322357, 2322359 and 2322360 accession numbers. The detailed experimental and geometric parameters are given in Table S1 and S2 in the Supplementary Information File (SI).

The single-crystal structures of polymorph I were determined at 295 K and 100 K, revealing that it belongs to an orthorhombic system with a chiral space group $P2_12_12_1$. The crystal structure of polymorph I was refined as a two-component inversion twin, with a refined twin component ratio of 0.6:0.4 at 295 K and 100 K. At 295 K, two crystallographically independent MHy cations are observed, both exhibiting disorder. The first is disordered in two positions with an occupancy ratio of 0.7:0.3, while the second one is disordered in two equivalent positions (0.5:0.5 occupancy ratio) and refined isotropically. While no phase transition was observed in polymorph I, cooling the crystal to 100 K revealed alterations in the organic part of the crystal structure. Both Mhy cations order and occupy one position in the structure with full occupancy. During the structural refinement of polymorph I, SHELXL restraint instructions (SADI, SIMU, DFIX) were used to manage disordered moieties.

Polymorph II crystallizes in the centrosymmetric monoclinic $P2_1/n$ space group. In the room-temperature phase, all four symmetry-independent MHy cations exhibit disorder, with two of them being disordered over two positions, having occupancies of 0.75(2) and 0.25(2), and 0.62(3) and 0.38(3), respectively. SADI restraints were employed to appropriately model the disordered cationic moiety. The atoms of the minor orientation were refined isotropically. The third and fourth organic moieties were refined only isotropically, and the disorder in the latter cation was modeled using a three-site model. In the high-temperature phase of polymorph II, two independent cations were disordered within equivalent positions. Refinement was conducted with SADI, SIMU and DFIX restraint to control disordered moieties. Due to the heavy twinning of polymorph II below 220 K, the single-crystal X-ray diffraction for the low-temperature phase experiment did not yield sufficient data for structure solution.

4.3. Thermal Analysis

DSC measurements were conducted using a Metler Toledo DSC 3 instrument. Polycrystalline samples were cooled and heated in the range of 120 K–360 K; ramp rate was 10 K/min.

4.4. Electrical Measurements

Electrical measurements were performed for polycrystalline samples in the temperature range of 180 K–300 K. The samples were painted with silver-conductive paint. Agilent E4980A Precision LCR Meter in the frequency range of 135 Hz–2 MHz was used. Temperature was stabilized and controlled by an INSTEC STC200. The procedures were carried out in a controlled nitrogen atmosphere.

4.5. Optical Measurements

The room temperature absorption spectra of the powdered samples were measured by using a Varian Cary 5E UV–Vis–NIR spectrophotometer (Varian, Palo Alto, CA, USA). Emission spectra at different temperatures under 375 nm excitation from a laser diode were measured with the Hamamatsu photonic multichannel analyzer PMA-12, equipped with a BT-CCD linear image sensor (Hamamatsu Photonics, Iwata, Japan). The temperature of the samples was controlled by using a Linkam THMS 600 Heating/Freezing Stage (Linkam, Tadworth, UK).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules29020455/s1, Figure S1: Temperature dependence of the real $\varepsilon'(\mathbf{a})$ and imaginary ε'' part (**b**) of the complex electric permittivity measured for the polymorph II in heating cycle; (c,d) thermal evolution of lattice parameters in polymorph II with cooling; Figure S2: (a) Second harmonic generation (SHG)-temperature dependence for Polymorph I; (b) SHG signal appears after the reconstructive phase transition from centrosymmetric polymorph II to non-centrosymmetric polymorph I, (c) the SHG signal from polymorph I at room temperature in relation to KDP. Figure S3: The independent parts of Polymorph I in 100 K (a) and 295 K (b). Displacement ellipsoids are drawn at the 50% and 30% probability levels for 100 K and 295 K, respectively. [Symmetry codes: (i) 1/2 + x, 3/2 - y, 1 - z]; Figure S4: The independent part of polymorph II is shown in 290 K (a) in the monoclinic phase $P2_1/n$ and at 365 K (b) in the orthorhombic phase $P2_12_12_1$. Displacement ellipsoids are drawn at the 30% probability levels. [Symmetry codes: (*i*, a) -1 + x, *y*, *z*; (*i*, b); -1/2 + x, 1/2 - y, 1 - z]; Figure S5: A view of the inorganic chains in the crystal structure of polymorph I along *a*-axis in 295 K (a) and 100 K (b); Figure S6: A view of the inorganic chains in the crystal structure of polymorph II along *a*-axis in 295 K (a) and 365 K (b); Figure S7: Diffuse reflectance spectra of investigated hybrid 1D MHy₂SbI₅ perovskites; Figure S8: Energy band gap of the $MHy_2SbI_5 P2_1/n$ crystals; Figure S9: Energy band gap of the MHy₂SbI₅ P2₁2₁2₁ crystals; Figure S10: Integrated intensity in function of temperature of the investigated hybrid 1D MHy₂SbI₅ perovskites; Figure S11: Energy activation for the thermal quenching of the MHy₂SbI₅ P2₁2₁2₁ crystals; Figure S12: Energy activation for the thermal quenching of the MHy₂SbI₅ $P2_1/n$ crystals; Table S1: Selected geometric parameters (Å, °) for polymorph I; Table S2: Selected geometric parameters (Å, °) for polymorph II. Table S3: Crystal data, collection and refinement results for (MHy)₂[SbI₅].

Author Contributions: Conceptualization, A.G. and R.J.; validation, M.R., A.G. and R.J.; investigation, M.R., A.G., T.J.B., D.S., J.K.Z. and R.J.; data curation, M.R.; writing—original draft preparation, M.R., D.S. and A.G.; writing—review and editing, A.G. and R.J.; visualization, T.J.B., D.S. and A.G.; supervision A.G.; project administration, A.G.; funding acquisition, A.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Science Centre, Poland, grant number 2021/43/B/ST5/01172. For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Experimental data will be available at https://doi.org/10.5281/zenodo. 10471676 accessed on 16 January 2024. Crystal structures have been deposited in CCDC with numbers 2249176, 2249177 and 2249178.

Conflicts of Interest: The authors declare no competing financial interests.

References

- Liu, M.; Johnston, M.B.; Snaith, H.J. Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* 2013, 501, 395–398. [CrossRef] [PubMed]
- Yoo, J.J.; Seo, G.; Chua, M.R.; Gwan Park, T.; Lu, Y.; Rotermund, F.; Kim, Y.-K.; Su Moon, C.; Joong Jeon, N.; Correa-Baena, J.-P.; et al. Efficient Perovskite Solar Cells via Improved Carrier Management. *Nature* 2021, 590, 587–593. [CrossRef] [PubMed]
- 3. Jeong, J.; Kim, M.; Seo, J.; Lu, H.; Ahlawat, P.; Mishra, A.; Yang, Y.; Hope, M.A.; Eickemeyer, F.T.; Kim, M.; et al. Pseudo-Halide Anion Engineering for α-FAPbI 3 Perovskite Solar Cells. *Nature* **2021**, *592*, 381. [CrossRef]
- 4. Zhou, Y.; Zhou, Z.; Chen, M.; Zong, Y.; Huang, J.; Pang, S.; Padture, N.P. Doping and Alloying for Improved Perovskite Solar Cells. J. Mater. Chem. A 2016, 4, 17623. [CrossRef]
- 5. Ono, L.K.; Juarez-Perez, E.J.; Qi, Y. Progress on Perovskite Materials and Solar Cells with Mixed Cations and Halide Anions. ACS Appl. Mater. Interfaces 2017, 9, 30197–30246. [CrossRef] [PubMed]
- 6. Shang, Y.; Liao, Y.; Wei, Q.; Wang, Z.; Xiang, B.; Ke, Y.; Liu, W.; Ning, Z. Highly Stable Hybrid Perovskite Light-Emitting Diodes Based on Dion-Jacobson Structure. *Sci. Adv.* **2019**, *5*, 8072–8088. [CrossRef]
- 7. Gao, X.; Zhang, X.; Yin, W.; Wang, H.; Hu, Y.; Zhang, Q.; Shi, Z.; Colvin, V.L.; Yu, W.W.; Zhang, Y. Ruddlesden–Popper Perovskites: Synthesis and Optical Properties for Optoelectronic Applications. *Adv. Sci.* **2019**, *6*, 1900941. [CrossRef]
- 8. Cortecchia, D.; Yin, J.; Petrozza, A.; Soci, C. White Light Emission in Low-Dimensional Perovskites. J. Mater. Chem. C 2019, 7, 4956. [CrossRef]
- 9. Kim, Y.H.; Cho, H.; Lee, T.W. Metal Halide Perovskite Light Emitters. *Proc. Natl. Acad. Sci. USA* 2016, 113, 11694–11702. [CrossRef]
- 10. Wang, Y.; Song, L.; Chen, Y.; Huang, W. Emerging New-Generation Photodetectors Based on Low-Dimensional Halide Perovskites. *ACS Photonics* **2020**, *7*, 10–28. [CrossRef]
- 11. Lun, M.-M.; Zhou, F.-L.; Fu, D.-W.; Ye, Q. Multi-Functional Hybrid Perovskites with Triple-Channel Switches and Optical Properties. *J. Mater. Chem. C* 2022, *10*, 11371–11378. [CrossRef]
- 12. Li, H.-J.; Liu, Y.-L.; Chen, X.-G.; Gao, J.-X.; Wang, Z.-X.; Liao, W.-Q. High-Temperature Dielectric Switching and Photoluminescence in a Corrugated Lead Bromide Layer Hybrid Perovskite Semiconductor. *Inorg. Chem.* **2019**, *58*, 10357–10363. [CrossRef]
- Chen, W.; Bhaumik, S.; Veldhuis, S.A.; Xing, G.; Xu, Q.; Grätzel, M.; Mhaisalkar, S.; Mathews, N.; Sum, T.C. Giant Five-Photon Absorption from Multidimensional Core-Shell Halide Perovskite Colloidal Nanocrystals. *Nat. Commun.* 2017, *8*, 15198. [CrossRef] [PubMed]
- Mączka, M.; Ptak, M.; Gagor, A.; Stefańska, D.; Zaręba, J.K.; Sieradzki, A. Methylhydrazinium Lead Bromide: Noncentrosymmetric Three-Dimensional Perovskite with Exceptionally Large Framework Distortion and Green Photoluminescence. *Chem. Mater.* 2020, 32, 1667–1673. [CrossRef]
- 15. Mączka, M.; Gagor, A.; Zaręba, J.K.; Stefanska, D.; Drozd, M.; Balciunas, S.; Šimėnas, M.; Banys, J.; Sieradzki, A. Three-Dimensional Perovskite Methylhydrazinium Lead Chloride with Two Polar Phases and Unusual Second-Harmonic Generation Bistability above Room Temperature. *Chem. Mater.* **2020**, *32*, 4072–4082. [CrossRef]
- Mączka, M.; Zaręba, J.K.; Gągor, A.; Stefańska, D.; Ptak, M.; Roleder, K.; Kajewski, D.; Soszyński, A.; Fedoruk, K.; Sieradzki, A. ₂PbBr₄, a Ferroelectric Hybrid Organic-Inorganic Perovskite with Multiple Nonlinear Optical Outputs. *Chem. Mater.* 2021, 33, 2331–2342. [CrossRef]
- Mączka, M.; Ptak, M.; Gagor, A.; Stefańska, D.; Sieradzki, A. Layered Lead Iodide of [Methylhydrazinium]₂PbI₄ with a Reduced Band Gap: Thermochromic Luminescence and Switchable Dielectric Properties Triggered by Structural Phase Transitions. *Chem. Mater.* 2019, *31*, 8563–8575. [CrossRef]
- Li, R.; Wang, Z.; Zhu, T.; Ye, H.; Wu, J.; Liu, X.; Luo, J. Stereochemically Active Lone Pair Induced Polar Tri-Layered Perovskite for Record-Performance Polarized Photodetection. *Angew. Chem. Int. Ed.* 2023, 62, e202308445. [CrossRef]
- 19. Shi, Z.; Guo, J.; Chen, Y.; Li, Q.; Pan, Y.; Zhang, H.; Xia, Y.; Huang, W.; Shi, Z.; Guo, J.; et al. Lead-Free Organic-Inorganic Hybrid Perovskites for Photovoltaic Applications: Recent Advances and Perspectives. *Adv. Mater.* **2017**, *29*, 1605005. [CrossRef]
- Chatterjee, S.; Pal, A.J. Tin(IV) Substitution in (CH₃NH₃)₃Sb₂I₉: Toward Low-Band-Gap Defect-Ordered Hybrid Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2018, 10, 35194–35205. [CrossRef]
- 21. Lu, L.; Pan, X.; Jonhua, L.; Sun, Z. Recent Advances and Optoelectronic ApplicationsofLead-Free HalideDoublePerovskites. *Chem. Eur. J.* **2020**, *26*, 16975–16984. [CrossRef] [PubMed]
- Zhao, J.; Xia, Z.; Chen, D.; Dai, F.; Hao, S.; Zhou, G.; Liu, Q.; Wolverton, C. Materials for Optical, Magnetic and Electronic Devices Crystal Structure and Luminescence Properties of Lead-Free Metal Halides (C₆H₅CH₂NH₃)₃MBr. *J. Mater. Chem. C* 2020, *8*, 7322–7329. [CrossRef]
- 23. Yang, W.; Chu, K.B.; Zhang, L.; Ding, X.; Sun, J.; Liu, J.Z.; Deng, J. Lead-free molecular ferroelectric [N,N-dimethylimidazole]3Bi2I9 with narrow bandgap. *Mater. Des.* **2020**, *193*, 108868. [CrossRef]

- 24. Zhang, W.; Tao, K.; Ji, C.; Sun, Z.; Han, S.; Zhang, J.; Wu, Z.; Luo, J. (C₆H₁₃N)₂BiI₅: A One-Dimensional Lead-Free Perovskite-Derivative Photoconductive Light Absorber. *Inorg. Chem.* **2018**, *57*, 4239–4243. [CrossRef]
- Skorokhod, A.; Mercier, N.; Allain, M.; Manceau, M.; Katan, C.; Kepenekian, M. From Zero- to One-Dimensional, Opportunities and Caveats of Hybrid Iodobismuthates for Optoelectronic Applications. *Inorg. Chem.* 2021, 60, 17123–17131. [CrossRef] [PubMed]
- Bi, W.; Leblanc, N.; Mercier, N.; Auban-Senzier, P.; Pasquier, C. Thermally Induced Bi(III) Lone Pair Stereoactivity: Ferroelectric Phase Transition and Semiconducting Properties of (MV)BiBr₅(MV= Methylviologen). *Chem. Mater.* 2009, 21, 4099–4101. [CrossRef]
- 27. Ju, D.; Jiang, X.; Xiao, H.; Chen, X.; Hua, X.; Tao, X. Narrow band gap and high mobility of lead-free perovskite single crystal Sn-doped MA₃Sb₂I₉. *J. Mater. Chem. A* **2018**, *6*, 20753. [CrossRef]
- 28. Zaleski, J.; Pietraszko, A. Structure at 200 and 298 K and X-ray Investigations of the Phase Transition at 242 K of [NH₂(CH₃)₂]₃Sb₂Cl₉ (DMACA). *Acta Crystallogr. B* **1996**, 52, 287–295. [CrossRef]
- 29. Matuszewski, J.; Sobczyk, L. Ferroelectricity and Phase Transitions in Tris (Dimethylammonium) Nonabromodiantimonate (III). *Ferroelectrics* **1987**, *74*, 339–345. [CrossRef]
- Louvain, N.; Mercier, N.; Boucher, F. α-to β-(Dmes)BiI₅ (Dmes) Dimethyl(2-Ethylammonium)Sulfonium Dication): Umbrella Reversal of Sulfonium in the Solid State and Short I···I Interchain ContactssCrystal Structures, Optical Properties, and Theoretical Investigations of 1D Iodobismuthates. *Inorg. Chem* 2009, *48*, 879–888. [CrossRef]
- 31. Li, Y.; Yang, T.; Liu, X.; Han, S.; Wang, J.; Ma, Y.; Guo, W.; Luo, J.; Sun, Z. A Chiral Lead-Free Photoactive Hybrid Material with a Narrow Bandgap. *Inorg. Chem. Front.* 2020, *7*, 2770. [CrossRef]
- 32. Wenhua Bi, B.; Louvain, N.; Mercier, N.; Luc, J.; Rau, I.; Kajzar, F.; Sahraoui, B.; Mercier, N.; Bi, W.; Louvain, N.; et al. A Switchable NLO Organic-Inorganic Compound Based on Conformationally Chiral Disulfide Molecules and Bi(III)I₅ Iodobismuthate Networks. *Adv. Mater.* **2008**, *20*, 1013–1017. [CrossRef]
- 33. Tao, K.; Li, Y.; Ji, C.; Liu, X.; Wu, Z.; Han, S.; Sun, Z.; Luo, J. A Lead-Free Hybrid Iodide with Quantitative Response to X-ray Radiation. *Chem. Mater.* **2019**, *31*, 5927–5932. [CrossRef]
- 34. Chen, Y.; Yang, Z.; Guo, C.-X.; Ni, C.-Y.; Ren, Z.-G.; Li, H.-X.; Lang, J.-P. Iodine-Induced Solvothermal Formation of Viologen Iodobismuthates. *Eur. J. Inorg. Chem* **2010**, *33*, 5326–5333. [CrossRef]
- Li, X.; Traoré, B.; Kepenekian, M.; Li, L.; Stoumpos, C.C.; Guo, P.; Even, J.; Katan, C.; Kanatzidis, M.G. Bismuth/Silver-Based Two-Dimensional Iodide Double and One-Dimensional Bi Perovskites: Interplay between Structural and Electronic Dimensions. *Chem. Mater.* 2021, 33, 6206–6216. [CrossRef]
- Gagor, A.; Banach, G.; Węcławik, M.; Piecha-Bisiorek, A.; Jakubas, R. The Lone-Pair-Electron-Driven Phase Transition and Order-Disorder Processes in Thermochromic (2-MIm)SbI₄ Organic-Inorganic Hybrid. *Dalton Trans.* 2017, 46, 16605–16614. [CrossRef]
- 37. Gagor, A.; Wecławik, M.; Bondzior, B.; Jakubas, R. Periodic and Incommensurately Modulated Phases in a (2-Methylimidazolium) Tetraiodobismuthate(III) Thermochromic Organic-Inorganic Hybrid. *CrystEngComm* **2015**, *17*, 3286–3296. [CrossRef]
- Mccall, K.M.; Morad, V.; Benin, B.M.; Kovalenko, M.V. Efficient Lone-Pair-Driven Luminescence: Structure–Property Relationships in Emissive 5s² Metal Halides. ACS Mater. Lett. 2020, 2, 1218–1232. [CrossRef]
- 39. Wang, Z.-P.; Wang, J.-Y.; Li, J.-R.; Feng, M.-L.; Zou, G.-D.; Huang, X.-Y. [Bmim]₂SbCl₅: A Main Group Metal-Containing Ionic Liquid Exhibiting Tunable Photoluminescence and White-Light Emission. *Chem. Commun.* **2015**, *51*, 3094–3097. [CrossRef]
- 40. Li, Z.; Li, Y.; Liang, P.; Zhou, T.; Wang, L.; Xie, R.-J. Dual-Band Luminescent Lead-Free Antimony Chloride Halides with Near-Unity Photoluminescence Quantum Efficiency. *Chem. Mater.* **2019**, *31*, 9363–9371. [CrossRef]
- 41. Zhou, C.; Worku, M.; Neu, J.; Lin, H.; Tian, Y.; Lee, S.; Zhou, Y.; Han, D.; Chen, S.; Hao, A.; et al. Facile Preparation of Light Emitting Organic Metal Halide Crystals with Near-Unity Quantum Efficiency. *Chem. Mater.* **2018**, *30*, 2374–2378. [CrossRef]
- Benin, B.M.; McCall, K.M.; Wörle, M.; Morad, V.; Aebli, M.; Yakunin, S.; Shynkarenko, Y.; Kovalenko, M.V. The Rb₇Bi_{3-3x}Sb_{3x}Cl₁₆ Family: A Fully Inorganic Solid Solution with Room-Temperature Luminescent Members. *Angew. Chem.* 2020, 132, 14598–14605. [CrossRef]
- Wang, Z.; Zhang, Z.; Tao, L.; Shen, N.; Hu, B.; Gong, L.; Li, J.; Chen, X.; Huang, X.; Wang, Z.; et al. Hybrid Chloroantimonates(III): Thermally Induced Triple-Mode Reversible LuminescentS Witching and Laser-Printable Rewritable LuminescentP Aper. *Angew. Chem.* 2019, 131, 10079–10083. [CrossRef]
- Morad, V.; Shynkarenko, Y.; Yakunin, S.; Brumberg, A.; Schaller, R.D.; Kovalenko, M. V Disphenoidal Zero-Dimensional Lead, Tin, and Germanium Halides: Highly Emissive Singlet and Triplet Self-Trapped Excitons and X-ray Scintillation. *J. Am. Chem. Soc.* 2019, 141, 9764–9768. [CrossRef] [PubMed]
- 45. Mccall, K.M.; Stoumpos, C.C.; Kostina, S.S.; Kanatzidis, M.G.; Wessels, B.W. Strong Electron–Phonon Coupling and Self-Trapped Excitons in the Defect Halide Perovskites A₃M₂I₉ (A = Cs, Rb; M = Bi, Sb). *Chem. Mater.* **2017**, *29*, 4129–4145. [CrossRef]
- Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J.C.; Van De Burgt, L.J.; Kountouriotis, K.; Xin, Y.; Holt, E.; et al. One-Dimensional Organic Lead Halide Perovskites with Efficient Bluish White-Light Emission. *Nat. Commun.* 2017, *8*, 14051. [CrossRef]
- Liu, K.; Deng, C.; Li, C.; Zhang, X.; Cao, J.; Yao, J.; Zhao, J.; Jiang, X.; Lin, Z.; Liu, Q. Hybrid Metal-Halide Infrared Nonlinear Optical Crystals of (TMEDA)MI₅ (M = Sb, Bi) with High Stability. *Adv. Opt. Mater.* 2021, *9*, 24. [CrossRef]

- 48. Li, P.-F.; Tang, Y.-Y.; Liao, W.-Q.; Ye, H.-Y.; Zhang, Y.; Fu, D.-W.; You, Y.-M.; Xiong, R.-G. A Semiconducting Molecular Ferroelectric with a Bandgap Much Lower than That of BiFeO₃. *NPG Asia Mater.* **2016**, *9*, e342. [CrossRef]
- Zhang, H.-Y.; Wei, Z.; Li, P.F.; Tang, Y.-Y.; Liao, W.Q.; Cai, H.; Xiong, R.-G. Thin Films The Narrowest Band Gap Ever Observedin-Molecular Ferroelectrics: Hexane-1,6-Diammonium Pentaiodobismuth(III). *Angew. Chem. Int. Ed.* 2018, 57, 526–530. [CrossRef] [PubMed]
- 50. Gao, J.-X.; Hua, X.-N.; Chen, X.-G.; Mei, G.-Q.; Liao, W.-Q. [C₆N₂H₁₈][SbI₅]: A Lead-Free Hybrid Halide Semiconductor with Exceptional Dielectric Relaxation. *Inorg. Chem.* **2019**, *58*, 4343. [CrossRef]
- Skorokhod, A.; Hleli, F.; Hajlaoui, F.; Karoui, K.; Allain, M.; Zouari, N.; Mercier, N. Layered Arrangement of 1D Wavy Chains in the Lead-Free Hybrid Perovskite (PyrCO₂H)₂BiI₅: Structural Investigations and Properties. *Eur. J. Inorg. Chem.* 2021, 2021, 1452–1458. [CrossRef]
- 52. Wang, Z.; Wang, P.; You, X.; Wei, Z. A Hybrid Organic-Inorganic Bismuth Iodine Material Showing High Phase Transition Point and Low Bandgap. *Eur. J. Inorg. Chem.* 2022, *18*, e202200172. [CrossRef]
- Mao, C.-Y.; Liao, W.-Q.; Wang, Z.-X.; Li, P.-F.; Lv, X.-H.; Ye, H.-Y.; Zhang, Y. Structural Characterization, Phase Transition and Switchable Dielectric Behaviors in a New Zigzag Chain Organic–Inorganic Hybrid Compound: [C₃H₇NH₃]₂SbI₅. *Dalton Trans.* 2016, 45, 5229–5233. [CrossRef] [PubMed]
- Izumi, K.M.F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44, 1272–1276.
- 55. Kubelka, P.; Munk, F. A Contribution to the Optics of Pigments. Z. Technol. Phys. 1931, 12, 593–599.
- 56. Tauc, J.; Grigorovici, R.; Vancu, A. Optical Properties And Electronic Structure of Amorphous Germanium. *Phys. Status Solidi B* **1966**, *15*, 627–637. [CrossRef]
- 57. López, R.; Gómez, R. Band-Gap Energy Estimation from Diffuse Reflectance Measurements on Sol-Gel and Commercial TiO₂: A Comparative Study. *J. Sol. Sci. Technol.* **2012**, *16*, 1–7. [CrossRef]
- 58. Makuła, P.; Pacia, M.; Macyk, W. How to Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *J. Phys. Chem. Lett.* **2018**, *9*, 6814–6817. [CrossRef]
- 59. Li, C.; Luo, C.; Zhou, W.; Zhang, R.; Zheng, D.; Han, P. Highly Efficient Emission in Lead-Free Inorganic Vacancy-Ordered Sb-Bi-Alloyed Halide Quadruple Perovskites. *Chem. Phys. Lett.* **2022**, *795*, 139536. [CrossRef]
- 60. Mcclure, E.T.; Ball, M.R.; Windl, W.; Woodward, P.M. Cs₂AgBiX₆ (X = Br, Cl): New Visible Light Absorbing, Lead-Free Halide Perovskite Semiconductors. *Chem. Mater.* **2016**, *28*, 1348–1354. [CrossRef]
- 61. Saparov, B.; Hong, F.; Sun, J.P.; Duan, H.S.; Meng, W.; Cameron, S.; Hill, I.G.; Yan, Y.; Mitzi, D.B. Thin-Film Preparation and Characterization of Cs₃Sb₂I₉: A Lead-Free Layered Perovskite Semiconductor. *Chem. Mater.* **2015**, *27*, 5622–5632. [CrossRef]
- 62. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [CrossRef]
- 63. Sheldrick, G.M. SHELXT—Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. A Found. Adv.* 2015, 71, 3–8. [CrossRef] [PubMed]
- 64. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. Acta Crystallogr. C Struct. Chem. 2015, 71, 3–8. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.