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Research Article

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Detailed Characterization of Methylammonium and Formamidinium Bismuth Iodide Perovskite Thin Films, Focusing on Electrical Properties for Optoelectronic Applications

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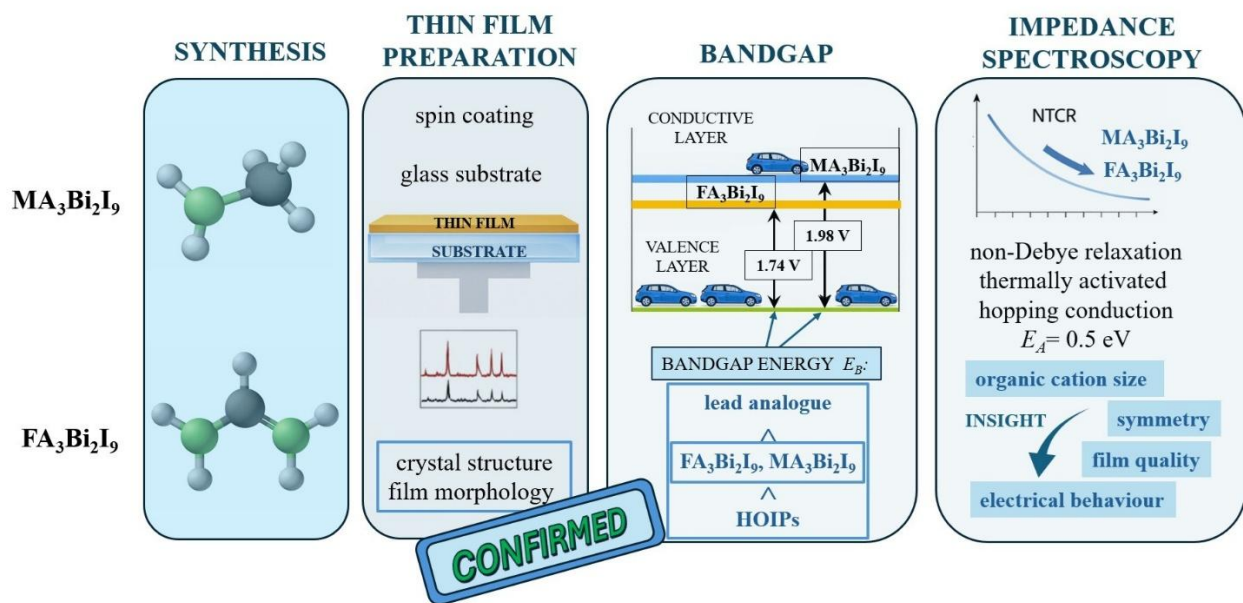
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Graphical abstract



Abstract

Bismuth-based halide perovskites have emerged as promising lead-free alternatives for optoelectronic applications due to their stability, low toxicity, and favorable semiconductor properties. In this study, methylammonium bismuth iodide ($\text{MA}_3\text{Bi}_2\text{I}_9$) and formamidinium

bismuth iodide ($\text{FA}_3\text{Bi}_2\text{I}_9$) were synthesized as single crystals and subsequently processed into thin films by spin-coating on activated glass substrates. Structural characterization using powder X-ray diffraction (XRD) confirmed the successful synthesis and revealed distinct crystallographic orientations. The uniform film morphology and stoichiometric composition were confirmed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), while UV-Vis spectroscopy was used to determine the indirect optical energy bandgap from the UV-Vis Tauc plot analysis giving values of 1.98 eV for $\text{MA}_3\text{Bi}_2\text{I}_9$ and 1.74 eV for $\text{FA}_3\text{Bi}_2\text{I}_9$. Both films have smooth uniform morphology and good overall quality. Temperature-dependent impedance spectroscopy revealed a negative temperature coefficient of resistance (NTCR) behavior, non-Debye relaxation, and thermally activated hopping conduction with activation energies around 0.5 eV, thereby defining the charge transport mechanism. The electrical modulus and conductivity analysis further confirmed the coexistence of long-range and localized conduction mechanisms. These findings highlight the influence of organic cation size and symmetry on electrical behavior, establishing $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ as good candidates for their use as perovskite solar cells and in other optoelectronic devices.

Keywords: methylammonium bismuth iodide, formamidinium bismuth iodide, perovskite, energy bandgap, impedance spectroscopy, thin films

1. Introduction

Bismuth-based halide perovskites have emerged as promising lead-free alternatives for optoelectronic applications due to their intrinsic stability, low toxicity, and tunable structural properties [1]. Among them, methylammonium bismuth iodide ($\text{MA}_3\text{Bi}_2\text{I}_9$) and formamidinium bismuth iodide ($\text{FA}_3\text{Bi}_2\text{I}_9$) have attracted considerable attention for their potential use in photovoltaic and photodetector devices [2,3]. Due to their excellent semiconductor properties, these perovskite materials are excellent candidates for the fabrication of solar cells [4].

Over the past decade, research on bismuth iodide perovskites has increasingly focused on the preparation and investigation of thin films deposited on diverse substrates [5–12]. The thin films of these perovskites have been improved not only by altering the substrate but also by doping with halogen elements or introducing alternative organic cations. Such modifications, together with variations in thin-film fabrication techniques, have led to notable differences in measured bandgap values. Reported approaches range from solution processing to direct substrate immersion in precursor solutions, each influencing the resulting optoelectronic performances [8,10,12,13]. Film synthesis routes strongly affect bandgap values, with surface roughness emerging as a critical parameter in solar cell efficiency [13]. Irregular crystal orientation and morphology can hinder charge transport, and reduce device efficiency [4]. Techniques such as spin-coating [1], thermal evaporation [14], doctor blading [12], and spray coating [15] often yield rough surfaces. Moreover, precursor composition, solvent engineering, and annealing

conditions decisively influence film uniformity. Careful optimization of these parameters has been shown to enhance charge-carrier mobility and improve reproducibility. In addition, the correlation between solvent choice, precursor concentration, and post-deposition annealing has been shown to dictate film uniformity and defect density [1,14]. These factors directly influence charge-carrier lifetimes [16] and recombination rates, making them crucial for device optimization.

Understanding the crystallographic structure of these materials is essential for optimizing their performance, particularly when processed as thin films. The effectiveness of organic–inorganic perovskites in solar cell applications is largely attributed to their structural motif: octahedra formed by metal cations and inorganic anions, and the connectivity between them. The type of octahedral connectivity is strongly influenced by the organic cation [4]. In this study, powder XRD was employed to confirm crystal structure and orientation, with diffractograms of bulk samples and thin films compared against established structural models. Even slight distortions in the octahedral framework can significantly alter optical absorption and carrier dynamics, highlighting the importance of precise structural characterization.

Performance evaluation in light-harvesting devices is primarily based on bandgap determination, which in this study, was carried out using UV-Vis spectroscopy. Additionally, temperature-dependent impedance spectroscopy was performed on bulk material, providing a powerful, non-destructive probe of electrical properties across a wide frequency range. This technique enables separation of bulk resistance, grain boundary effects, and electrode polarization, with Nyquist plots offering direct insight into charge transport and relaxation mechanisms in perovskite thin films.

Previous studies have characterized $\text{MA}_3\text{Bi}_2\text{I}_9$, both in bulk, thin films [9] and devices [17]. The bandgap of $\text{FA}_3\text{Bi}_2\text{I}_9$ [18] and the optoelectronic properties based on the A-site cations [19] have also been reported. Based on these studies, the present work focuses on comparative impedance spectroscopy analysis of MA- versus FA-based bismuth iodide perovskites. To our knowledge, this is the first systematic impedance study of $\text{FA}_3\text{Bi}_2\text{I}_9$ films, enabling direct comparison of charge transport, relaxation behavior, and conduction mechanisms between MA and FA cations in bismuth iodide systems. This comparative approach provides new insight into the influence of the organic cation size and symmetry to the electrical response and film quality, thereby advancing the understanding of lead-free perovskite analogues for optoelectronic applications.

In addition to impedance spectroscopy, complementary characterization techniques, including scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy, were also employed to provide a comprehensive understanding of composition, morphology, and microstructure prior to device integration. The methods applied in this study establish a

framework for evaluating bismuth-based perovskites, ensuring that both fundamental properties and practical device considerations are addressed in a unified manner.

2. Experimental

Synthesis

The synthesis of **formamidinium bismuth iodide**, $[\text{CH}(\text{NH}_2)_2]_3\text{BiI}_9$, denoted as FA_3BiI_9 , was carried out under temperature-controlled heating with constant stirring. Pre-synthesized formamidinium iodide and BiI_3 [20,21] were dissolved in 57 % HI (57 % w/w, aqueous solution, stabilized with 1,5 % H_3PO_2 , Carlo Erba reagents). The process was allowed to proceed for 2 h and 30 min and then allowed to cool down to room temperature. It is important to pay attention to the temperature while heating because it must not exceed 130 °C. During cooling, crystallization of the perovskite occurs. After the solution reached room temperature, the perovskite crystals were removed and washed three times with dry ether (anhydrous diethyl ether, ≥ 99.0 %, ≤ 0.03 % water, Merck). The crystals were vacuum-dried and stored in a desiccator.

The synthesis of **methylammonium bismuth iodide**, $(\text{CH}_3\text{NH}_3)_3\text{BiI}_9$, denoted as MA_3BiI_9 , was conducted in the same manner as of the synthesis of FA_3BiI_9 . The pre-synthesized methylammonium iodide (10 % excess, w/w) and BiI_3 were dissolved in 57 % HI (w/w). As with the previous synthesis, it is important to carefully monitor the temperature (as in the FA_3BiI_9 synthesis).

Thin film preparation

Thin films were prepared by deposition of the perovskite solution on microscope glass slides with dimensions 20×25 mm. Before deposition, the substrates were thoroughly cleaned by sequential immersion in NaOH and HNO_3 solutions with a molar concentration of 1 mol/L. The slides were left in each solution for 2 h and then rinsed with distilled water. Afterwards, the surface activation of the glass was achieved by treatment with piranha solution ($V(\text{H}_2\text{SO}_4) : V(\text{H}_2\text{O}_2) \approx 3 : 1$) for 8 h. The activation of the slides was concluded by washing with distilled water and ethanol, as well as subsequent drying under ambient conditions. They were stored in a vacuum desiccator.

Solutions of MA_3BiI_9 and FA_3BiI_9 (w/w = 6 %) in dry acetonitrile (> 99.9 %, for HPLC, VWR Chemicals) were used to make the thin film by the spin-coating process. The perovskite layer was spin-coated on the pre-activated glass slides by adding the solution dropwise at 5000 rpm and then annealed at 100 °C for 15 minutes. A total volume of 0.25 mL has been deposited on the glass substrate in 5 consecutive drops (0.05 mL each), and 10 seconds span between the addition. All processes were performed under ambient conditions. The representative images of the prepared thin films are shown in Fig. 1.

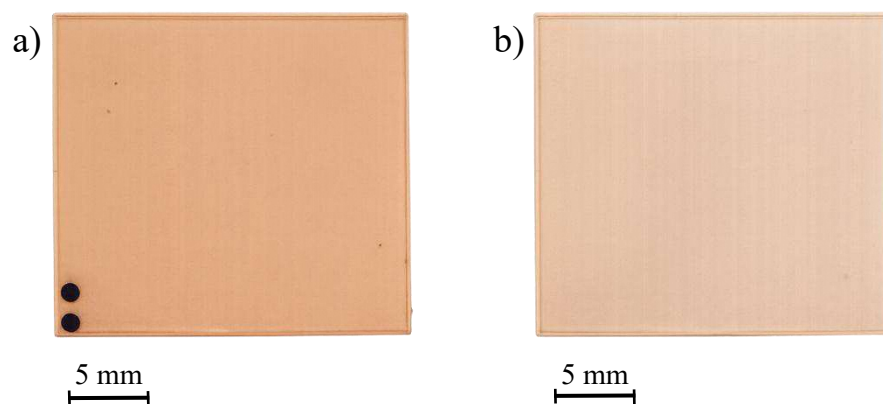


Fig. 1. Thin films prepared by spin-coating, a) $\text{MA}_3\text{Bi}_2\text{I}_9$ and b) $\text{FA}_3\text{Bi}_2\text{I}_9$.

X-ray diffraction

Powder X-ray diffraction (XRD) patterns of the bulk samples and the thin films were collected at room temperature in air. The diffractograms were recorded using a Rigaku Ultima IV, Japan powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and a high-speed D/teX Ultra detector within the range 2θ starting from $5/10$ up to $60\text{-}90^\circ$ with $5\text{-}10^\circ/\text{min}$ scanning speed. All diffractograms were analyzed using the MATCH! 4.1 software [22].

Scanning electron microscopy and EDX

The morphology of the samples was studied by field emission scanning electron microscopy (FE-SEM) on the Thermo Fisher Scientific Apreo 2S (Thermo Fisher, USA), operating at an acceleration voltage of 2 kV with a working distance of approximately 5.5 mm. For elemental characterisation, comprehensive elemental qualitative and quantitative mapping and composition analyses of the powders were performed using the energy-dispersive detector (EDS) and AZtec X-ray microanalysis software (both Oxford Instruments, UK) using 20 kV and $\sim 10 \text{ mm}$ of working distance.

The samples were put onto graphite tape and were not gold sputtered prior to the microscopy. Images were taken using In-lens and/or standard Evernhart-Thornley secondary electron (SE) detectors.

UV-Vis measurements

The optical spectra of the thin films were obtained using Varian Cary 50 spectrophotometer. The spectra were recorded in the spectral range from 300 to 800 nm at room temperature (25°C). The data obtained were analyzed using Origin software [23] in order to obtain the values of the bandgap.

Measurement of the electrical properties

For electrical measurements, the pellets of $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ samples were electroded with air-drying high-purity silver paste. The dimensions of the plates were approximately 12.5 mm in diameter and 1 mm thick. Impedance spectroscopy of the samples was investigated using the standard four-probe technique with Hewlett-Packard 4192 A LCR meter in the temperature range 28 - 69 °C with a heating rate of 1 °C min⁻¹ and in the frequency range from 5 Hz to 10 MHz.

3. Results and Discussion

To confirm the successful synthesis, first, $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ were synthesized, and then, the obtained crystals were used to prepare the solution used for the preparation of the thin films. The diffractograms of the bulk material were obtained in order to confirm the successful synthesis, and then the thin films on the glass substrate were also recorded (Fig. 2).

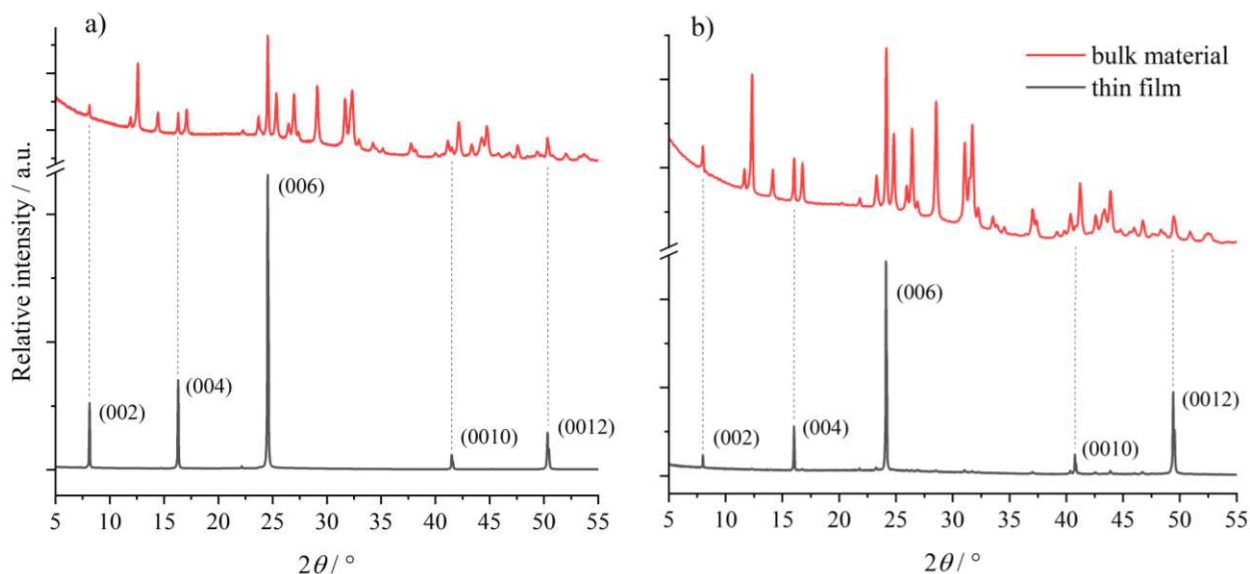


Fig. 2. XRD patterns from the bulk materials (red lines) used for preparation of the thin films on glass substrate (black lines) obtained by spin-coating, for a) $\text{MA}_3\text{Bi}_2\text{I}_9$ and b) $\text{FA}_3\text{Bi}_2\text{I}_9$.

The results from the EDX spectroscopy show that the stoichiometric ratio between the Bi and I is 2:9, as expected by the determined structure [20,24,25]. Since the EDX results ($w(\text{Bi})_{\text{MA}_3\text{Bi}_2\text{I}_9} = 25.03\%$, $w(\text{I})_{\text{MA}_3\text{Bi}_2\text{I}_9} = 69.15\%$, $w(\text{Bi})_{\text{FA}_3\text{Bi}_2\text{I}_9} = 24.40\%$, $w(\text{I})_{\text{FA}_3\text{Bi}_2\text{I}_9} = 67.55\%$) were comparable to the previously reported values [20], and the theoretically calculated values for the proposed composition, further elemental (CHN) analysis was not performed. As additional confirmation, the obtained powder X-ray diffractograms are also in line with the ones from the bulk samples. These analyses confirm the stoichiometry of $\text{A}_3\text{B}_2\text{X}_9$, i.e., $\text{A}_3\text{Bi}_2\text{I}_9$.

The SEM micrographs of the obtained thin films with perovskites are shown in Figs. 3 and 4. Both $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ thin films show smooth, continuous layers, confirming good film quality. This observation is consistent with the powder XRD diffractograms where the low intensity of certain peaks support the presence of well-ordered structures. A slight difference can

be noted between the two systems. $\text{FA}_3\text{Bi}_2\text{I}_9$ tends to form a somewhat more regular and clearer surface compared to $\text{MA}_3\text{Bi}_2\text{I}_9$ (Fig. 3 and Fig. 4), indicating marginally improved crystallization. Nevertheless, both films demonstrate uniform morphology and satisfactory smoothness, supporting their suitability for optoelectronic applications. Residual traces of the mother solution and substance residues of the same phase are occasionally observed on the surfaces (Figs. 3b and 4b), where in the case of $\text{MA}_3\text{Bi}_2\text{I}_9$ are somewhat more pronounced. Similar conclusions can be drawn from the SEM images of the corresponding single crystals [20].

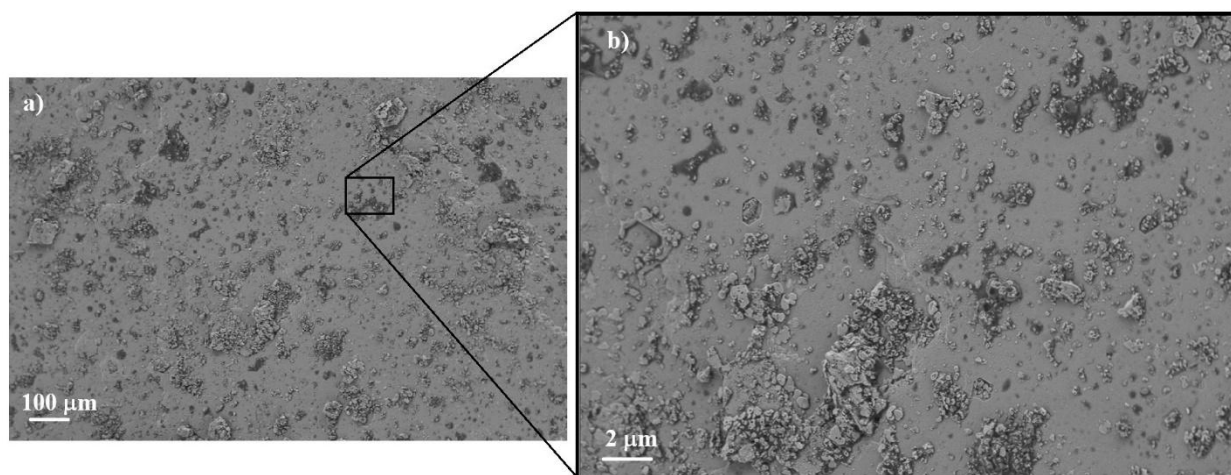


Fig. 3. SEM image of $\text{MA}_3\text{Bi}_2\text{I}_9$ thin film at room temperature: a) $\times 350$ magnification and b) $\times 20,000$ magnification.

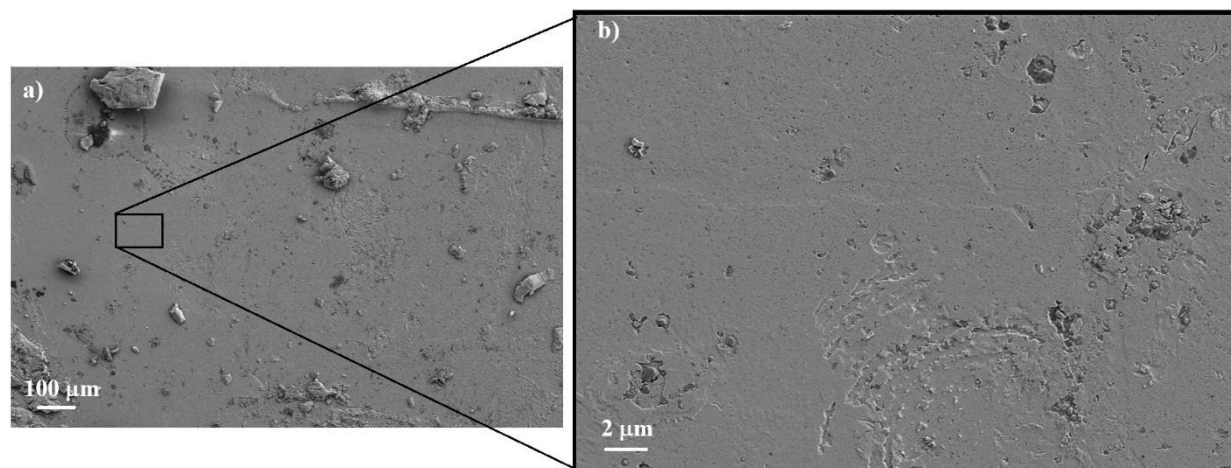


Fig. 4. SEM image of $\text{FA}_3\text{Bi}_2\text{I}_9$ thin film at room temperature: a) $\times 350$ magnification and b) $\times 20,000$ magnification.

X-ray diffraction

The diffractograms obtained by XRD performed on the thin films of $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ show distinct crystallographic features characteristic of their structural organization and phase

purity. In Fig. 2, the XRD patterns of the bulk material were used to obtain the thin films by spin-coating, and the patterns of the thin films are shown. The diffractograms confirm not only the successful synthesis of the material but also the successful preparation of the films. Since both compounds exhibit multiple stable phases at different temperatures [20,26], it was essential to ensure that, following the annealing of the thin films, sufficient time was allowed for the films to stabilize on the substrate.

Based not only on the diffraction patterns shown in Fig. 2, but also on the SEM images (Figs. 3 and 4), it can be concluded that in both films there is a high level of crystal orientation, and the film has formed evenly on the surface of the substrate via spin-coating, having sharp diffraction peaks. The XRD pattern of the MA₃Bi₂I₉ film has peaks with high intensity that correspond to the (006) planes, suggesting a preferred orientation along that plane. In contrast, the XRD pattern of the FA₃Bi₂I₉ film has slightly shifted positions compared to the bulk material, implying that there is a reduction of crystallinity and possible lattice distortion due to the larger formamidinium cation. The results obtained for the crystal structures of the bulk materials [17,20,24,27,28] and the thin films [6,19,29,30] are consistent with previously reported literature data.

Additionally, the higher crystallinity of the MA₃Bi₂I₉ film can be confirmed by the relative peak intensity of the MA₃Bi₂I₉ diffractogram (Fig. 2a) compared to the FA₃Bi₂I₉ (Fig. 2b). The differences can be ascribed to the kinetics of the film formation [31] and the interactions with the solvent during the film formation. In both cases, no secondary phases or impurities were detected, once again confirming that the films obtained were chemically homogeneous. In the diffraction pattern of the MA₃Bi₂I₉ film, five distinct diffraction peaks appear at $2\theta = 8.13^\circ, 16.33^\circ, 24.55^\circ, 41.49^\circ$, and 50.32° can be noted. They are assigned to (002), (004), (0010), and (0012) lattice planes, respectively [6,32,33]. The MA₃Bi₂I₉ bulk material and film are indexed as a hexagonal system having the space group *P*6₃/*mmc* [20,24].

For FA₃Bi₂I₉ film, the diffraction peaks from the same lattice planes as in MA₃Bi₂I₉ appear with slightly different values for 2θ ($7.99^\circ, 16.01^\circ, 24.13^\circ, 40.76^\circ$, and 49.39°). The FA₃Bi₂I₉ bulk and the film, like the methylammonium analogue, are determined to have the hexagonal crystal structure, with space group *P*6₃*mc* [20,25].

UV-Vis spectroscopy

Optical absorption measurements made at room temperature show that the UV-Vis spectra are very similar for MA₃Bi₂I₉ and FA₃Bi₂I₉. Both compounds show excellent absorption up to 430 nm of the visible region of light with a high absorption coefficient (Fig. 5a and 6a). Compared to purely lead-based perovskite materials [34], bismuth-based materials absorb light at the higher energy side of the spectrum, which results in a distinct color difference in MA₃Bi₂I₉ and FA₃Bi₂I₉ compared to the lead iodide analogs. While the lead iodides are either black or yellow,

the bismuth iodides (both MA and FA based) have a dark red (as bulk material) or orange color (as thin films).

The similarities of MA and FA lead iodides on one hand and the corresponding bismuth iodides on the other hand, are expected if the ionic radii of MA^+ and FA^+ are taken into consideration [35]. Their performances as materials for solar cells can be predicted based on the UV-Vis spectra and can be correlated to the similar behavior of the MAPbI_3 and $\alpha\text{-FAPbI}_3$ [36–39]. The substitution of MA with FA leads to a peak shift to higher values for the wavelengths. Due to this, the energy bandgap decreases in the case of formamidinium analogs. Figs. 5c and 6c show this trend in the case of $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$. The absorption peak maximum appears at 500 and 510 nm for the MA and FA bismuth iodides, respectively, compared to the 780 and 800 nm values for MAPbI_3 and FAPbI_3 [36–39]. Based on these results, the high differences in the absorption maxima can be attributed to the nature of the BI_6 octahedra. The polarizability of the B cation influences on the way the octahedra are interconnected, and at the same time, the influence of the A cation contributes to the BI_6 network [40].

The results from the UV-Vis measurements and the spectra of both lead and bismuth analogs reflect their optical energy bandgap values. The direct and indirect optical bandgap have been extracted from the Tauc plot [41] using the formula:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where A is a constant, α is the absorption coefficient, and E_g is the energy gap between HOMO and LUMO, and n refers to the mode of transitions. Here, $n = 2$ for the allowed direct transition and $n = 0.5$ for the allowed indirect transition.

Based on the Tauc plot, the estimated **direct bandgaps** (E_g) of $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ are found to be 2.54 eV and 2.43 eV, respectively, while the values of the **indirect bandgaps** are 1.98 eV and 1.74 eV, respectively (Fig. 5). After the fit of the linear part of the Tauc plot, it was concluded that the optical energy bandgaps of the bismuth analogs suggest that both compounds behave as an indirect-gap semiconductor at room temperature. This conclusion was made based on the R^2 value from the linear fit of the Tauc plots for both compounds and it is in line with the data available in the literature [6,42]. Additionally, this can be concluded based on the steep absorption edge in the UV-Vis absorption spectra (Fig. 5 a, Fig. 6 a) [12].

Even though the values for the optical energy bandgap are higher than those of MAPbI_3 [43,44] and FAPbI_3 [43–45], the achieved E_g of these compounds is still lower than most of the other HOIPs, especially of the methylammonium-based bismuth chloride perovskites [46].

The reported bandgaps values for these compounds vary widely, ranging from 1.65 to 2.94 eV (Tables 1 and 2). In addition, different studies have described the conduction mechanism as either direct and indirect. Such inconsistencies exist since the earliest characterization of these

materials, and even after more than a decade, no consensus has been reached regarding the true nature of their bandgap.

To understand the origin of these discrepancies, both in the bandgap values and in the assignment of direct versus indirect conduction, we compared results across multiple studies, taking into account the synthesis methods, measurement techniques, and experimental conditions. A major factor is whether the measurements were performed on bulk samples or thin films. Other influences include the choice of substrate (quartz, glass, FTO-TiO₂, ITO), the solvents employed, and the technique used to determine the bandgap (UV-Vis, photoluminescence, Spectroscopic Ellipsometry or DFT calculations). Furthermore, synthesis routes and deposition methods (solvent, CVD, SP) strongly affect crystallinity and film morphology, while measurement temperature can also play a role.

The diversity of reported values has led to speculation about mixed conduction mechanisms and the possibility of a “mixed” bandgap character. For example, studies on MAPbI₃ perovskites suggest that an indirect bandgap may arise from Rashba splitting. In compounds containing heavy atoms such as bismuth and iodine, strong spin–orbit coupling (SOC) modifies the electronic structure. At surfaces or interfaces, SOC generates an effective magnetic field that lifts spin degeneracy, splitting the valence and conduction band edges and resulting in an indirect bandgap [47].

Additional spectral features also support indirect behavior. The long absorption tail is often attributed to sub-bandgap emission from trap states [48], possibly linked to weak connectivity between A-site cations and the Bi₂I₉ anions. A slight bathochromic shift of the excitonic absorption band may also be an indication of a less localized exciton state [49]. Taken together, these observations point toward the presence of indirect conduction pathways in these materials.

However, taken into consideration all other factors mentioned before and addressed in Tables 1 and 2, the conduction type cannot be generally defined. The wide variation in reported bandgap values reflects the strong dependence on synthesis and characterization approaches. In our study, however, the indirect Tauc plot fitting provided a slightly better match than the direct model, supporting the conclusion that the conduction is best described as indirect in this exact case.

Table 1. Reported direct and indirect bandgap values of MA₃Bi₂I₉ from different studies.

Reference	Sample preparation	Direct E_g / eV	Indirect E_g / eV	Methodology	Year
Park <i>et al.</i> [5]	modified TiO ₂ -FTO electrodes	2.1		UV-Vis	2015
Öz <i>et al.</i> [17]		2.8 - 2.9		UV-Vis	2016

	film on ITO	1.65		PL	
	glass	2.94		DFT	
Eckhard <i>et al.</i> [24]	SC	1.94	1.67	UV-Vis	2016
Hoye <i>et al.</i> [6]	film (quartz)	2.1	2.04	PL	2016
		2.1		DFT	
Lyu <i>et al.</i> [4]	film FTO-TiO ₂		2.11	UV-Vis	2016
	SC		2.25	TC	
Chen <i>et al.</i> [7]	film on glass (CVD)		1.8	UV-Vis	2017
Zhang <i>et al.</i> [50]	film on FTO-TiO ₂	2.26		UV-Vis	2017
		2.15		PL	
McDonald <i>et al.</i> [2]	film ITO-TiO ₂	2.08	1.88	UV-Vis	2018
		1.89	1.77	DFT	
Mohammad <i>et al.</i> [8]	film on FTO-TiO ₂ (SP)	2.24		UV-Vis	2019
Maiti <i>et al.</i> [51]	film on quartz	1.97 - 2.04		UV-Vis	2019
Lan <i>et al.</i> [18]	film on FTO-TiO ₂	2.25		UV	2019
Jin <i>et al.</i> [52]	film		2.04	UV-Vis	2020
Tailor <i>et al.</i> [49]	film on ITO		2.10	UV-Vis	2021
Shah <i>et al.</i> [9]	film on FTO-TiO ₂		1.85 - 2.00	UV-Vis	2022
Valastro <i>et al.</i> [53]	SC	2.81		SE	2024
		2.79		DFT	
Kumaresan <i>et al.</i> [12]	film (FTO)		2.24, 2.25	UV-Vis	2025
Zhao <i>et al.</i> [54]	film on Bi	2.14 - 2.26		UV-Vis	2025
		1.8		PL	
This work	film on glass	2.57	1.98	UV-Vis	

PL - photoluminescence, SE - Spectroscopic Ellipsometry, SC - Single Crystal, TC - Theoretically Calculated, ITO - Indium Tin Oxide, FTO - Fluorine-doped Tin Oxide, CVD - Chemical Vapor deposition, SP - Spray Coating.

Table 2. Reported direct and indirect bandgap values of FA₃Bi₂I₉ from different studies.

Reference	Sample preparation	Direct E_g / eV	Indirect E_g / eV	Methodology	Year
Lan <i>et al.</i> [18]	film on FTO-TiO ₂	2.19		UV-Vis	2019
Szklarz <i>et al.</i> [25]	powder in nujol	1.85		UV-Vis	2019
		1.89		DFT	
Nishikubo <i>et al.</i> [55]	film on quartz	2.21		UV-Vis	2020

Tailor <i>et al.</i> [49]	film on ITO		2.10	UV-Vis	2021
Ünlü <i>et al.</i> [19]	Film on FTO-TiO ₂	2.6	1.7	UV-Vis	2021
Li <i>et al.</i> [56]	SC	2.08		UV-Vis	2021
Tailor <i>et al.</i> [57]	Nanocrystals in solution	2.21 1.82	2.13 1.78	UV-Vis DFT	2025
Kumaresan <i>et al.</i> [58]	powder	2.46 or 2.13		UV-Vis	2025
This work	film on glass	2.43	1.74	UV-Vis	

SC - Single Crystal, ITO - Indium Tin Oxide, FTO - Fluorine-doped Tin Oxide.

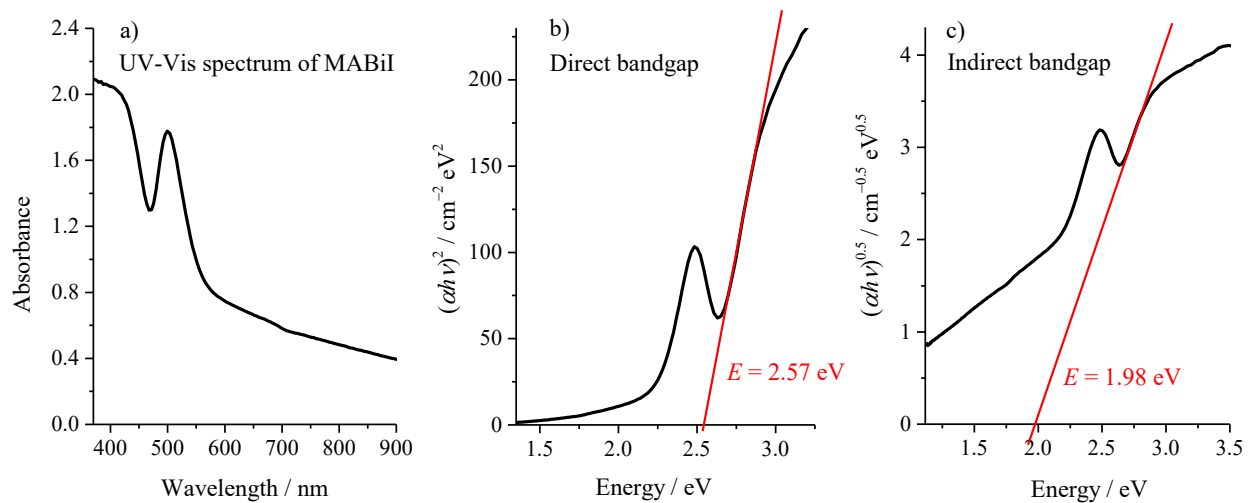


Fig. 5. a) UV-Vis spectrum of MA₃Bi₂I₉ deposited on activated glass, b) Tauc plot for calculating the direct energy bandgap, and c) Tauc plot for calculating the indirect energy bandgap.

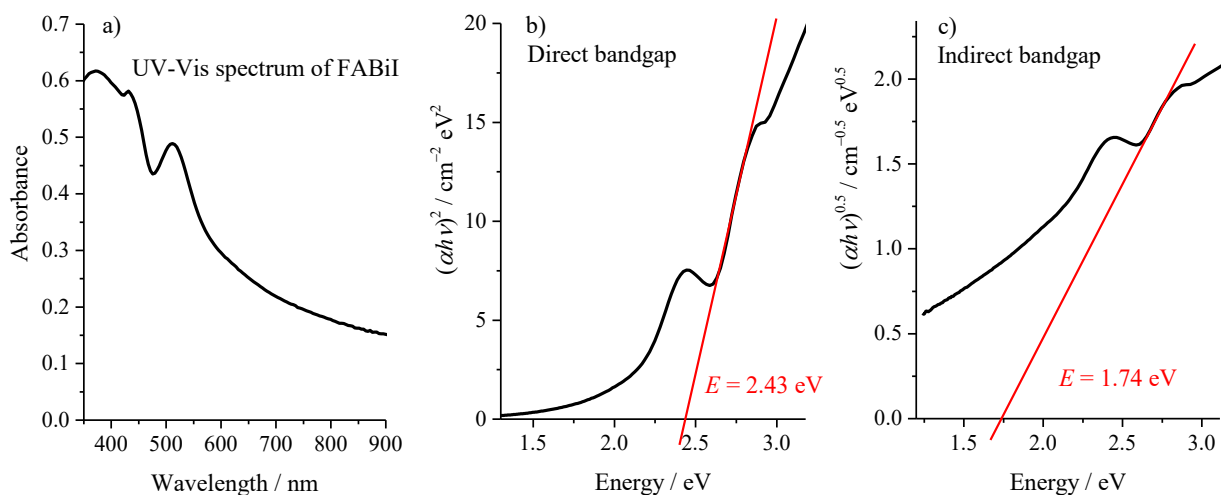


Fig. 6. a) UV-Vis spectrum of FA₃Bi₂I₉ deposited on activated glass, b) Tauc plot for calculating the direct energy bandgap, and c) Tauc plot for calculating the indirect energy bandgap.

Impedance spectroscopy

The electrical properties of the as-synthesized MA₃Bi₂I₉ and FA₃Bi₂I₉ have been investigated through complex impedance spectroscopy in the frequency range of 5 Hz to 13 MHz with temperature variation from 28 °C to 69 °C during cooling process. The measurements were repeated on same samples and similar results were obtained.

The frequency variation of the imaginary part Z'' of complex impedance with different temperatures for MA₃Bi₂I₉ and FA₃Bi₂I₉ is shown in Fig. 7. For these materials, the relaxation peak reduces with temperature, i.e., the resistance decreases and shifts toward higher frequencies, indicating the negative temperature coefficient of resistance (NTCR)-type behavior of both MA₃Bi₂I₉ and FA₃Bi₂I₉ [59,60]. This type of behavior confirms the rise in ac conductivity due to the rise of mobility of charge carriers, as well as the reduction of trapped charge density within MA₃Bi₂I₉ and FA₃Bi₂I₉.

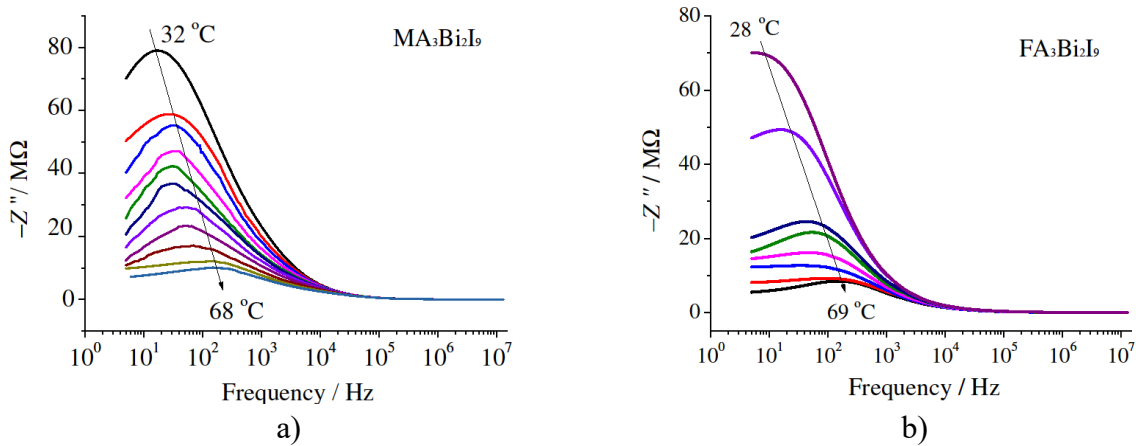


Fig. 7. Imaginary part of impedance vs frequency for a) $MA_3Bi_2I_9$ and b) $FA_3Bi_2I_9$.

In the high frequency region, Z'' exhibits a temperature-independent nature, which indicates the presence of space charge in this material [61]. The semicircles observed in the complex impedance spectra, appearing in the high-frequency, intermedial-frequency, and low-frequency regions, are conventionally ascribed to the grain interior, grain boundaries, and electrode/film interface, respectively [62]. The grain boundary contribution typically dominates in the low- to intermediate-frequency interval (often ranging from $\sim 10^{-2}$ Hz to $\sim 10^4$ Hz), situated between the higher-frequency response of the grain interiors (bulk) ($\sim 10^4$ Hz to GHz) and the lower-frequency response of the electrode interfaces ($< 10^{-2}$ Hz) [63,64].

The plots presenting the difference in contribution of grain, grain boundary, and electrode polarization for both samples are very similar. For both $MA_3Bi_2I_9$ and $FA_3Bi_2I_9$, the peak of Z'' is in the interval where grain boundary contribution is dominant [65], possibly overlapped with electrode polarization. Both materials confirm the characteristic semiconducting behavior of perovskites, decrease of impedance with rise in temperature due to generation of new electron hole pairs [66], mainly through the grain boundaries, considering high values of impedance in the low/medium range of frequency.

The complex impedance plot, also called the Nyquist plot, is a supplementary method for representing bulk (grain) and grain boundary phenomena of materials. A Nyquist plot is a graphical representation on the complex plane showing the relationship between the real part and imaginary part of impedance, for variable frequency [67]. In Fig. 8, as we can see that both materials exhibit one incomplete semicircle at medium frequencies, confirming the domination of high-resistive grain boundaries in the total resistance.

The semicircles are depressed, and their centers are shifted down to the real axis, implying distributions of relaxation time. Depressed semicircles in Nyquist plots are classic indicators of non-Debye relaxation [68]. In fact, in perovskite materials, the grain boundaries are more

resistive than the grains. The difference between these two resistive values leads to a huge increase in the number of space charges at the grain boundaries due to polarization.

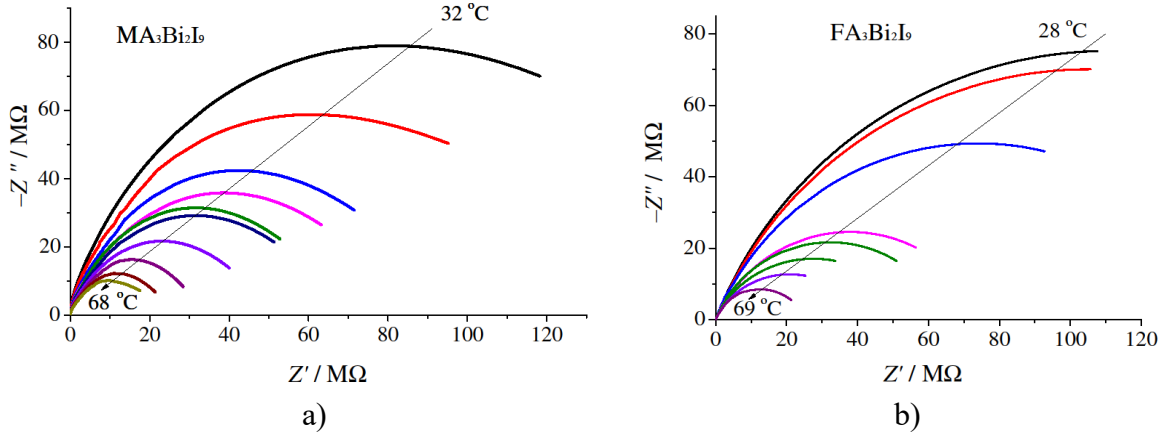


Fig. 8. Nyquist plots for: a) $\text{MA}_3\text{Bi}_2\text{I}_9$ and b) $\text{FA}_3\text{Bi}_2\text{I}_9$.

It is well known that close relaxation times of different contributions (corresponding to grain, grain boundary, electrode polarization, etc.) are very hard to be separated from the usual Nyquist plot showing up as a single semicircular arc. It is possible that two processes overlap and two transport mechanisms, through grains and grain boundaries are seen as one single arc [61]. In order to separate grain boundary part from grain part, the impedance data are presented in a Z' versus Z''/f plot, as suggested by Abrantes *et al.* [69], shown in Fig. 9.

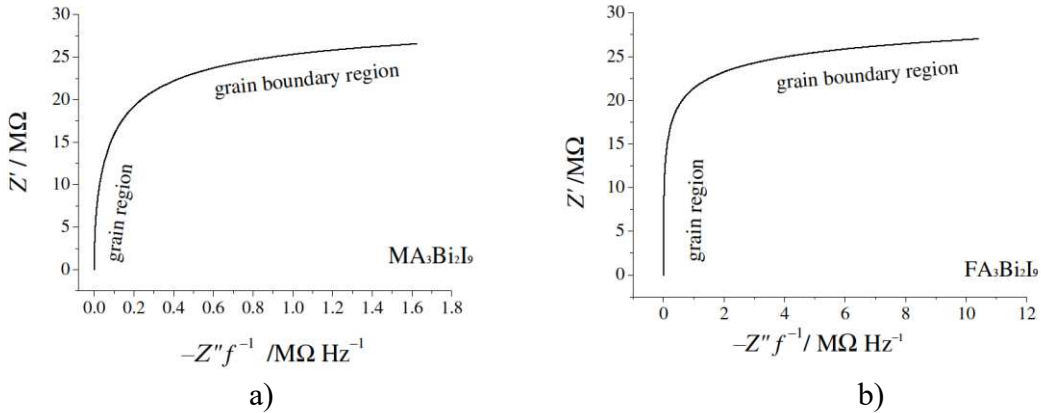


Fig. 9. Another presentation of the impedance, Z' vs $-Z''/f$, (Abrantes plot), emphasizing different regions of conductivity a) $\text{MA}_3\text{Bi}_2\text{I}_9$ at 61 °C, b) $\text{FA}_3\text{Bi}_2\text{I}_9$ at 69 °C.

The data clearly reveals two regions with different slopes corresponding to grains and grain boundaries. The interfacial relaxation between the sample and the electrode is not of interest and

is not shown. This confirms that the interfacial polarization in MA₃Bi₂I₉ and FA₃Bi₂I₉ originates from the blocking of charge carriers at the grain and grain boundary interface [69].

The conductivity analysis provides information about the type of transport of charge carriers (electrons, holes, or cations, anions) that predominate the conduction process and their response as a function of temperature and frequency. For the investigated temperature range, the dependence of $\ln \sigma_{dc}$ on $1000/T$ (Fig. 10) reveals that dc conductivity, σ_{dc} follows the Arrhenius relation:

$$\sigma_{dc} = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is the pre-exponential factor, and E_a represents the activation energy of the conduction process. The activation energy has been obtained from the Arrhenius plot, as shown in Fig. 10, and confirms semiconducting behavior - the conductivity increases on heating the sample.

Estimated values of the activation energy from the temperature dependence of σ_{dc} are: $E_a = 0.505 \text{ eV} \pm 0.003 \text{ eV}$ for MA₃Bi₂I₉ and $0.498 \text{ eV} \pm 0.003 \text{ eV}$ for FA₃Bi₂I₉. Calculated values for activation energy extracted from the imaginary part of the impedance are $0.501 \text{ eV} \pm 0.006 \text{ eV}$ for MA₃Bi₂I₉ and $0.503 \text{ eV} \pm 0.006 \text{ eV}$ for FA₃Bi₂I₉.

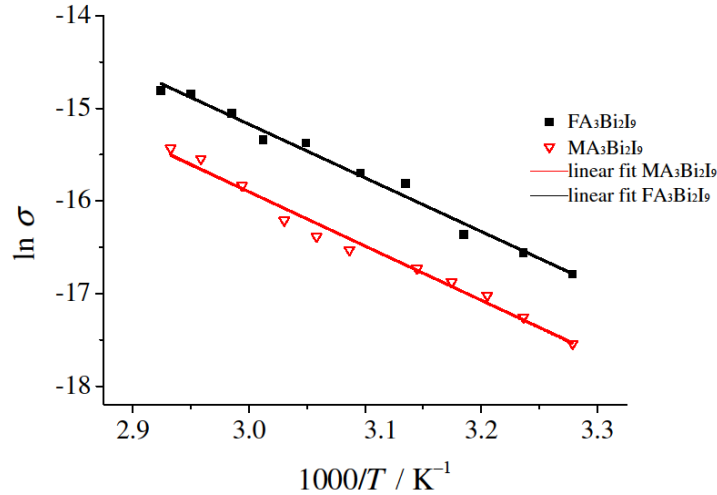


Fig. 10. Dependence of $\ln \sigma_{dc}$ versus $1000/T$ for MA₃Bi₂I₉ and FA₃Bi₂I₉, used to obtain the activation energy.

The ac conductivity measured at different frequencies and temperatures for both samples (Fig. 11) increases with temperature. In the low frequency region, the conductivity is dominated by real component σ_{dc} , and at high frequencies, dispersion is observed, implying hopping-type conduction. The frequency-dependent electrical conductivity has been fitted by Jonscher's power law [70], according to equation:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

where ($0 < n < 1$), A represents the temperature-dependent pre-exponential constant, connected to the strength of polarization, and n is the frequency exponent, which depends on the type of the

process, intrinsic or extrinsic. The lines in Fig.11 represent fitted results from the experimental measurements using Jonscher's universal power law.

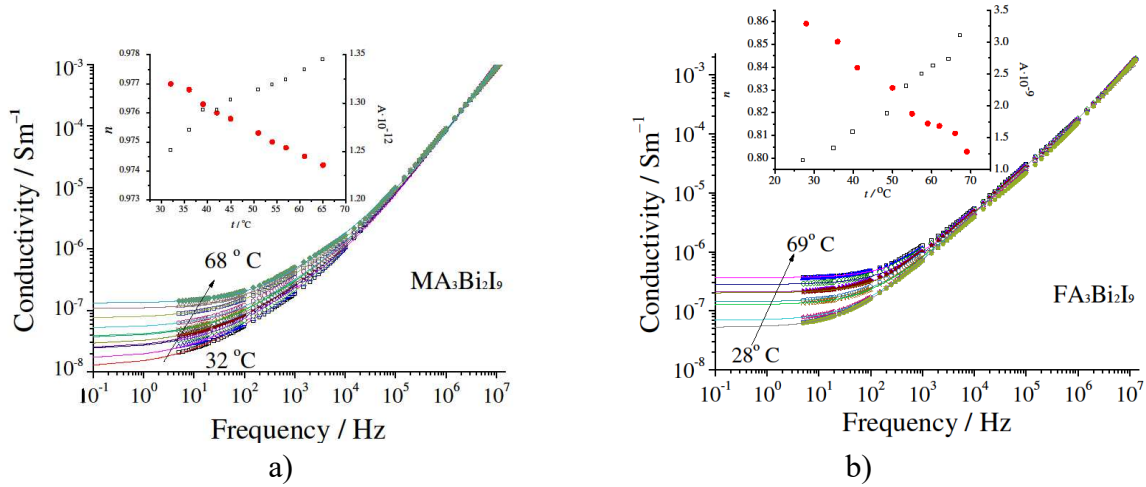


Fig. 11. Ac conductivity for a) $\text{MA}_3\text{Bi}_2\text{I}_9$ and b) $\text{FA}_3\text{Bi}_2\text{I}_9$ at different temperatures. The lines are fits for the experimental measurements using Jonscher's universal power law. The inserted graphs represent the variation of exponent n and pre-exponential constant A with temperature. The values of n and A were obtained with error less than 0.5 %.

According to the behavior of n , different theoretical hopping models for conduction mechanism are proposed in literature: *correlated barrier hopping* (CBH) [71], *small polaron hopping* (SPH) [72], *quantum mechanical tunneling* (QMT) [72], *overlapping large polaron tunneling* (OLPT) [73] and *non-overlapping small polaron tunneling* (NSPT) model [71].

In the investigated temperature interval, the estimated values of n for $\text{MA}_3\text{Bi}_2\text{I}_9$ show decrease with temperature from 0.977 to 0.939, and for $\text{FA}_3\text{Bi}_2\text{I}_9$, from 0.859 to 0.803. They are found to be less than unity, which confirms that the conductivity in these samples is governed by hopping of charge carriers [74]. Constant A for $\text{MA}_3\text{Bi}_2\text{I}_9$ increases with temperature from $1.25 \cdot 10^{-12}$ to $1.35 \cdot 10^{-12}$, and from $1.19 \cdot 10^{-9}$ to $3.10 \cdot 10^{-9}$ for $\text{FA}_3\text{Bi}_2\text{I}_9$. The temperature dependence of the n parameter in the investigated temperature interval could be described by the so-called correlated-barrier-hopping model [75]. In this model, the value of n decreases linearly with increasing temperature, which is attributed to an increase in the movement of charge carriers through the localized states [76].

Further, the electrical behavior of the investigated samples is examined by the electric modulus, defined as the reciprocal value of the dielectric constant [77]:

$$M^* = (1/\varepsilon^*(\omega)) = M' + jM''$$

The electrical modulus corresponds to the relaxation of the electric field in the materials when the electric displacement remains constant. It suppresses electrode polarization and gives importance to a circuit element having a small capacitance value. The relaxation phenomenon

inside MA₃Bi₂I₉ and FA₃Bi₂I₉ causes a characteristic peak in frequency dependence of imaginary part of modulus M'' which tends to shift toward higher frequencies with the increase in temperature. The frequency variation of M'' consists of two regions: the left side (i.e., below peak frequency $f_{\max}$) is related to the hopping of mobile charge carriers over a long-range inside the material and the right side (i.e., above $f_{\max}$) is related to the short-range or localized motion of charge carriers within the potential wells [68]. Hence, the relaxation peak indicates the transition from the long-range to the short-range mobilization of charge carriers in both MA₃Bi₂I₉ and FA₃Bi₂I₉. The frequency and temperature dependence of the M'' is shown in Fig. 12, where a slightly asymmetric peak at each temperature is observed (more pronounced for FA₃Bi₂I₉).

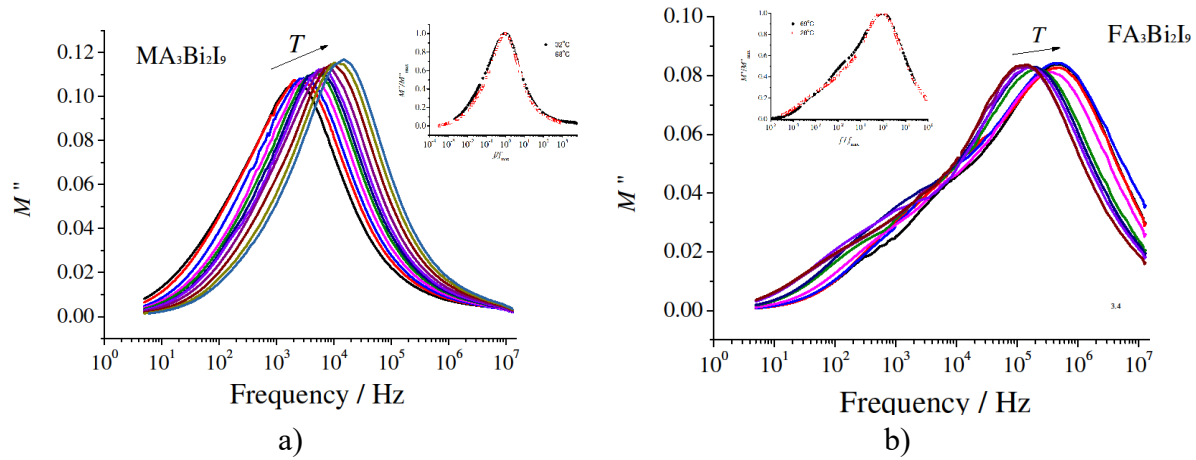


Fig. 12. Frequency variation of M'' of (a) MA₃Bi₂I₉ and (b) FA₃Bi₂I₉. The insets show a plot of $M''/M''_{\max}$ vs $\log(f/f_{\max})$.

The peak shifts toward higher frequencies with the increase in temperature. This supposes the presence of a correlation between the mobile charge carriers movement. The peaks are broad, which can be attributed to the distribution of relaxation time due to a non-Debye nature of the material [78]. The asymmetry in peak broadening shows the spread of relaxation times with different time constants. The nature of the observed modulus spectra confirms the existence of a hopping mechanism in the electrical conduction of the material [79]. Inside the graphs in Fig. 13, Arrhenius plots for relaxation times and the plots of $M''/M''_{\max}$ vs $\log(f/f_{\max})$ at 32 - 68 °C for MA₃Bi₂I₉ and 28 - 69 °C FA₃Bi₂I₉, are given. The nearly perfect overlap of the curves for all temperatures into a single master curve indicates that the relaxation describes the same mechanism at various temperatures. Fig. 13 gives Arrhenius plots for relaxation times for same temperatures given in the previous figure. The relaxation mechanism was analyzed by the thermally activated Arrhenius behavior:

$$\tau_M = \tau_{M0} \exp\left(\frac{E_{a,M}}{k_B T}\right)$$

where $E_{a,M}$ is the activation energy required for the relaxation process, τ_{M0} is the pre-exponential factor and τ_M corresponds to the peak frequency of M'' for a given temperature. The activation

energies for relaxation processes, obtained from the plot $\ln \tau$ vs $1000/T$ are $0.482 \text{ eV} \pm 0.003 \text{ eV}$ for $\text{MA}_3\text{Bi}_2\text{I}_9$ and $0.487 \text{ eV} \pm 0.003 \text{ eV}$ for $\text{FA}_3\text{Bi}_2\text{I}_9$, close to the activation energy extracted from conductivity.

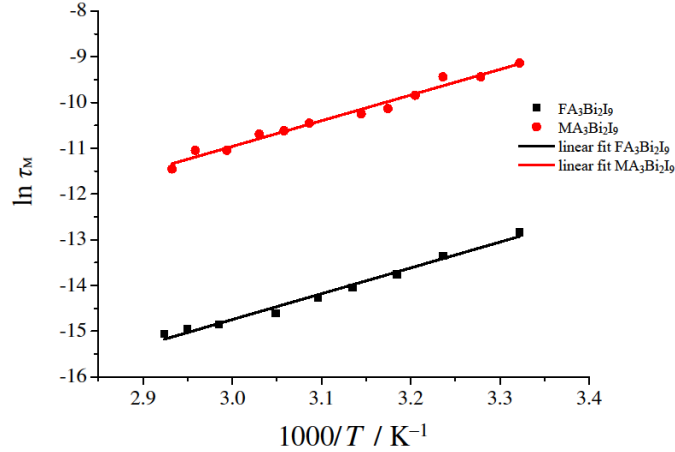


Fig.13. $\ln \tau_M$ vs $1000/T$, for $\text{MA}_3\text{Bi}_2\text{I}_9$ (red circles) and $\text{FA}_3\text{Bi}_2\text{I}_9$ (black squares).

To our knowledge, there is no available data for Bi-based HOIPs. Similar cases for reported values of activation energy for Bi-based perovskites are CuBiI_4 and Ag_3BiI_6 which showed activation energy of 0.44 eV [80].

A comparison of the impedance with electrical modulus data can distinguish between the long-range and localized conduction mechanisms, i.e., defect relaxation or non-localized conduction (ionic or electronic conductivity). Grain boundaries' contribution is highlighted in the $-Z''$ plots, while grains contribution is highlighted in the M'' plots. It has been shown that for a long-range process, peaks in $-Z''$ and M'' versus $\log f$ plots will occur at the same frequency, and for conduction involving short-range migration of charge carriers the peaks are at different frequencies [81]. Thus, one can separate the various contributions. A combined plot of M''/M''_{max} and Z''/Z''_{max} versus frequency for lowest and highest temperatures (a) for $\text{MA}_3\text{Bi}_2\text{I}_9$ and (b) for $\text{FA}_3\text{Bi}_2\text{I}_9$ is shown in Fig. 14. For the present systems, the M'' and Z'' peaks are separated and do not overlap, suggesting the presence of components from both long-range and localized relaxation in both $\text{MA}_3\text{Bi}_2\text{I}_9$ and $\text{FA}_3\text{Bi}_2\text{I}_9$ [81].

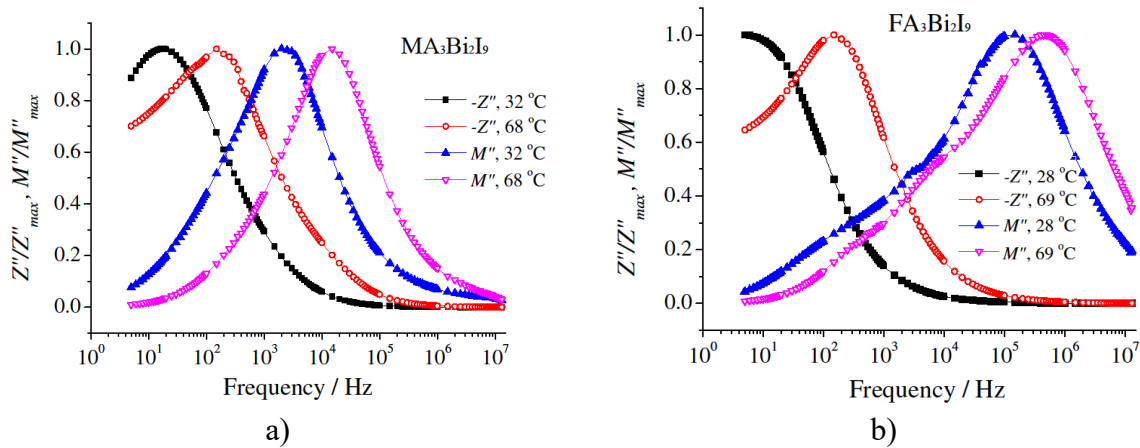


Fig. 14. M''/M''_{max} and Z''/Z''_{max} versus frequency for the lowest and the highest temperatures for (a) MA₃Bi₂I₉ and (b) FA₃Bi₂I₉.

When compared to lead-based perovskites such as MA₃Bi₂I₉ and FA₃Bi₂I₉, the bismuth analogues MA₃Bi₂I₉ and FA₃Bi₂I₉ exhibit different electrical transport behavior. Impedance spectroscopy of MAPbI₃ and FAPbI₃ typically reveals lower activation energies (0.2 - 0.3 eV) [82], faster charge transport [83], and less resistive grain boundaries [82,83], which underpin their high photovoltaic efficiencies exceeding 20 %. In contrast, MA₃Bi₂I₉ and FA₃Bi₂I₉ show activation energies around 0.5 eV, pronounced grain boundary resistance, and non-Debye relaxation, indicating slower thermally activated hopping conduction. While this limits their charge-carrier mobility compared to lead perovskites, the coexistence of long-range and localized conduction mechanisms confirms their semiconducting nature. Importantly, the reduced toxicity and enhanced stability of bismuth-based perovskites make them attractive lead-free alternatives, even if further optimization of film morphology and grain boundary engineering is required to approach the performance of lead-based systems. Also, based on the comparable energy bandgaps, similar structures as well as their activation energies, make them an ideal doping material [84] for improving the properties of the other perovskites for their use in different devices.

4. Conclusion

Thin films of formamidinium bismuth iodide, [(CH(NH₂)₂)₃Bi₂I₉], FA₃Bi₂I₉, and methylammonium bismuth iodide, [CH₃NH₃]₃Bi₂I₉, MA₃Bi₂I₉ were prepared and analyzed using different techniques for structure characterization (XRD and SEM imaging). In addition, their electrical properties were studied in detail. The main focus of the prepared thin films was directed towards analyzing the energy bandgap using UV-Vis spectroscopy. According to the obtained diffractograms, the crystal structure of these compounds and the successful preparation of the thin films were confirmed. Additionally, elemental analysis (EDX) confirmed the successful synthesis and the purity of the films. The SEM imaging gave insight into the

morphology of the thin layer that was deposited on the glass surface. The SEM images helped to reveal the homogeneity of the film.

The observed structural differences between MA₃Bi₂I₉ and FA₃Bi₂I₉ thin films highlight the influence of organic cation size and symmetry on crystallographic orientation and film quality, which are critical parameters for optimizing optoelectronic performance.

Based on the results obtained from the Tauc plot fitting on the linear part of the function, it was established that both MA₃Bi₂I₉ and FA₃Bi₂I₉ behave as indirect-gap semiconductor having values of 1.98 and 1.74 eV, respectively for the indirect optical energy bandgap at room temperature. These values are somewhat higher than the lead analogs, but still, they are lower than most of the HOIPs, having up to 2.3 eV [85,86]. The relatively low values of the optical bandgap give the opportunity to obtain low-energy bandgap perovskites with Bi mixed B-position cations.

According to impedance spectroscopy, both compounds behave in the same manner. In the high frequency region, based on the Z'' , these materials show the presence of space charge. Both materials confirm the characteristic semiconducting behavior of perovskites, mainly through the grain boundaries that are highly resistive.

Activation energies of σ_{dc} plots are estimated to 0.505 eV for MA₃Bi₂I₉ and 0.498 eV for FA₃Bi₂I₉, suggesting thermally activated hopping conduction above room temperature in both materials. Similar values were obtained from impedance and modulus analysis. From the ac conductivity study, we found that the correlated-barrier-hopping model explains the mechanism of charge transport for both MA₃Bi₂I₉ and FA₃Bi₂I₉. A scaling investigation of modulus spectra defines temperature independent relaxation mechanism for both materials.

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6. Statements and Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.