

Molecular Ink-Based Synthesis of $\text{Bi}(\text{S}_z\text{Se}_{1-z})(\text{I}_x\text{Br}_{1-x})$ Solid Solutions as Tuneable Materials for Sustainable Energy Applications

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Q-1D van der Waals chalcogenides emerge as promising materials for advanced energy applications, combining tunable optoelectronic properties and composed by earth-abundant and non-toxic elements. However, their widespread application remains hindered by challenges such as anisotropic crystal growth, composition control and lack of knowledge on optoelectronic properties. A deeper understanding of the intrinsic limitations of these materials, as well as viable defect mitigation strategies like the engineering of solid solutions, is critical. This work presents a low-temperature synthesis route based on molecular ink deposition enabling direct crystallization of tunable $\text{Bi}(\text{S}_z\text{Se}_{1-z})(\text{I}_x\text{Br}_{1-x})$ solid solutions without need for binary chalcogenide precursors. This approach yields phase-pure films with precise control over morphology, composition, and crystallographic orientation. XRD analysis and DFT calculations confirm the formation of homogeneous solid solutions, while optoelectronic measurements reveal the distinct roles of halogen and chalcogen anions in tuning bandgap energy and carrier type, with Se shifting downwards the conduction band. The versatility of this synthesis technique enables morphology control ranging from compact films to rod-shaped microcrystals, expanding the functional adaptability of these materials. These findings offer a foundational framework for defect engineering and the scalable integration of chalcogenides in next-generation energy technologies, including photovoltaics, photocatalysis, thermoelectrics, and chemical sensing.

1. Introduction

2D van der Waals (vdW) materials, such as MoS_2 and graphene, have garnered significant attention for functional applications due to their high surface area, excellent carrier mobility, and mechanical robustness.^[1–5] However, their limited tunability in terms of bandgap and electronic properties restricts their versatility, highlighting the need for alternative materials with greater compositional and structural adaptability. In this context, Q-1D vdW materials, such as MChX ($\text{M} = \text{Sb, Bi}$; $\text{Ch} = \text{S, Se}$; $\text{X} = \text{I, Br}$) chalcogenides, are emerging as promising candidates for next-generation functional applications.^[6,7] Chalcogenide materials crystallize in an orthorhombic crystalline structure with symmetry characterized by the Pnma space group and consisting of $(\text{M}_2\text{Ch}_2\text{X}_2)_n$ covalently bonded ribbons extending along one crystallographic axis, with weak vdW interactions binding the ribbons in orthogonal directions. The Q-1D nature originates from the ns^2 lone pair of

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DOI: 10.1002/smt.202501723

pnictogen cations, which distorts their coordination environment and creates an asymmetric electronic density.^[8] This structure has been proposed to lead to perovskite-like electronic characteristics like defect tolerance, high dielectric constants, and efficient charge transport resulting in unique, anisotropic optoelectronic properties. Their intrinsic anisotropy in transport and optical properties makes them promise for directional control in electronic and photonic systems. The strong quantum confinement and edge-dominated surfaces enhance their tunability and chemical reactivity, offering a wide bandgap range, from 1 to 3.5 eV.^[9–12] Importantly, the presence of heavy elements in many MChX compounds enhances phonon scattering, making them suitable for thermoelectric applications.^[7,13,14]

Despite their promising optoelectronic properties, the current performance of chalcogenide-based optoelectronic devices remains significantly poor.^[15–17] These results underscore the urgent need for further investigation into the fundamental limitations of chalcogenide semiconductors and the development of strategies to overcome them. One key challenge arises from their intrinsic anisotropy. While enabling high carrier mobility along covalent directions, it promotes ribbon-like crystallite growth, hindering the formation of compact, uniform films and leading to poor in-plane conductivity and inefficient charge extraction. Advancing morphology control techniques for Q-1D materials is crucial to unlocking their full potential in energy applications. Also, although chalcogenides have been suggested to exhibit defect tolerance, recent experimental and theoretical studies^[18,19] suggest that deep defect states still play a detrimental role. Among the strategies proposed to mitigate these effects,

the use of solid solutions has shown promise due to ionic radius mismatch suppressing ion exchangeability and increasing the formation energy of point defects.^[19]

Various physical and chemical synthesis routes for Bi-based chalcogenides have been established in the literature. They include hydrothermal deposition, co-evaporation of precursor binary chalcogenides followed by reactive annealing in a halogen-rich atmosphere, or sonochemical methods using elemental compounds.^[20–25] However, these methods are often limited to one or two materials within the chalcogenide family. The use of molecular inks has also been reported,^[16,17] and this method has proven its effectiveness in the synthesis of other chalcogenides. “Alkahest” systems based on hydrazine or amine-thiols, as well as metal–organic–chalcogen complex-based systems, have reached a high level of maturity in producing high-efficiency devices.^[25–30] Chalcogenourea ligands (thioureas/selenoureas) are powerful enablers for low-temperature conversion of molecular inks into metal chalcogenides. They combine facile chalcogen transfer chemistry, tunable coordination to metal centers, and decomposition kinetics that can be tailored by ligand substitution.^[31,32] Seminal work from the Owen group showed that substituted thioureas act as single-source or co-precursors whose reactivity spans many orders of magnitude.^[33] By choosing ligand substituents one can control the conversion rate, nucleation density and ultimately crystal size and composition during mild thermolysis. Recent studies have extended this concept to selenoureas and other chalcogen-rich precursors, demonstrating low-temperature formation of metal selenides and solution-processed chalcogenide thin films from molecular formulations.^[34]

Building on this knowledge, we develop a general chemical ink for synthesizing chalcogenides. We synthesize for the first time the complete Bi-chalcogenide family, including BiSI, BiSBr, BiSeI, and BiSeBr, and their corresponding solid solutions, using the same solvent system, with precise control over morphology, stoichiometry, and optoelectronic properties. The approach is based on the spin-coating of precursor inks dissolved in *N,N*-dimethylformamide (DMF), followed by a low temperature thermal annealing step to drive crystallization of the ternary phase (Figure 1). The synthesis and characterization of Bi-based chalcogenide solid solutions have been explored as a foundation for future material engineering strategies. In the first part of the study, we show the phase purity of the synthesized compounds with no segregation of secondary phases. In-depth investigation of their structural characteristics is performed through X-ray diffraction analysis. We demonstrate excellent compositional control, supporting the viability of this direct synthesis method without the need for binary chalcogenide precursor layers.^[35] Also, we develop strategies that facilitate control of orientation and film morphology, crucial for functionality. In the second part, we analyze the optoelectronic properties of solid solutions, disentangling the individual roles of the chalcogen and halogen anions in tuning charge carrier type, and optical absorption, highlighting their potential for band structure engineering. Density Functional Theory (DFT) calculations were conducted to complement the analysis of the optoelectronic and structural properties of solid solutions. This combination of tunable material chemistry and scalable processing places chalcogenide semiconductors as promising candidates for a wide range of applications

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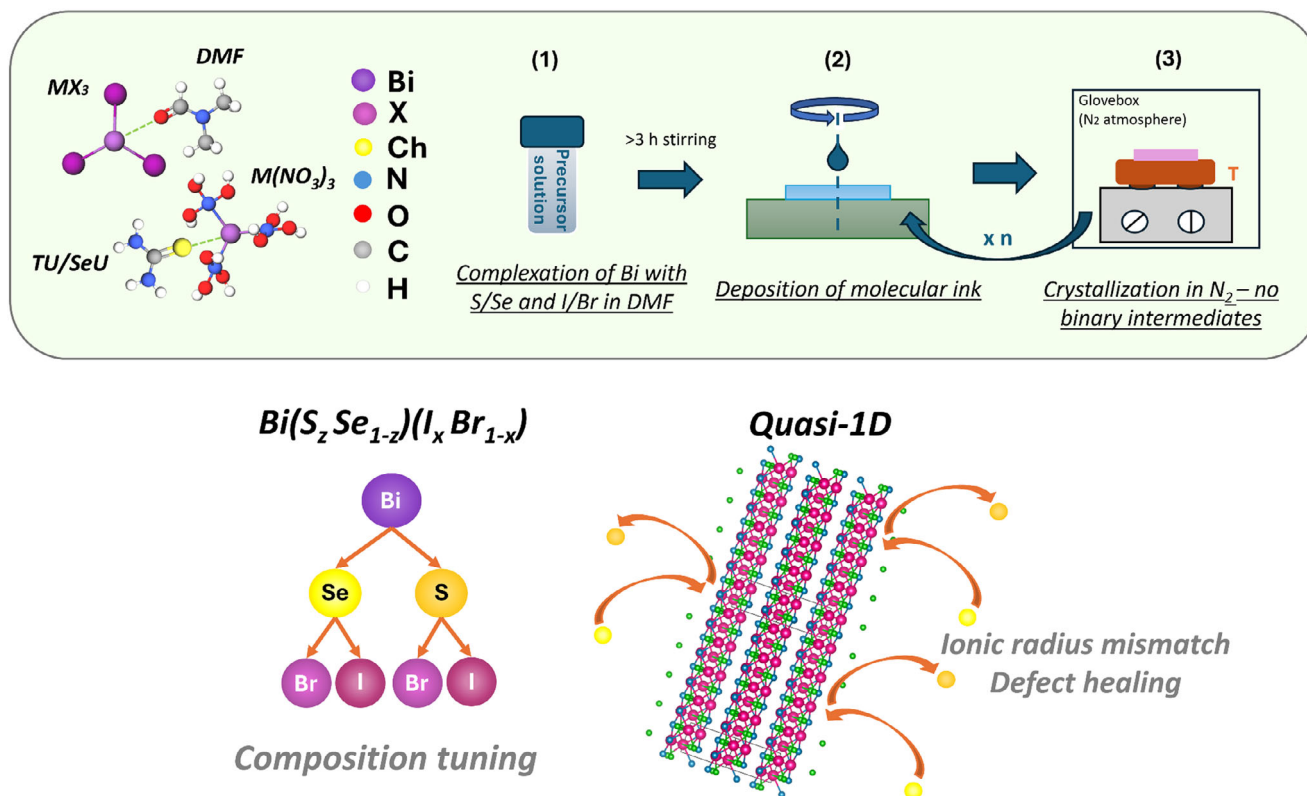


Figure 1. The solution-processed synthesis enables direct formation of Bi-based chalcogenides with controlled composition and crystallinity. The resulting solid solutions offer both optoelectronic tunability and intrinsic point-defect healing through lattice strain relaxation.

including photovoltaics, photocatalysis, thermoelectricity, and sensing.

2. Results and Discussion

2.1. Solid Solution Phase Verification

The characteristic X-ray diffraction (XRD) patterns for the complete set of Bi-chalcogenide compounds listed in Table S1 (Supporting Information) are shown in Figure 2. A magnified view of the peak corresponding to the (110) plane is included to highlight the shift in its position for the solid solutions. Quantitative pattern matching refinement, performed using the Le Bail method, confirmed an orthorhombic structure with a Pnma space group for all compounds.^[36] The samples analysed were synthesized on fluorine doped tin oxide (FTO) coated glass (SnO₂, tetragonal structure with P42/mnm space group), whose diffraction peaks are marked with grey dashed lines. For the halogen solid solutions BiSI_{0.5}Br_{0.5} and BiSI_{0.7}Br_{0.3}, a minor bromine-poor phase, Bi_{12.89}Br_{2.85}S_{17.15}, was detected. The refined fittings and variation of cell parameters are provided in the Supporting Information.

Figure 2d,f clearly illustrate the shift in the position of the (110) peak. The gradual substitution of sulfur with selenium in BiSBr results in a shift toward lower angles, indicating an expansion of the unit cell due to the larger ionic radius of selenium. Conversely, when iodine is replaced with bromine in BiSI, the unit cell contracts, causing the diffraction peaks to shift toward higher

angles. This behavior is further elucidated by the refined lattice parameters of the final structures.

For the four parent compounds (BiSI, BiSBr, BiSeI, and BiSeBr), the obtained lattice parameters were $a = 8.45(12)$; $8.10(29)$; $8.64(71)$; $8.21(41)$ Å, $b = 10.11(92)$; $9.77(73)$; $10.49(28)$; $10.44(73)$ Å, and $c = 4.17(13)$; $4.04(39)$; $4.19(91)$; $4.11(05)$ Å, respectively. These values are in excellent agreement with previously reported data.^[35,37–40]

When inspecting the cell parameters of the solid solutions (illustrated in Figures S1 and S2, Supporting Information), the lattice expansion or contraction resulting from ion substitution can be quantitatively observed. Substituting ions with smaller radii for those with larger radii leads to an increase in the unit cell volume. This trend is typically described through Vegard's rule which states that the lattice parameter of an alloy varies linearly with the concentration of its constituent elements.^[41] Both chalcogen and halogen solid solutions appears to follow reasonably well Vegard's Rule (see Figure 2e,g). This supports the formation of a continuous solid solution, a structural stability across the range and the systematic incorporation of the substituent into the lattice.

In the chalcogen solid solution, a clear linear increase in all lattice parameters is observed as sulfur is progressively replaced by selenium. Particularly significant is the expansion of the b -parameter, which increases by 6.86%, from 9.77 Å in BiSBr to 10.44 Å in BiSeBr. In contrast, for the a - and c -parameters the increase is much lower, 1.37% and 1.64% respectively. This fact strongly confirms that the

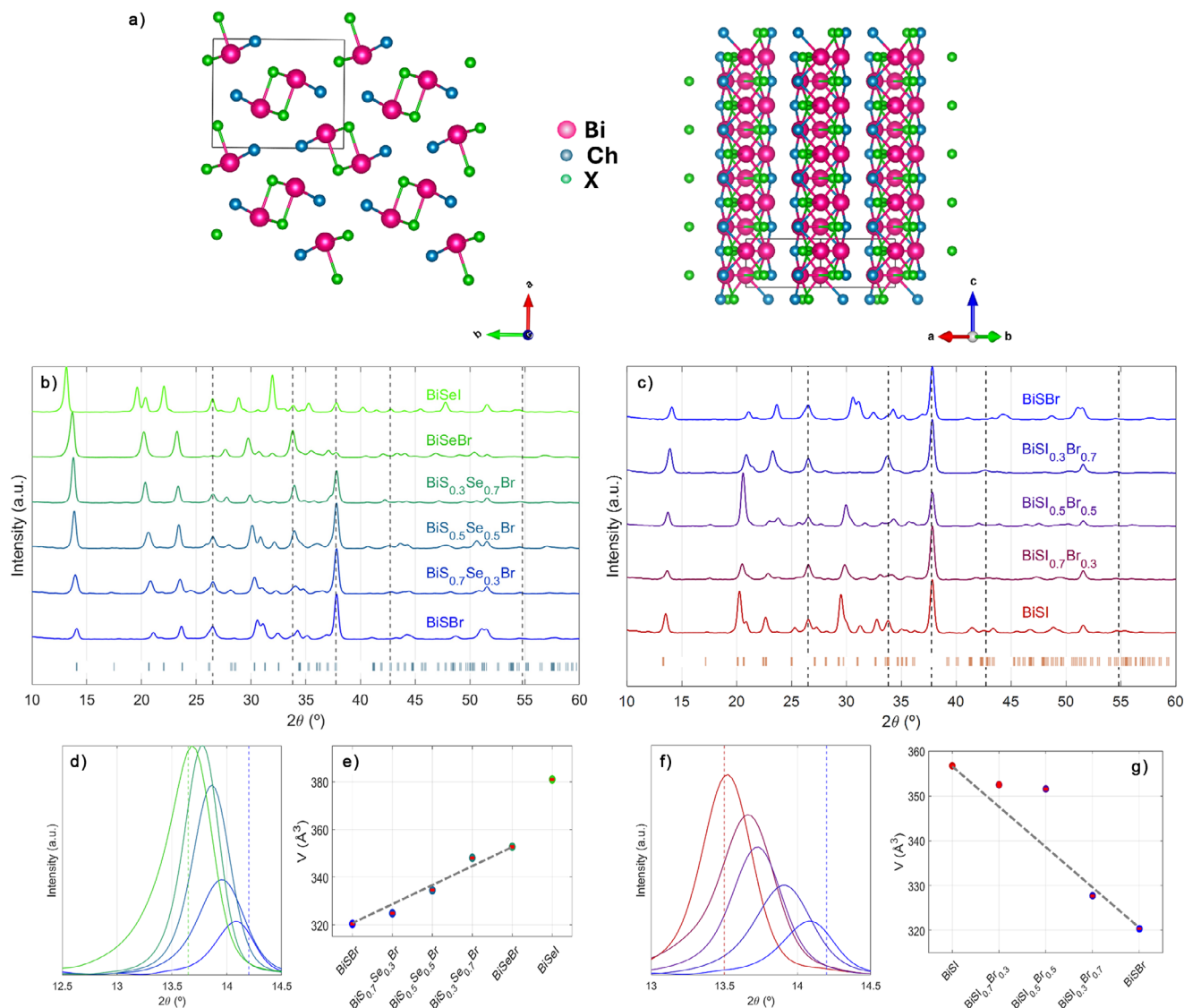


Figure 2. a) Crystal structure of MChX b,c) XRD patterns for the Bi-chalcholides solid solutions and parent compounds, with the reference (hkl) peaks of BiSBr and BiSI highlighted in blue and red, respectively. FTO peaks are indicated as grey dashed lines d,f) Magnified views of the peak corresponding to the (110) plane of the chalcholides. e,g) Unit cell volume for Bi-chalcholides solid solutions. The dashed line indicates the theoretical evolution following Vegard's Rule (error bars shown in red).

b-direction corresponds to the one where Bi-Ch interactions are predominant.

In contrast, the halogen solid solution does not exhibit a strictly linear decrease in lattice parameters upon substituting iodine with bromine; instead, a negative bowing effect is observed. (Figure S2, Supporting Information). A plateau in the lattice values is observed until bromine becomes the dominant halide ($x \geq 0.5$), beyond which the parameters drop sharply toward the values of BiSBr. Additionally, the relative variation in lattice dimensions is slightly greater along the *a*-axis (4.28%) than along the *b*- and *c*-axes (3.37% and 3.05%, respectively), differently to the trend observed in the chalcogen series. This is in agreement with the fact that the Bi-X interactions are mostly placed in the *a*-direction.

These results highlight the distinct local bonding effects that define the structural behavior of these materials, which consist

of Q-1D motifs. The structure combines covalent bonding within the 1D ribbons (along the *c*-axis) and vdW interactions between the ribbons in the *ab*-plane. Chalcogen and pnictogen ions constitute the core of the 1D ribbons, while halogen ions are located on the edges. Halogen substitution influences interchain interactions predominantly through halogen-halogen vdW interactions and does not strictly follow Vegard's law. Unlike strong covalent bonding, vdW interactions rely on the presence of transient dipoles. The easier it is to distort the electron cloud of an ion, the larger the induced dipole moment and, consequently, the stronger the dispersion forces. These interactions are therefore strongly governed by the polarizability of the constituent ions. These vdW interactions are prominently affected by the polarizability of the ions involved. The higher polarizability of I^- may provide stronger and stiffer interactions, especially in the

Table 1. DFT values of lattice parameters for the four Bi-chalcogenide parent compounds with the representative of the vdW interaction energy.

	a[Å]	b[Å]	c[Å]	vdW interaction energy [meV/ Å ³]
BiSI	8.342	10.024	4.144	7.39
BiSBr	8.056	9.518	4.032	6.25
BiSeBr	8.079	10.704	4.083	7.05
BiSeI	8.550	10.304	4.190	8.19

ribbon-stacking direction. When iodine is the dominant halogen, this stronger inter-ribbon locks the lattice parameters, having a rigid structure. As bromine content increases, the weaker vdW interactions that introduces thanks to its lower polarizability possibly relax these constraints, allowing lattice parameters to adjust more freely. Then, a sharp drop in lattice constants is observed when bromine becomes the predominant halogen. Consequently, halogen substitution is expected to play a key role in determining morphology and stacking stability of the Q-1D structures in these materials (see Morphology Control Section).

To further support this hypothesis, ab initio calculations based on DFT were carried out for the four parent compounds to quantify the strength of vdW interactions (see [Experimental Section](#) for more details). The results are summarized in [Table 1](#). The computed lattice parameters, included in [Table 1](#), show good agreement with the experimental values, with a slight underestimation. This consistency serves as a validation of the reliability of the performed simulations. Importantly, iodine-based compounds display higher normalized vdW energy differences compared to their bromine counterparts (BiSeI > BiSI > BiSeBr > BiSBr). In particular, the highest vdW interaction energy (i.e., the difference between total ground energies calculated with and without dispersion interactions) is obtained for BiSeI, with 8.19 meV Å⁻¹,^[3] significantly higher than the 6.25 meV Å⁻³ of BiSBr. Analyzing the impact of halogen and chalcogen substitutions reveals distinct trends: replacing S with Se in BiSI and BiSBr increases the vdW interaction energy by 10.8% and 12.8%, respectively, while substituting Br with I in BiSBr and BiSeBr results in larger increases of 18.2% and 16.2%. These results highlight the stronger influence of halogen substitution—particularly iodine—on enhancing vdW interactions. These theoretical results support the general wisdom that enhanced inter-ribbon interactions are formed with iodine, contributing to greater structural rigidity and anisotropy. The higher polarizability of I⁻ ions leads to stronger vdW interactions that effectively lock the lattice volume, maintaining it nearly constant until a significant substitution of iodine by bromine occurs. Consequently, a non-linear trend in the lattice parameter evolution is expected and justifies the observed deviation from Vegard's law. These stronger interactions likely restrict atomic rearrangement in the ab-plane while favoring ribbon elongation, resulting in highly anisotropic, needle-like morphologies in iodine-rich compositions.

Raman spectroscopy was additionally performed on the Bi-based parent compounds and four of their solid solutions. The corresponding spectra is presented in [Figure S3](#) (Supporting Information). The Raman spectra can be divided into two distinct regions: vibrational modes below 150 cm⁻¹ are attributed to Bi–

X (halogen) bonds, while those above 150 cm⁻¹ correspond to Bi–Ch (chalcogen) bonds.^[35] In both regions, the solid solution samples exhibit broader peaks, with increased full width at half maximum (FWHM), relative to the parent compounds, indicating higher lattice disorder. Moreover, the absence of sharp, well-resolved peaks and the continuous shift of a single set of modes, rather than the coexistence of two distinct sets, provides strong evidence for the formation of a true solid solution, rather than a physical mixture of separate crystalline phases. This interpretation is consistent with the XRD results.

2.2. Elemental Composition Analysis

Elemental characterization of all Bi-chalcogenides, Bi(S_zSe_{1-z})(I_xBr_{1-x}), was performed at the micrometre scale using Ion Beam Analysis (IBA) techniques. A combination of Particle-Induced X-ray Emission (PIXE) and Elastic Backscattering Spectrometry (EBS) were employed in a scanning nuclear microprobe to quantify elemental concentrations and assess depth profiles. PIXE enables high-precision elemental composition analysis without the need for calibration, detecting elements with atomic numbers above Z = 11 at ppm resolution.^[42,43] EBS provides non-destructive in-depth information, enabling the determination of both layer thickness and composition.

PIXE 2D scanning maps of 113 × 113 μm² size were first performed in each sample to determine the elemental distribution homogeneity. Then, point analyses were carried out in selected regions to obtain a more precise elemental composition. In each measurement we first fit the EBS spectrum with a depth profile. Once this composition profile is correctly fitted, we use it as an initialization parameter in the PIXE spectrum fitting to accurately extract the bulk elemental concentration of the region selected.

[Figure 3a–c](#) presents the EBS-fitted and PIXE spectra for BiS_{0.3}Se_{0.7}Br sample, and the elemental distribution in the 2D maps. The IBA measurements for all the studied compounds are presented in the [Supporting Information](#). The 2D maps show the micrometre-scale homogeneity of the films, with no exposed substrate. Interestingly, in Se-containing samples, inhomogeneous regions are observed where the thickness of the active layer increases (the silicon signal from the Soda-Lime-Glass (SLG) decreases) and appear to be richer in bismuth and selenium. Therefore, these abnormal regions may originate from amorphous precipitates from bismuth-selenium complexes within the solution. The 2D-PIXE map, [Figure 3c](#), also reveals a uniform distribution of both sulfur and bromine in the film, with no distinguishable domains. This supports even more the formation of a true solid solution, rather than separate crystalline domains as determined in the structural and vibrational characterizations (XRD and Raman).

Combining EBS and PIXE spectra from different point analyses the average elemental composition of the films was performed. [Table 2](#) presents the obtained atomic percentage of each element in the chalcogenide films. Although PIXE also detects elements from the substrate, the interlayer element diffusion observed in EBS spectra is attributed to morphology and rugosity effects rather than actual elemental diffusion (discussion in [Supporting Information](#)). Only Bi, S, Se, I, and Br were considered as part of the chalcogenide layer.

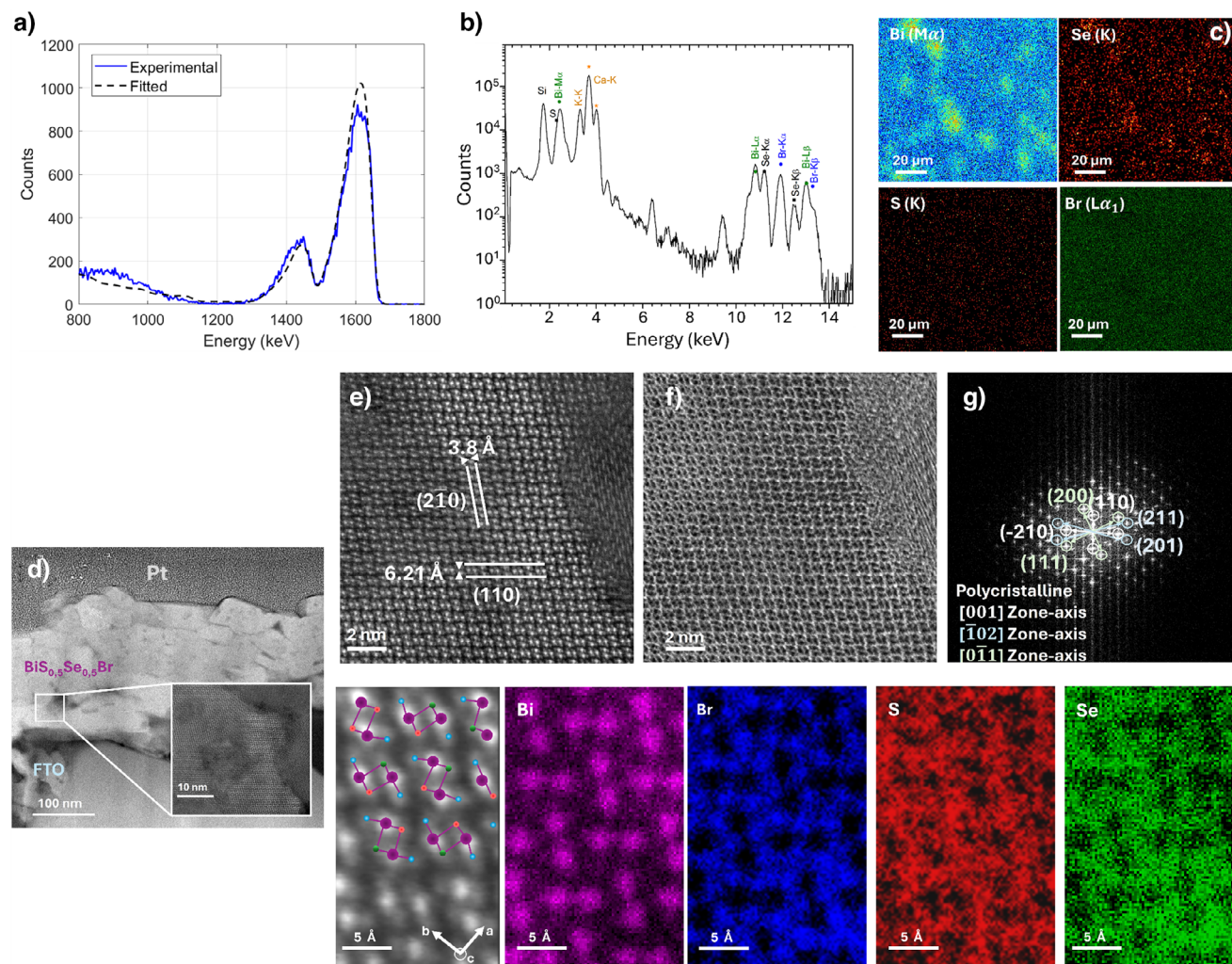


Figure 3. a) EBS (experimental and fitted), b) PIXE spectra and c) elemental maps ($113 \times 113 \mu\text{m}^2$) for $\text{BiS}_{0.3}\text{Se}_{0.7}\text{Br}$ solid solution film on glass. d) STEM cross-section of the $\text{BiS}_{0.3}\text{Se}_{0.5}\text{Br}$ on FTO with high-resolution image insert. e) HAADF-STEM image showing ribbon-like atomic arrangement of heavy atoms (brightest spots being Bi atoms). f) ABF-STEM image revealing the spatial distribution of lighter elements (S, Se, Br) around Bi atoms. g) FFT pattern for the selected region. Bottom: HAADF-STEM image of with corresponding EELS elemental maps for Bi-M, Br-L, S-K and Se-L lines.

The obtained composition of the solid solutions closely aligns with the molecular precursor ratios in the formulated solutions. This confirms that for $\text{BiSI}_x\text{Br}_{1-x}$ and $\text{BiS}_z\text{Se}_{1-z}\text{Br}$, the intended x and z values in the precursor ink are effectively transferred to the final film composition without significant losses of material during the thermal treatment. These results highlight the strength of the methodology employed in this work, as it enables precise control over the film composition.

High-Resolution Transmission Electron Microscopy (HRTEM) was conducted on a Bi-chalcogenide solid solution to investigate its crystallinity and composition at the atomic scale. $\text{BiS}_{0.5}\text{Se}_{0.5}\text{Br}$ was selected for analysis due to the observation of certain inhomogeneities in the chalcogen solid solutions during IBA measurements. Consequently, this sample was examined to confirm the absence of compositional segregation. HRTEM analysis of the lamella revealed a polycrystalline structure, composed of chalcogenide Q-1D structures stacking both transversely and longitudinally (Figure 3d). Transversal sections

displayed single-crystalline domains with lateral dimensions corresponding to the Q-1D structure diameter, $\approx 50 \text{ nm}$. In contrast, longitudinal sections, along the column axis, exhibited multiple crystalline domains stacked vertically. These observations suggest that each Q-1D structures consists of vertically stacked crystalline domains, with each domain spanning the full width of the column. This result provides insight into the film growth mechanism. Since the deposition involves multiple spin-coating steps to achieve the desired thickness, each layer can introduce a crystalline extension on top of the initial Q-1D structure, potentially with a different crystallographic orientation. As a result, a quasi-epitaxial growth of the columns along the vertical direction with stacking fault formation is proposed between spin-coating steps.

Figure 3e–g show magnified STEM maps of the region highlighted in Figure 3d, along with the corresponding Fast Fourier Transform (FFT) pattern. From the FFT, interplanar distances of the crystalline planes were extracted and assigned to specific

Table 2. Elemental concentration of Bi-chalcogenide solid solutions obtained from PIXE spectra.

	Bi [at%]	S [at%]	Se [at%]	I [at%]	Br [at%]
BiSI	34.3 ± 0.11	33.9 ± 0.12	—	31.7 ± 0.01	—
BiS _{0.7} Br _{0.3}	35.6 ± 0.18	30.8 ± 0.68	—	23.4 ± 0.90	9.9 ± 0.37
BiS _{0.3} Br _{0.7}	32.9 ± 0.93	31.3 ± 1.54	—	9.8 ± 0.35	25.9 ± 1.63
BiSBr	32.9 ± 1.73	33.9 ± 1.82	—	—	33.0 ± 3.55
BiS _{0.7} Se _{0.3} Br	36.3 ± 0.76	23.2 ± 0.76	10.1 ± 0.47	—	30.3 ± 0.50
BiS _{0.3} Se _{0.7} Br	34.8 ± 0.82	10.6 ± 1.48	25.1 ± 1.62	—	29.4 ± 0.96
BiSeBr	40.5 ± 0.01	—	31.9 ± 0.01	—	27.5 ± 0.01
BiSeI	36.2 ± 0.47	—	26.1 ± 0.22	37.6 ± 0.53	—

Miller indices. Strong agreement exists between the refined lattice parameters and the interplanar distances measured from the FFT. For example, the (210) plane, which has a calculated interplanar spacing of 3.76 Å based on the fitted diffraction data, appears with a spacing of 3.80 Å in the FFT pattern. Moreover, the FFT reveals signals from three different zone-axes: The (200) and (110) planes belonging to [011] zone-axis, the (210) and (110) corresponding to [001] zone-axis and the (201) and (211) planes associated to [102] zone-axis. This indicates the presence of three crystalline domains within the selected region. In the HAADF-STEM image (Figure 3-Bottom), the central crystalline domain exhibits an arrangement of atom pairs alternating in vertical and horizontal orientations, characteristic of the [001] zone-axis, viewed along the *c*-axis. These atom pairs represent the covalently bonded ribbons of the vdW structure, as projected onto the *ab* plane.

Electron Energy Loss Spectroscopy (EELS) measurements conducted on the crystalline domain oriented along the [001] zone axis (Figure 3-Bottom) allowed direct visualization of the atomic distribution, where bismuth atoms form alternating vertical and horizontal pairs surrounded by lighter elements. Elemental maps for Bi, Br, S, and Se were obtained and show excellent agreement with the theoretical structure of the material (overlaid on the STEM image for comparison). Quantitative analysis of the EELS spectra was also performed to determine the elemental composition (Figure S4, Supporting Information). Three distinct regions, each measuring 15 Å × 30 Å, were analysed. The resulting average composition was 32 ± 5 at% Bi, 32 ± 3 at% Br, 17.1 ± 1.5 at% S, 16.7 ± 1.9 at% Se, which is in good agreement with the expected stoichiometry from the precursor solution, and are consistent with those obtained from IBA measurements. This confirms the formation of an actual solid solution, with stoichiometric composition with no segregation or formation of nanodomains.

2.3. Morphology Control

Beyond precise control over composition and phase, the synthesis approach presented in this study enables systematic tuning of the morphology of chalcogenide compounds. As the optimal orientation and packing density of the material can vary depending on the target application, this morphological flexibility significantly enhances the potential for incorporating chalcogenides into diverse fields. For photovoltaic devices, compact and continuous thin films are essential to ensure proper top contact deposition and efficient extraction of photogenerated carriers

(Figure 4b). For sensing and catalysis, a high aspect ratio is preferred to maximize surface exposure and enhance interaction with the surrounding environment—making long, vertically aligned Q-1D structures more suitable (Figure 4b). For thermoelectric applications, a horizontal alignment of the rods is desirable to optimize in-plane transport (Figure 4b). Four parameters have been identified to play a critical role in this morphology tuning: substrate skewness and kurtosis, Bi(NO₃)₃·5H₂O:BiX₃ ratio in the precursor solution, spin-coating steps with different solution concentrations, and the solid-solution formulation (Figure 4a).

The choice of substrate proves to be the most critical parameter for controlling the orientation of the chalcogenide films. Hydrophilic substrates are preferred, as they promote good wettability of the precursor solution, ensuring uniform coverage and film formation. However, if the contact angle is too low, the solution may spread too thinly during spin-coating, resulting in a very thin layer that leads to the formation of sparse and under-sized chalcogenide rods after annealing. Figure S5 (Supporting Information) presents the measured contact angles and surface tensions for various substrates. Among them, ZnOS, CdS, TiO₂, FTO, and np-ZnO exhibit optimal surface tension that support desirable film morphology. In contrast, ZnSnO was found to be highly hydrophobic. Nevertheless, wettability alone does not fully account for the observed differences in morphology. As shown in Figures S6 and S7 (Supporting Information), films deposited under identical conditions on TiO₂ and ZnOS substrates exhibit markedly different morphologies, despite having similar surface tensions. On CdS and ZnOS, the chalcogenide rods tend to grow more vertically, whereas on TiO₂ they tend to lie parallel to the substrate. Compared to TiO₂-based sample, the ZnOS substrate yields a more compact film, characterized by a merging of adjacent rods.

Atomic Force Microscopy (AFM) was performed on the substrates used for the growth of chalcogenide films (Figure S8, Supporting Information). Notable differences in surface morphology between substrates are observed. FTO, molybdenum, and TiO₂ exhibit relatively smooth, grainy surfaces, while CdS, ZnOS, and ZnSnO display grains with small protuberances. Nevertheless, the root mean square (RMS) roughness (Table 3) show no clear trend. For instance, FTO exhibits a relatively high RMS roughness of 8.99 nm, greater than that of CdS or ZnOS.

To better quantify these surface features, we explored additional statistical descriptors of the height distribution: skewness and kurtosis, which represent the asymmetry and sharpness of

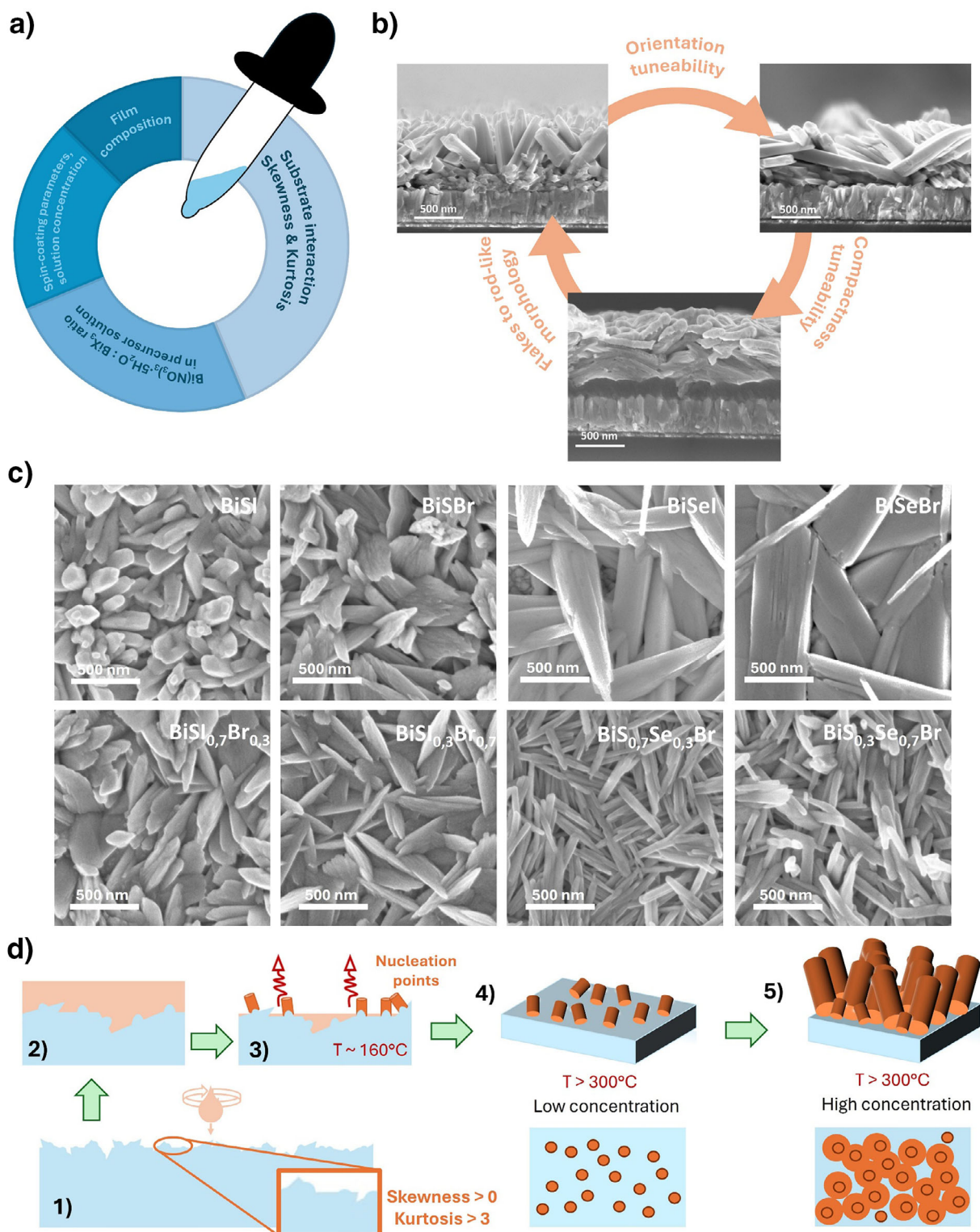


Figure 4. a) Diagram summarizing the key parameters controlling morphology, with different weights depending on the observed influence on crystal structure. b) SEM cross-sectional images of BiSBr films grown under varying conditions reveal three morphologies: horizontally and vertically tilted ribbons, and compact film. c) Top-view SEM images of Bi-chalcogenide solid-solutions on FTO/ZnOS substrates. d) Solution-based synthesis method for compact films (substrates with skewness > 0 and kurtosis > 3). The process involves: (1-2) spin coating a low-concentration precursor solution, (3) mild annealing to nucleate grains at surface features, (4) high-temperature annealing to crystallize a seed layer, and (5) deposition of a higher-concentration solution, followed by crystallization to produce a dense film.

Table 3. Roughness, skewness and kurtosis values in the seven substrates studied obtained by AFM.

	RMS [nm]	Skewness	Kurtosis
Mo	7.38	−0.197	3.49
FTO	8.99	−0.18	3.70
np-ZnO	2.56	0.13	3.20
CdS	6.72	0.29	12.20
ZnOS	8.71	0.78	14.40
TiO ₂	8.16	−0.33	8.35
ZnSnO	12.26	0.19	7.01

the height profile, respectively. A positive skewness suggests the presence of more surface peaks than valleys, while a kurtosis above 3 indicates sharp, narrow features that contribute to a non-uniform topography.^[44]

As shown in Table 3, only CdS, ZnOS, ZnSnO, and np-ZnO exhibit both positive skewness and kurtosis values greater than 3, consistent with the visually observed surface protuberances. Notably, skewness is particularly pronounced for CdS, ZnOS, and ZnSnO, likely a consequence of their chemical bath deposition (CBD) synthesis method. These findings are further supported by the height distribution plots (Figure S9, Supporting Information), where these substrates show sharp, non-Gaussian profiles, in contrast to the more symmetric and smoother distributions seen for molybdenum or FTO.

Based on these results, it can be concluded that substrates with asymmetric height distributions—i.e., those exhibiting surface protuberances—promote the vertical alignment of chalcogenide rods by acting as preferential nucleation sites during the annealing process. Due to the sharpness of these surface features, localized evaporation of the precursor solution occurs more rapidly at these points, triggering early-stage crystallization of the chalcogenide rods (as illustrated in steps 2 and 3 of Figure 4d).

Furthermore, a higher density of surface protuberances likely enhances the number of nucleation sites, which in turn leads to the formation of more compact thin films, as adjacent rods coalesce. This merging can be maximized through a two-step deposition strategy: first, a low-concentration precursor solution is used to grow small chalcogenide rods during annealing (step 4 in Figure 4d), forming a seed layer; then, a second, higher-concentration solution is deposited, which promotes vertical and radial growth and merging into a dense compact film (step 5 in Figure 4d). The seed layer formation is clearly observed in Figure S10 (Supporting Information) for the CdS and ZnOS substrates, where high crystalline grains are formed at the earlier growth stages.

Conversely, if a high aspect ratio and rod dispersion are desired—for instance, in sensing applications—a substrate with negative skewness and kurtosis below 3 should be chosen, as it offers fewer nucleation points and favours the isolated growth of rods.

Furthermore, noticeable morphological differences are observed across the various Bi-chalcogenides compositions. Compounds incorporating selenium tend to crystallize into thicker and more well-defined rods compared to their sulfur-based counterparts (Figure 4c). In contrast, the halogen has a more pro-

nounced influence on the shape rather than the size of the structures: iodine-based compounds typically form ribbon-like morphologies, whereas bromine-based compounds exhibit flake-like features. This confirms that the halogen significantly affects the crystal growth in the *ab*-plane, as shown previously by XRD analysis. As discussed previously, the lower polarizability of bromine likely weakens the vdW interactions between ribbons, promoting lateral rearrangement and facilitating a more isotropic growth. This results in the formation of more 2D morphologies rather than Q-1D structures.

Beyond material composition, precursor solution formulation plays a crucial role in controlling the morphology, particularly influenced by the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} : \text{BiX}_3$ ratio (noted as X in Table S1, Supporting Information). In the multistep spin-coating process, redissolution of earlier layers occurs in the absence of bismuth nitrate, mainly affecting smaller crystallized rods. As a result, only larger rods persist, serving as heterogeneous nucleation sites that preferentially grow during subsequent steps. This leads to the formation of isolated, large macroscopic rods sparsely distributed across the substrate (Figure S11, Supporting Information). Increasing the bismuth nitrate content and decreasing BiX_3 results in smaller rods and a denser, more compact film. This behavior can be attributed to two key factors: (1) the water introduced through bismuth nitrate pentahydrate decreases the solvation power of the solution, which helps preserve smaller rods from earlier layers and promotes a more uniform solute distribution during subsequent spin-coating steps; and (2) the reduced halogen content brings the precursor solution closer to stoichiometric proportions, thereby limiting abrupt halogen evaporation during crystallization at temperatures above 300 °C, which in turn minimizes material loss and enhances film integrity.

2.4. Optoelectrical Properties

Photothermal Deflection Spectroscopy (PDS) was employed to determine the optical bandgap, assess the Urbach energy, and detect any possible sub-bandgap absorption features. Unlike UV-vis spectroscopy, PDS allows the reliable detection of subtle spectral features such as Urbach tails, defect states, and sub-gap transitions.^[45] Figure 5a,b show the absorption coefficients derived from PDS measurements for Bi-chalcogenide solid solutions with varying halogen and chalcogen content, respectively. A systematic redshift in the absorption onset is observed with progressive anion substitution, indicating tunability of the bandgap. The optical bandgaps and Urbach energies were extracted using a combined Urbach–Tauc fitting model incorporating both UV-vis and PDS datasets.^[46,47] Through this approach the reliability of the extracted optical parameters is enhanced.

In the Supporting Information, we present the Tauc plots for all measured samples using both direct and indirect bandgap analysis methods. In each case, a linear trend is observed near the absorption onset, suggesting the coexistence of both direct and indirect bandgaps in these chalcogenide materials, with the indirect bandgap consistently lower in energy. These experimental results were compared with DFT calculations of the band structure showing good agreement. The DFT data confirm that these materials exhibit both direct and indirect transitions, with energy differences typically below 0.2 eV, and with the

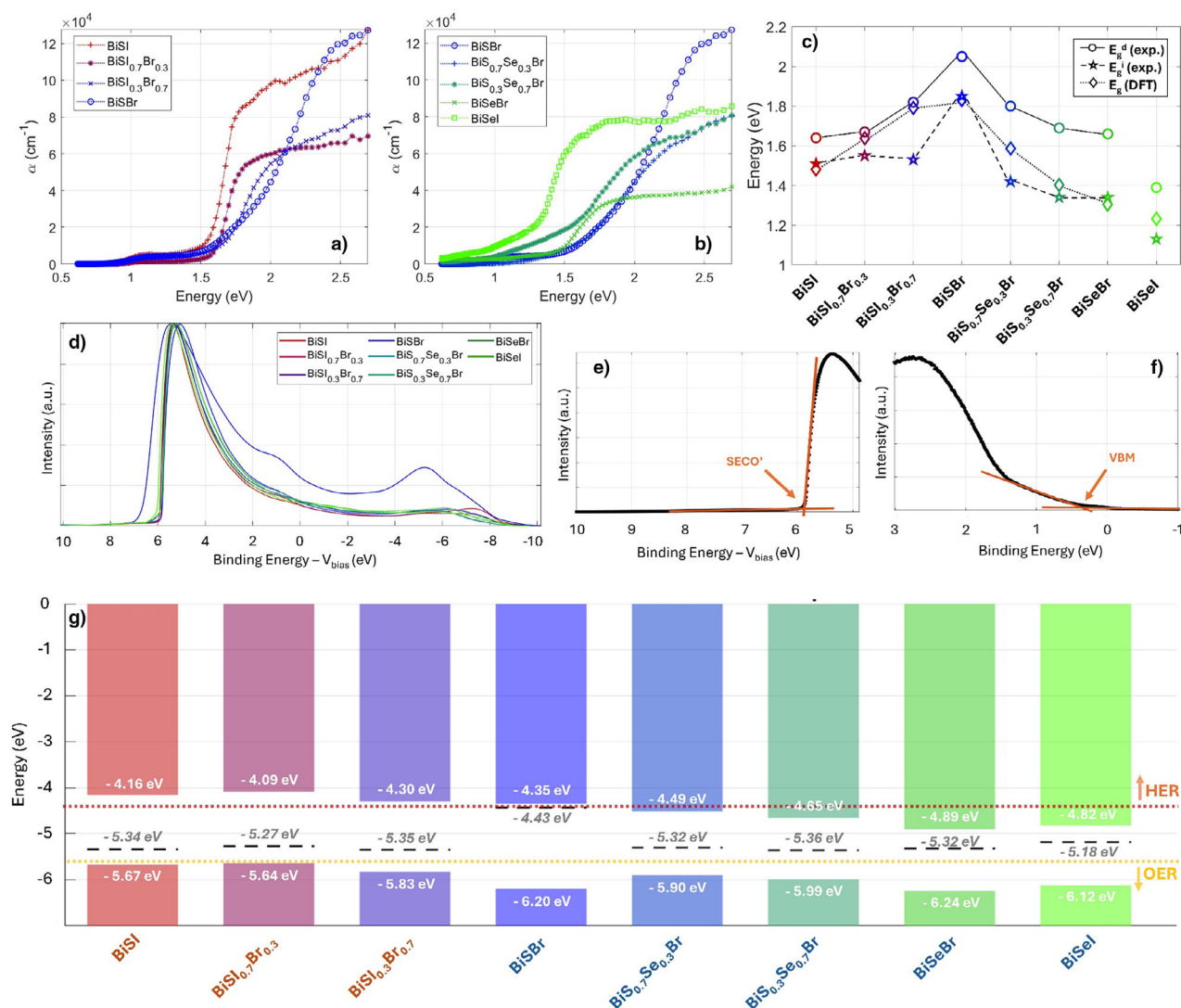


Figure 5. Absorption coefficient spectra for a) halogen and b) chalcogen solid solutions obtained via PDS characterization. c) Experimental and computational values for Bi-chalcoholides bandgaps, where “d” and “i” subindexes denote for direct and indirect bandgap. d) UPS spectra for all Bi-chalcoholide compounds, measured with 10 eV bias voltage. e) Magnified view of the bias UPS signal in the near vacuum level range with the graphical determination of SECO*. f) Magnified view of the UPS signal in the near Fermi level range and the VBM graphical determination. g) Energy band structure reconstruction for all Bi-chalcoholide compounds referenced to the vacuum level.

indirect bandgap always being the lowest.^[48] Interestingly, while the indirect bandgap remains largely invariant with anion substitution, the direct bandgap shows greater sensitivity with a trend close to the one predicted by DFT (Figure 5c). We observe a systematic tuning of the direct bandgap with halide and chalcogen substitution, in contrast to the indirect bandgap, which remains relatively unaffected. This tunability enables tailoring of the optical absorption edge, providing a pathway to optimize the material for specific spectral regions in light-harvesting devices.

Figure S13 (Supporting Information) shows the absorption coefficient fitted using the combined Urbach–Tauc model, which accounts for the coexistence of both direct and indirect bandgaps. This dual-gap approach is crucial for accurately extracting the Urbach energy, as neglecting the indirect bandgap can lead to a significant overestimation of the Urbach edge. The low Urbach ener-

gies observed for the parent compounds reflect their high structural and electronic quality. In particular, the iodine-containing compounds, BiSI and BiSeI, exhibit the lowest Urbach energies, 42 and 56 meV, respectively, indicating minimal disorder and high crystallinity. Furthermore, the absence of multistep absorption onsets supports the phase purity of these samples, with no detectable phase segregation. Upon anion substitution, the Urbach energy increases substantially, indicating a deterioration in lattice quality due to increased disorder in the solid solution. This effect is particularly pronounced in the chalcogen-substituted series: for example, Se incorporation into the BiSBr parent compound results in an order-of-magnitude increase in Urbach energy. This may be attributed to the preferential incorporation of chalcogen atoms into the covalent bonding direction, rather than the vdW gap, as suggested by Le Bail refinements. Such increased

lattice distortion introduced by chalcogen substitution likely perturbs the electronic density of states near the band edges, which can negatively impact the optoelectronic quality of the semiconductor.

In the case of the halogen solid solutions $\text{BiSi}_{0.7}\text{Br}_{0.3}$ and $\text{BiSi}_{0.3}\text{Br}_{0.7}$, a sub-bandgap absorption feature is observed at ≈ 1 eV, as highlighted in the logarithmic scale of Figure S13 (Supporting Information). However, we exclude the possibility that this absorption corresponds to a true band edge transition, as it does not correlate with any linear region in the Tauc plots. To account for this feature, we included a Gaussian-shaped discrete energy state in the Urbach–Tauc fitting model of the absorption coefficient. In both compositions, this localized state was centered at 1.12 eV, suggesting the presence of a deep defect level that could potentially hinder charge transport and reduce device performance when the material is used in optoelectronic applications. Similarly, the work by Dolcet et al. on photoluminescence (PL) spectroscopy of BiSeI microcrystals revealed a pronounced deep emission band centred at $E_M = 1.108$ eV in low-temperature PL measurements.^[18] This emission closely matches the sub-bandgap absorption feature observed in our study, reinforcing the presence of a deep electronic state. López and collaborators^[19] performed DFT calculations on the point defect landscape of BiSeI , identifying chalcogen vacancies as among the most detrimental intrinsic defects in Bi-based chalcogenides. These vacancies were predicted to introduce deep states with band-to-defect transition energies near 1 eV, in good agreement the sub-gap absorption observed experimentally.

Interestingly, a similar sub-gap state was also detected in parent compounds synthesized using $\text{Bi}(\text{NO}_3)_3$ -rich molecular inks, where it was accompanied by elevated Urbach energies (Figure S14, Supporting Information). Reducing the $\text{Bi}(\text{NO}_3)_3$ content in the precursor solution suppressed the discrete state and significantly lowered the Urbach energy. From XRD and SEM characterization one can observe that increasing the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ content in the molecular ink reduces the crystallinity of the Q-1D chalcogenide structures, as reflected by broader XRD peaks and the development of more compact and dense morphologies. Since similar defect states are observed in solid-solution configurations where structural order is reduced, this suggests that crystalline distortion and partial amorphization promote the formation of deep defect states. Therefore, for the halogen solid solution series, implementing a post-deposition annealing step may help relax the structure and eliminate such defects, mirroring the improvements observed with optimized precursor formulations in parent compounds. Additionally, shifting the precursor composition toward chalcogen-rich conditions could further mitigate these defects, which have been theoretically attributed to sulfur or selenium vacancies.^[19]

Ultraviolet Photoelectron Spectroscopy (UPS) was performed on all Bi-chalcogenide samples to analyze their electronic structure. Prior to measurement, the sample surfaces were gently sputtered for 1 min to remove superficial oxidation without significantly altering the underlying semiconductor. The sputtering time was intentionally limited to minimize compositional changes learned from X-ray Photoelectron Spectroscopy (XPS) measurements that could arise from the differential sputtering yields of the elements involved, which could oth-

erwise result in electronic structure modifications. Figure 5d presents the UPS spectra of the samples, while Figure 5e illustrates a representative example of the secondary electron cut-off (SECO') both measured under an applied bias voltage of 10 eV. Figure 5f illustrate a representative example of the valence band maximum (VBM) in an unbiased sample.^[49,50] Accordingly, the actual SECO is calculated as: $\text{SECO} = \text{SECO}' + V_{\text{bias}}$.

From these SECO and VBM values, the work function (WF) and ionization energy (IE) of the Bi-chalcogenide semiconductors were calculated using the following relationships: $\text{WF} = h\nu - \text{SECO}$ and $\text{IE} = h\nu - (\text{SECO} - \text{VBM})$. By combining these UPS-derived values with the optical bandgaps obtained from PDS measurements, we constructed the electronic band diagrams for all studied Bi-chalcogenide compositions, as shown in Figure 5g. The sulfur–iodine compounds exhibit clear p-type conductivity, which progressively becomes more intrinsic as iodine is partially replaced by bromine. In the fully substituted BiSBr , the material shows a marked n-type behavior, indicating a shift in Fermi level position across the solid solution series. Given its low Urbach energy, moderate bandgap (≈ 1.6 eV), and p-type nature, BiSI emerges as the most promising Bi-chalcogenide candidate for optoelectronic devices. In contrast, the larger bandgap and strong n-type conductivity of BiSBr make it a suitable material for use as an electron transport layer (ETL) in various photovoltaic architectures.

Similar n-type conductivity is observed for the BiSeI and BiSeBr parent compounds. However, upon substituting sulfur with selenium in BiSBr , the material transitions toward a more intrinsic behavior, accompanied by a downward shift of the conduction band minimum (CBM). This trend suggests that selenium orbitals dominate the conduction band density of states (DOS) and play a critical role in determining the electronic transport properties. This strong influence of selenium on the conduction DOS is consistent with DFT calculations reported by López et al.,^[48] reinforcing the excellent agreement between theoretical predictions and experimental observations for this class of materials. Moreover, these findings are further supported by XPS measurements, which show a shift in the Bi 4f peak (Figures S15 and S16, Supporting Information), and XRD analysis (Figure S1, Supporting Information), which reveal greater lattice distortion along the covalently bonded directions in selenium-rich compositions. Together, these results highlight the pivotal role of the chalcogen anion—particularly selenium—in shaping the electronic structure and conduction properties of Bi-based chalcogenide semiconductors.

Moreover, analysis of the VBM and CBM positions reveals the potential suitability of these semiconductors for photoelectrochemical (PEC) water splitting.^[35] Based on this band alignment analysis, BiSI , $\text{BiSi}_{0.7}\text{Br}_{0.3}$ and $\text{BiSi}_{0.3}\text{Br}_{0.7}$ emerge as promising candidates for photocathodes, while $\text{BiS}_{0.7}\text{Se}_{0.3}\text{Br}$, $\text{BiS}_{0.3}\text{Se}_{0.7}\text{Br}$, BiSeBr , and BiSeI are more suitable as photoanodes in PEC water splitting.^[51,52] Interestingly, BiSBr possesses a band alignment that enables operation in both configurations, underscoring the tunable and versatile nature of chalcogenide semiconductors. These findings highlight the potential of this material family not only for photovoltaic applications but also for solar-driven fuel generation, broadening their relevance to emerging renewable energy technologies.

3. Concluding Remarks

In this work, we present a novel low-temperature synthesis method based on molecular ink deposition, capable of producing a wide range of pnictogen chalcogenide materials with excellent morphological and compositional control. This methodology is notable for its simplicity, direct formation of ternary alloys, and the elimination of the need for pre-synthesized chalcogenide binary films. Using this approach, we explored the feasibility of forming solid solutions in Bi-based chalcogenides, motivated by their potential for defect engineering in next-generation high-efficiency devices. A thorough structural characterization confirmed the successful synthesis of phase-pure solid solutions and revealed a pronounced structural anisotropy intrinsic to their vdW layered nature. Additionally, we demonstrated precise compositional control, with a strong correlation between the molecular ink formulation and the final film composition, and no signs of phase segregation at either the micro- or nanoscale. Moreover, the ink-based deposition route is inherently scalable and compatible with large-area, solution-processing techniques, offering a pathway toward low-cost and industrially viable fabrication. Importantly, the molecular design concept underlying this approach is generalizable beyond Bi-based systems, enabling its adaptation to a broader class of chalcogenides and low-dimensional semiconductors.

Through comprehensive optoelectronic characterization, we were able to disentangle the individual roles of the chalcogen and halogen anions in tuning electrical conductivity and optical absorption, emphasizing the versatility and tunability of this material family. Notably, we identified the emergence of deep defect states upon introducing lattice disorder and proposed a passivation strategy based on post-synthesis thermal treatments for lattice relaxation. Beyond photovoltaics, we discussed the application potential of these materials in areas such as photoelectrocatalysis and thermoelectrics, enabled not only by their favourable optoelectronic properties, but also by the ability to precisely control their morphology. In this context, we identified the key parameters governing morphological evolution and demonstrated the growth of chalcogenides ranging from film-like layers to rod-shaped microcrystals.

Altogether, the fundamental insights and methodological advances presented here lay a solid foundation for the future integration of chalcogenides into high-efficiency optoelectronic and energy conversion technologies, including photovoltaics, photoelectrocatalysis, and thermoelectrics.

4. Experimental Section

Materials: Thiourea (>99%), cadmium sulfate hydrate (98%), N,N-Dimethylformamide, and fluorine-doped tin oxide (FTO) substrates were purchased from Sigma-Aldrich. Bismuth (III) bromine powder (>99%), bismuth (III) iodide powder (>99.999%), bismuth (III) nitrate pentahydrate (>99.999%), selenourea (98%), and Titanium(diisopropoxide)bis(2,4-pentanedionate) (75% in ethanol), ammonium hydroxide (28–30% in water), 2-propanol (>99%) were purchased from ThermoScientific. Zinc sulfate heptahydrate (>99.5%) was purchased from Chem-Lab. Liquinox critical cleaning liquid detergent was purchased from Alconex. Molybdenum substrates were purchased from Suzhou ShangYang Solar Technology. Zinc oxide nanoparticles (2.5% in mixture of alcohols) were purchased from Avantama.

Synthesis of Bi-Chalcogenides: Film synthesis was done through molecular ink deposition. A single molecular ink consisting of thiourea or selenourea ($\text{SC}(\text{NH}_2)_2$, $\text{SeC}(\text{NH}_2)_2$) as the chalcogen source, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) as the Bi-salt, and bismuth iodide or bromide (BiI_3 , BiBr_3) as the halogen salt was employed. These salts were sequentially dissolved in DMF in the order listed, in a way that the metal cations preferentially coordinate with the thione sulfur (or selenone) atoms rather than with the carbonyl oxygen of DMF. The total ratio of Bi/Ch in the solution was maintained at 1:1 to avoid the formation of the binary chalcogenide phases ($\text{Bi}_2(\text{S,Se})_3$). However, the ratio of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and BiX_3 can be adjusted towards halogen-rich regions as the excess of halogen will be released during the temperature treatment (Table S1, Supporting Information). Different concentrations have been studied for all the precursor species, ranging from 0.05 to 1 M. After dissolution, 50 μL of the molecular ink was transferred onto the selected substrate using a micropipette. The substrates were pre-cleaned to ensure proper adhesion. The precursor was then spin-coated at 1000–2000 rpm for 30 s, after which the sample was transferred to a hotplate for soft annealing. A pre-annealing step was performed at 150 $^\circ\text{C}$ for 3 min to gently remove the solvent. Subsequently, the temperature was increased to the crystallization temperature of the material, 300–350 $^\circ\text{C}$, and maintained for a minimum of 3 min. All the preparation was carried out in an inert atmosphere (using a glovebox system) with controlled oxygen and water levels (<1 and <30 ppm, respectively).

Substrate Preparation: Molybdenum and fluorine-doped tin oxide (FTO) coated glass substrates were initially cleaned manually using Liquinox and deionized water, followed by immersion in 2-propanol for 10 min in an ultrasonic bath. A final rinse with ultrapure deionized water was performed to ensure complete removal of contaminants. Various functional substrate layers were studied, most of which were deposited on top of FTO.

Titanium dioxide (TiO_2) layers were prepared via spray pyrolysis using a 5% ethanol solution of titanium(IV) diisopropoxide bis(2,4-pentanedionate), followed by thermal annealing at 500 $^\circ\text{C}$ for 20 min. Zinc oxide (ZnO) layers were prepared by spin-coating ZnO nanoparticle slurry onto FTO, followed by annealing at 120 $^\circ\text{C}$ for 10 min.

Cadmium sulphide (CdS) and zinc oxysulphide (ZnOS) layers were deposited via chemical bath deposition (CBD) on FTO substrates, using thiourea as the sulfur source and cadmium sulphate (CdSO_4) or zinc sulphate (ZnSO_4) as the metal precursor in an ammonia-based aqueous solution.

Finally, zinc tin oxide (ZnSnO) layers were grown on FTO by atomic layer deposition (ALD) using diethylzinc [$\text{Zn}(\text{C}_2\text{H}_5)_2$, DEZ], tetrakis(diethylamido)tin(IV) [$\text{Sn}(\text{N}(\text{CH}_3)_2)_4$, TDMASn], and deionized water as precursors. The deposition was performed at a substrate temperature of 150 $^\circ\text{C}$ under a continuous argon (Ar) carrier gas flow.

Material Characterization: X-ray diffraction was performed in a PANalytical X'Pert PRO MPD powder diffractometer in Bragg–Brentano geometry, 240 millimetres of radius $\theta/2\theta$ goniometer, enabled to obtain the X-ray diffraction patterns, using nickel filtered $\text{Cu K}\alpha_{(1+2)}$ radiation, $\lambda_{\text{average}} = 1.5418 \text{ \AA}$, with a work power of 45 kV – 40 mA. A divergence slit of 0.25 $^\circ$, a mask defining a length of the beam over the sample in the axial direction of 12 millimetres and incident and diffracted beam Soller slits of 0.04 radians were used. An 1D PIXcel Detector with an active length of 3.347 $^\circ$ was employed. The measurements consisted of $2\theta/\theta$ scans from 4.5 to 145 $^\circ$ 2θ with a step size of 0.026 $^\circ$ and a measuring time of 200 s per step. The patterns have been analysed with X'Pert HighScore software. Pattern matching refinement (via Le Bail method) has been performed using the FullProf suite and ensuring a weighted profile R-factor (R_{wp}) below 5%. The corresponding crystallographic information files (CIF) were available through the Crystallography Open Database (COD). The following COD entries were used as initial structures for the refinements: COD 1535800 (BiI), COD 1535795 (BiSBr), COD 2010577 (BiSeI), COD 7711569 ($\text{Bi}_{12.89}\text{Br}_{2.85}\text{S}_{17.15}$), and COD 1000062 (SnO_2).

Raman spectroscopy measurements were carried out with a Renishaw inVia Qontor instrument with 532 nm excitation wavelength, and nominal 100 mW output power, coupled with 2400 lines per mm visible grating

and Leica DM2700 microscope (with 100x objective) for confocal measurements. For data collection, between 0.5% and 5% of the nominal power was used. The optimal laser power was defined as the highest power at which no changes in the spectral parameters were detected. 20 accumulations with 3 s of exposure time for each accumulation over 3 different areas of each sample were performed on each compound.

Ion beam analysis (IBA) measurements were carried out under vacuum conditions with the Oxford-type nuclear microprobe installed at the 2.5 MV Van de Graaff accelerator, in Lisbon (Portugal). For a detailed depth profiling analysis, the experiment was performed using two types of ion beams: protons at 1750 keV and alpha particles at 1800 keV. In both cases the beam current was ≈ 300 pA. The use of alpha particles increases the elemental mass resolution and in-depth sensitivity when considering the EBS spectra. X-rays were detected using a 30 mm² Bruker SDD detector with a 145 eV resolution, positioned at 135° relative to the beam direction. When the proton beam was used, a 50 μ m thick Mylar filter was placed in front of the detector. Backscattered particles were detected by means of a 200 mm² PIPS detector, positioned at 140° with the beam direction in Cornell geometry.

The OMDAQ software package was used for beam control, data acquisition, data processing and postdata treatment. PIXE and EBS maps were obtained by selecting the regions of interest (ROIs) in each spectrum using the list mode playback mode. PIXE spectra were analysed by the GUPIX code. For the quantification of elemental concentrations, Bi-M α_1 , S-K, Se-L α_1 , Br-K, I-L α_1 shell emission lines were selected to their higher signal-to-noise ratio, ensuring more accurate calculations.

XPS measurements have been done with a monochromatic focused X-ray source (Aluminium K α line of 1486.6 eV) calibrated using the 3d^{5/2} line of Ag with a full width at half maximum (FWHM) of 0.6 eV. The analysed area was a circle of 100 μ m of diameter, sample placed at 45° with respect to the analyser axis, and the selected resolution for the spectra was 224 eV of Pass Energy and 0.8 eV per step for the general spectra, and 27 eV of Pass Energy and 0.1 eV per step for the high-resolution spectra of the selected elements. Measurements were referenced to the C^{1s} signal, whose binding energy was equal to 284.8 eV in adventitious carbon (from atmospheric contamination).

On the other hand, UPS measurements have been done using a Helium source (He I line of 21.22 eV) calibrated using an Ag sample in which the work function (WF) calculated was of 4.27 eV. The analysed area was a spot of ≈ 1.5 mm of diameter, sample placed at 90° with respect to the analyser axis, and the selected resolution for the spectra was 1.3 eV of Pass Energy and 0.01 eV per step. Both XPS and UPS measurements were made in an ultra-high vacuum (UHV) chamber at a pressure between 5×10^{-10} and 5×10^{-9} Torr. Moreover, to measure beyond the surface avoiding surface contamination sputtering with monoatomic Ar⁺ ion gun (at 4 keV and 6 mm $\times$ 6 mm raster) was done. The analysis and fitting of the spectra were carried out with Multipak V. 9.9.2 program.

The setup for Photothermal Deflection Spectroscopy (PDS) consists of a 100 W tungsten halogen lamp, PTI 01-0002 monochromator, and Thorlabs MC1000 optical chopper (4 Hz light modulation frequency). A Signal Recovery 7265 lock-in amplifier was connected to Hamamatsu C10442-02 PSD position sensitive detector to measure the deflection of the MC6320C laser probe beam (10 mW). Samples were located in a quartz cell filled with Fluorinert TM FC-40 liquid. UV-vis data were also used to calibrate the PDS signal by normalizing the absorption coefficient in the high-absorption region. Optical analyses were performed by UV-vis-NIR spectroscopy using a PerkinElmer Lambda 950 spectrophotometer operated with UV WinLab software. Measurements were carried out with a 150 mm integrating sphere, enabling global transmittance and reflectance acquisition over the 200–2500 nm wavelength range. The instrument was equipped with two detectors: a photomultiplier tube (PMT) for the UV-vis region and a PbS detector for the NIR region.

Scanning electron microscopy was performed with a Zeiss Series Auriga field-emission microscope, with acceleration voltage of 5 kV and working distance ranging between 3 to 4 mm was employed to get top-view and cross-section images of the samples fabricated. No gold or carbon coatings were needed.

A VEECO Dimension 3100 equipment was used for the atomic force microscope measurements. The TAP150-G-10 probe with 10 nm tip radius, spring constant of 5 N per mm and resonant frequency of 150 kHz was acquired from Ted Pella, INC. Gwyddion software was used for the data treatment.

Water contact angle (WCA) measurements were conducted with a KRÜSS Drop Shape Analyzer (DSA25E). Precisely 1 μ L of water was dropped onto the surface of the sample for every measurement. The acquired data were further examined utilizing the Sessile Drop module in the KRÜSS Advance program.

STEM-HAADF, STEM-EELS and STEM-EDXS data were acquired using a JEOL ARM 200cF (NEOARM), operated at 200 kV accelerating voltage. The microscope was equipped with a cold FEG electron gun and an aberration corrector in the condenser system. STEM-EELS data were acquired using a Gatan GIF Continuum K3 IS energy filter. STEM-EDXS data were acquired using the dual JEOL DrySD windowless detectors. The acquired data was processed through the software DigitalMicrograph from Gatan, INC. Plane identification in FFT were made using PDF reference 01-089-7110, with lattice parameters refined through Le Bail refinement for Bi_{0.5}Se_{0.5}Br: $a = 4.035$ Å; $b = 10.05$ Å; $c = 8.12$ Å.

DFT Calculations: First-principles calculations based on density functional theory (DFT)^[53] were carried out as implemented in the VASP code.^[54] The projector augmented-wave method^[55] was used to represent the ionic cores^[56] and for each element the maximum possible number of valence electronic states was considered. Wave functions were represented in a plane-wave basis typically truncated at 850 eV. By using these parameters and a dense k-point grid for Brillouin zone integration of $10 \times 5 \times 4$ centered at Γ , the resulting zero-temperature energies were converged to within 1 meV per formula unit. In the geometry relaxations, a tolerance of 0.005 eV Å⁻¹ was imposed in the atomic forces.

To address the limitations of semi-local functionals,^[57] the range-separated hybrid functional HSEsol containing an exact Hartree-Fock exchange fraction of 25% was employed,^[58,59] which was based on the Perdew–Burke–Ernzerhof exchange-correlation functional revised for solids.^[60–62] Additionally, spin–orbit coupling (SOC) effects, which were particularly relevant for Bi-based compounds, were explicitly included^[58,61,63] for the estimation of the optoelectronic properties, with a plane-wave basis truncated at 550 eV and a $5 \times 3 \times 2$ Γ -centered mesh.

Solid solutions were modelled by means of the virtual crystal approximation (VCA),^[64] which assumes the presence of virtual atoms on potentially disordered sites, interpolating between the electronic traits of the actual components. VCA supercells match the size of the primitive cell, making them computationally tractable while providing reliable results for isoelectronic atom substitutions.^[48,65]

The strength of the long-range dispersion interaction in these materials was quantified using the vdW D3 correction scheme.^[66] The energy of the vdW interaction was defined as the difference between the total ground energies calculated with and without the D3 correction. To facilitate the comparison across different chalcogenides, single-shot energy calculations was performed without structural relaxation, ensuring that the exact same atomic configuration (BiSI structure) was used for all chalcogenides. Thus, when normalizing any energy by units of volume the BiSI's unit cell volume was used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research has received funding from the European Union H2020 Framework Program under the SENSATE project: the Low-dimensional semi-conductors for optically tunable solar harvesters (grant agreement Number 866018) and the Renew-PV European COST action (CA21148). E.S. and J.P. acknowledge financial support of the Spanish Ministry of Science and Innovation from the CURIO-CITY project

(PID2023-148976OB-C41), and ACT-FAST project (PCI2023-145971-2), from the CETP-Partnership Program 2022. This work was part of Maria de Maetzu Units of Excellence Programme CEX2023-001300-M, funded by MCIN/AEI/10.13039/501100011033. D.R. acknowledges support by Generalitat de Catalunya under grant FI SDUR 2023 (ref. BDNS 699313) (DOGC Núm. 8929 – 02.06.2023). This research was funded by MCIN/AEI/10.13039/501100011033, grant number PID2022-138434OB-C53. Funding for the IBA measurements conducted in Lisbon, Portugal, was provided by the European Union's Horizon Europe Research and Innovation programme under Grant Agreement No 101057511 (EUROLABS). V.C. and L.C.A. acknowledge Fundação para a Ciência e Tecnologia, Portugal (Center for Nuclear Sciences and Technologies). J. W. T. and R. A. are grateful to the National Science Foundation for funding support through grants 1735282-NRT (SFEWS) and 10001536 (INFEWS). C.L. acknowledges support from the Spanish Ministry of Science, Innovation and Universities under a FPU grant. C.C. acknowledges support by MICIN/AEI/10.13039/501100011033 and ERDF/EU under grants TED2021-130265B-C22, TED2021-130265B-C21, PID2023-146623NB-I00, PID2023-147469NB-C21 and RYC2018-024947-I and by the Generalitat de Catalunya under grants 2021SGR-00343, 2021SGR-01519 and 2021SGR-01411. Computational support was provided by the Red Española de Supercomputación under grants FI-2025-2-0027, FI-2025-2-0028 and FI-2025-2-0006. Access to the JEOL ARM200F – NEOARM at CCIUB was granted through the Spanish Singular Scientific Technical Infrastructure (ICTS) ELECMI via a competitive call (project code ELC349-2023). E.S. acknowledges the ICREA Academia program.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

chalcogenides, optoelectronic tuneability, Q-1D materials, molecular inks, solid solutions

Received: August 29, 2025
Revised: October 23, 2025
Published online:

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