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**Sintesi e caratterizzazione di $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$:
dalle polveri ai film sottili**

**Synthesis and Characterization of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$:
From Powders to Thin Films**

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Abstract

Le *metal halide perovskites* (MHPs) hanno suscitato negli ultimi anni un notevole interesse scientifico grazie alla combinazione di proprietà ottiche ed elettroniche particolarmente favorevoli, che le rendono promettenti per numerose applicazioni optoelettroniche, tra cui celle solari, fotodetettori, LED e dispositivi emissivi. In particolare, le perovskiti alogenure al piombo hanno raggiunto prestazioni nel campo del fotovoltaico molto elevate, grazie all'alto coefficiente di assorbimento, alla possibilità di modulare il band gap mediante variazioni composizionali e strutturali, all'efficiente trasporto di carica e alla notevole tolleranza ai difetti. Queste caratteristiche, unite alla possibilità di ottenere film cristallini mediante tecniche di deposizione relativamente semplici e a basso costo, hanno reso le perovskiti una delle classi di materiali semiconduttori più studiate nell'ultimo decennio. Nonostante questi successi, la scalabilità commerciale delle MHPs incontra due importanti ostacoli: la tossicità intrinseca del piombo, regolamentata da restrizioni severe come la direttiva europea RoHS, e la scarsa stabilità chimico-strutturale in condizioni ambientali, in particolare in presenza di umidità, ossigeno, radiazione UV e sollecitazioni termiche. Per superare tali limitazioni, la comunità scientifica ha sviluppato un crescente interesse per materiali privi di piombo ispirati alle perovskiti, i cosiddetti *Perovskite-Inspired Materials* (PIMs).

Le *metal halide perovskites* presentano una struttura cristallina tridimensionale generalmente descritta dalla formula ABX_3 , in cui A è un catione organico o inorganico, B un catione metallico e X un anione alogenuro. Il catione B è coordinato ottaedricamente da sei anioni X, formando unità $[BX_6]^{4-}$ che condividono vertici e costituiscono il reticolo tridimensionale, mentre i cationi A occupano gli spazi interstiziali tra gli ottaedri. Tra le diverse strategie per sostituire il Pb^{2+} nei PIMs, riveste particolare interesse l'impiego di cationi trivalenti, per esempio Bi^{3+} e Sb^{3+} , come alternative non tossiche per il sito B. La diversa valenza rispetto al Pb^{2+} rende tuttavia necessario un riarrangiamento della struttura perovskitica, dando origine a materiali definiti *defect-ordered* con formula generale $A_3B_2X_9$, in cui solo due terzi dei siti B sono occupati. I composti appartenenti a questa famiglia presentano proprietà strutturali ed elettroniche interessanti e, in diversi casi, una maggiore stabilità chimica rispetto alle perovskiti a base di Pb o Sn. I materiali a base di bismuto e antimonio, in particolare $Cs_3Bi_2I_9$ e $Cs_3Sb_2I_9$, sono caratterizzati da una struttura costituita da unità bioottaedriche $[M_2I_9]^{3-}$, con $M = Bi^{3+}$ o

Sb^{3+} (**Figura 1**) e sono studiati per diverse applicazioni, tra cui dispositivi fotovoltaici, fotodetettori e processi fotocatalitici. Tuttavia uno dei principali limiti di questi materiali è rappresentato dall'elevato band gap, che riduce la porzione dello spettro solare che può essere efficacemente assorbita.

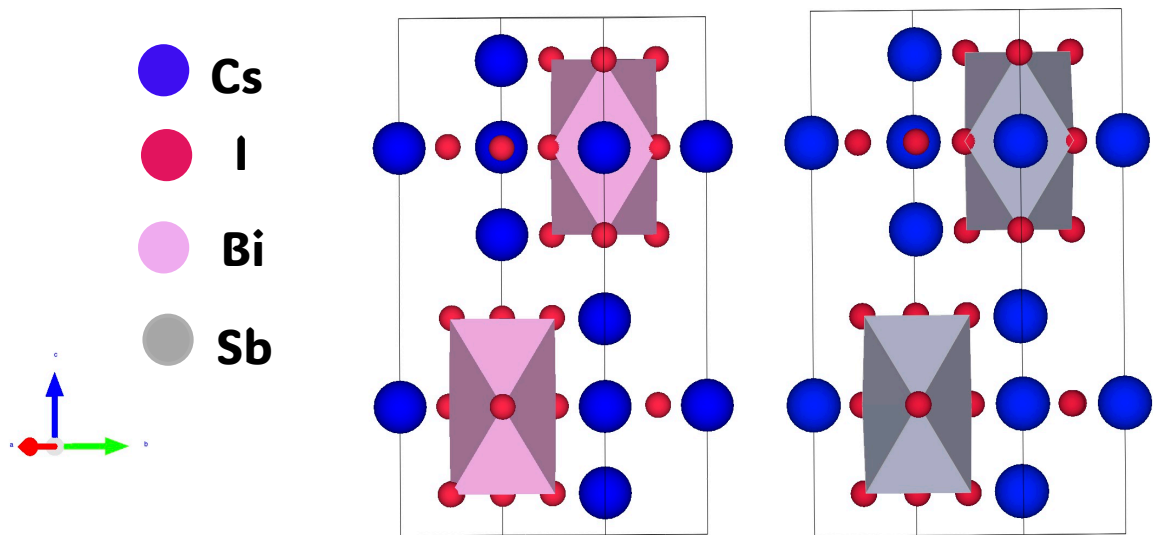


Figura 1: Rappresentazione schematica della struttura cristallina di $\text{Cs}_3\text{Bi}_2\text{I}_9$ e $\text{Cs}_3\text{Sb}_2\text{I}_9$.

Un ulteriore ostacolo riguarda la realizzazione di film sottili di elevata qualità. I metodi di deposizione da soluzione, comunemente impiegati per la preparazione di film di materiali perovskitici, possono infatti portare a una cristallizzazione rapida e non uniforme, con conseguente formazione di superfici dalla texture ruvida, *pinholes*, elevata densità di difetti e distribuzione non omogenea delle dimensioni dei grani. Inoltre l'utilizzo di solventi può rappresentare un limite dal punto di vista ambientale e può rendere più complessa la deposizione sequenziale di più strati. In questo contesto, le tecniche di deposizione da fase vapore rappresentano un'alternativa interessante. In particolare, il *Physical Vapor Deposition* (PVD) permette di ottenere film sottili in vuoto, senza utilizzare solventi durante la deposizione, e offre un controllo elevato sui parametri di crescita. Tra le tecniche PVD, il *radio-frequency magnetron sputtering* (RF magnetron sputtering) è particolarmente rilevante per la deposizione di materiali non conduttivi o semiconduttori e consente di controllare parametri quali potenza

RF, pressione di lavoro, flusso del gas, distanza target-substrato e temperatura del substrato. La possibilità di utilizzare direttamente polveri pressate come target rende inoltre questa tecnica particolarmente interessante grazie alla semplicità di preparazione, alla possibilità di depositare materiali multicomponente e al suo potenziale utilizzo in processi su larga scala.

La presente tesi si inserisce quindi nell'ambito dello sviluppo di materiali *perovskite-inspired* privi di piombo e si propone di studiare il sistema $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ investigando l'intera serie di composizioni con $x = 0, 0.5, 1, 1.5$ e 2 . Il lavoro affronta in modo sistematico entrambe le problematiche fondamentali legate a questi materiali: l'ampiezza della banda proibita e lo sviluppo di un protocollo per la deposizione in fase vapore di film sottili di elevata qualità. L'obiettivo centrale è stato lo studio e il controllo delle proprietà strutturali, ottiche e morfologiche delle soluzioni solide, combinando strategie innovative e sostenibili.

La prima fase del lavoro riguarda la preparazione delle polveri mediante sintesi meccanochimica. Le diverse composizioni sono state ottenute a partire da quantità stechiometriche dei precursori (CsI , BiI_3 e SbI_3) utilizzando un *vibratory ball miller*. Questo approccio presenta diversi vantaggi rispetto ai metodi convenzionali, tra cui semplicità, ridotto impiego di solventi e possibilità di preparare direttamente quantità pure e omogenee di materiale.

La seconda parte sperimentale riguarda la deposizione dei film sottili mediante RF magnetron sputtering. Le polveri precedentemente sintetizzate sono state utilizzate direttamente come materiali target, dopo essere state pressate su un supporto di rame. I film sono stati depositati su substrati di quarzo utilizzando una potenza RF di 50 W, una pressione di lavoro di 2.3×10^{-2} mbar, un flusso di argon di 30 sccm e una distanza target-substrato di 10 cm. Le condizioni sono state mantenute costanti per l'intera serie, consentendo di studiare l'effetto della composizione sulle proprietà dei film senza introdurre ulteriori variabili sperimentali. I pattern di diffrazione da raggi X su polveri (PXRD) hanno confermato che la sintesi meccanochimica conduce alla formazione di fasi cristalline monofasiche per tutte le composizioni studiate. Entrambi i termini puri ($\text{Cs}_3\text{Bi}_2\text{I}_9$ e $\text{Cs}_3\text{Sb}_2\text{I}_9$) e le miscele intermedie cristallizzano nel gruppo spaziale esagonale $P6_3/mmc$, caratterizzato da unità biottaedriche isolate $[\text{M}_2\text{I}_9]^{3-}$. Il raffinamento Rietveld condotto mediante il software TOPAS v6 ha

evidenziato una contrazione continua e regolare dei parametri di cella (a e c) e del volume della cella unitaria all'aumentare del contenuto di antimonio (x), come mostrato in **Figura 2**

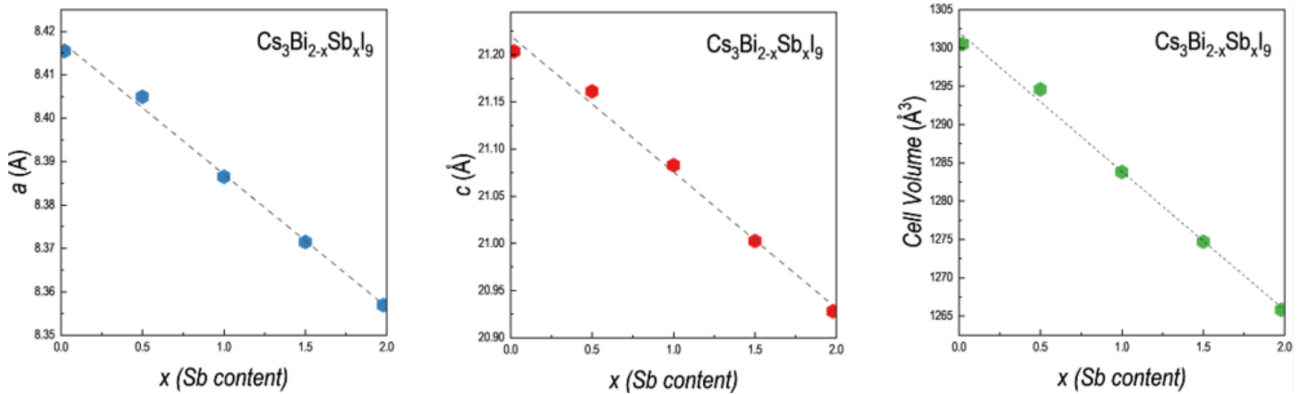


Figura 2: Parametri reticolari e volume di cella in funzione della composizione dei campioni.

L'andamento lineare dei parametri reticolari in funzione della frazione molare di Sb è giustificato dal minor raggio ionico di Sb^{3+} (0.76 Å) rispetto a Bi^{3+} (1.03 Å) e soddisfa perfettamente la legge di Vegard, dimostrando l'effettiva formazione di una soluzione solida sostitutiva continua. La diffrazione XRD sui film sottili depositati su substrati di quarzo (spessore di circa 400 nm misurato via profilometria) ha confermato la completa ritenzione della fase cristallina delle polveri target. Si può inoltre osservare la presenza di un marcato orientamento preferenziale lungo la direzione cristallografica ($00l$), a prova del fatto che la crescita dei cristalliti sul substrato avviene in modo fortemente anisotropo lungo l'asse c . Lo spostamento progressivo verso angoli 2θ più elevati del picco principale (006) conferma il mantenimento della contrazione reticolare nei film sottili (**Figura 3**).

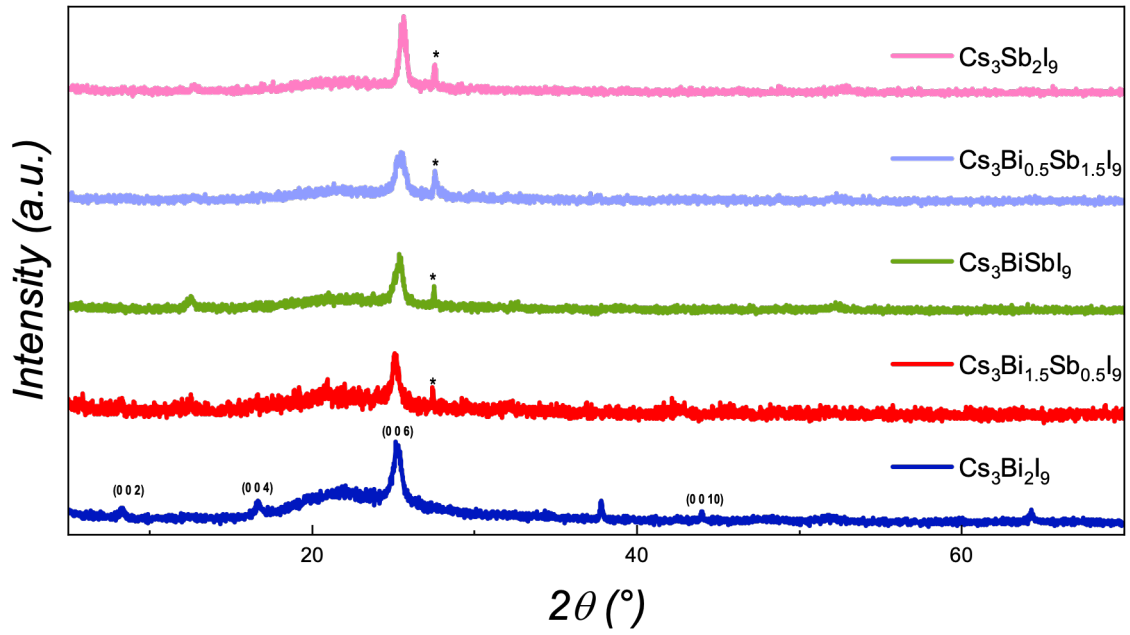


Figura 3: Pattern di diffrazione a raggi X dei film sottili della serie $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$).

La spettroscopia Micro-Raman (laser a 638 nm) condotta sia su polveri che su film ha permesso di esplorare la dinamica reticolare e l'ambiente di coordinazione locale degli ottaedri. Nella regione tra 40 e 180 cm^{-1} sono stati identificati i modi vibrazionali caratteristici di stretching e bending dei legami Bi–I e Sb–I all'interno delle unità bioctaedriche $[\text{M}_2\text{I}_9]^{3-}$ e la variazione graduale della frequenza dei picchi Raman al variare della composizione conferma l'assenza di segregazioni di fase su scala microstrutturale.

Una parte centrale del lavoro ha riguardato lo studio delle proprietà ottiche mediante spettroscopia UV–Vis. Per le polveri sono state fatte misure di riflettanza diffusa, successivamente elaborate mediante la funzione di Kubelka–Munk e il metodo di Tauc. Per i film sottili sono state invece acquisite misure in trasmittanza, dalle quali sono stati ricavati l'assorbanza e il coefficiente di assorbimento, permettendo la successiva costruzione dei Tauc plot. In entrambi i casi è stata considerata una transizione indiretta permessa, coerentemente con quanto riportato in letteratura per gli *end-members* e per sistemi correlati. L'analisi ottica ha evidenziato uno dei risultati più significativi della tesi: l'energia dell'assorbimento ottico non varia linearmente con la composizione, ma presenta un marcato band-gap bowing, graficamente evidente dalla **Figura 4** ed evidenziato dai dati riportati in **Tabella 1**.

Absorbition edge (eV)

x	Thin films	Powders
0	1.87	1.85
0.5	1.83	1.77
1	1.76	1.71
1.5	1.77	1.74
2	1.91	1.89

Tabella 1: Valori del band gap ottico di film sottili e polveri in funzione della composizione dei campioni estrapolati tramite il metodo di Tauc.

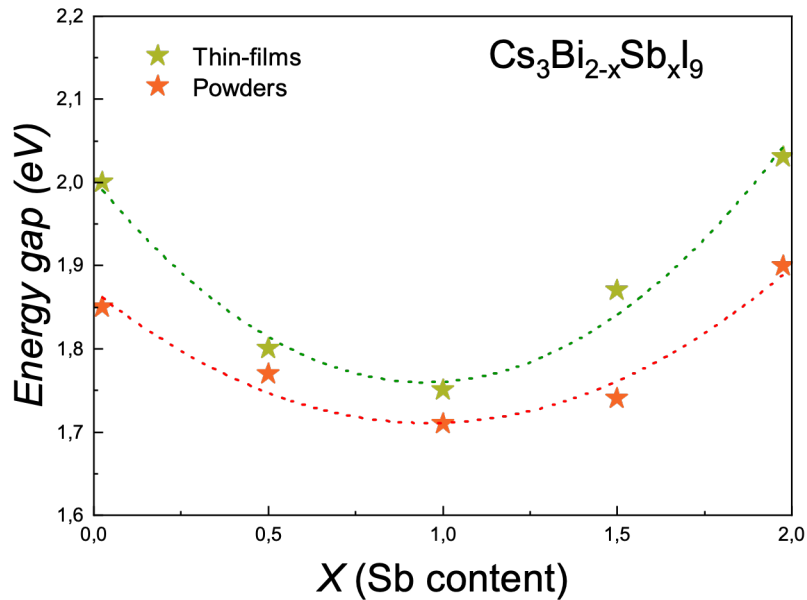


Figura 4: Valori delle energie del band-gap in funzione del contenuto di Sb (x).

La composizione equimolare $\text{Cs}_3\text{BiSbI}_9$ ($x = 1$) mostra il valore minimo assoluto del band gap, pari a 1.71 eV nelle polveri e 1.76 eV nei film sottili. Questo rappresenta il valore più basso mai riportato in letteratura per fasi inorganiche derivate da perovskiti a base di alogenuri di bismuto ed antimonio. La spiegazione fisica di questo fenomeno risiede nell'allineamento sfalsato (*staggered band alignment*) degli stati elettronici di $\text{Cs}_3\text{Bi}_2\text{I}_9$ e $\text{Cs}_3\text{Sb}_2\text{I}_9$: la loro interazione induce uno spostamento simultaneo verso l'alto del massimo della banda di valenza (VBM) ed un abbassamento del minimo della banda di conduzione (CBM), riducendo l'intervallo di energia proibita nelle miscele intermedie, come mostrato in **Figura 5** per un sistema simile.

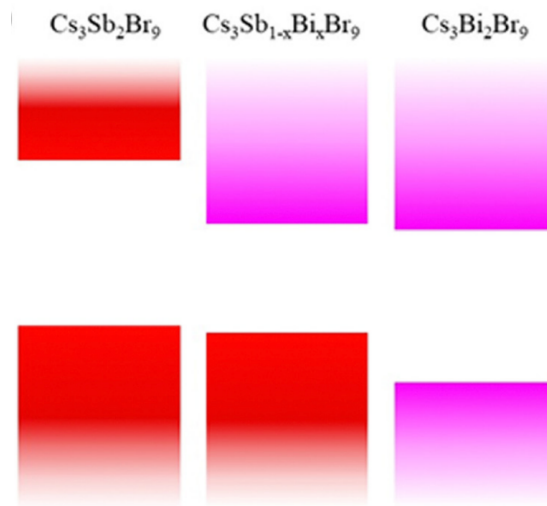


Figura 5: Schema dell'allineamento sfalsato degli stati elettronici nel sistema $Cs_3(Sb_{0.5}Bi_{0.5})_2Br_9$.²⁶

Il confronto tra polveri e film è particolarmente significativo. Sebbene i valori assoluti dell'*absorption edge* presentino piccole differenze, attribuibili alle diverse caratteristiche microstrutturali dei due tipi di campione, l'andamento composizionale è praticamente lo stesso. Le polveri, ottenute mediante macinazione meccanochimica, presentano particelle irregolari e una maggiore quantità di imperfezioni strutturali, mentre i film depositati per sputtering mostrano una morfologia più continua e uniforme. Nonostante queste differenze entrambi i sistemi presentano lo stesso andamento a campana rovesciata del band gap, dimostrando che il fenomeno osservato è una caratteristica intrinseca della soluzione solida e non un semplice effetto della morfologia o del processo di deposizione. La microscopia a forza atomica (AFM) in modalità *tapping* ha mostrato che il rapporto Bi/Sb esercita un impatto profondo sulla cinetica di nucleazione e sulla texture dei campioni. Il film di $Cs_3Bi_2I_9$ presenta una superficie estremamente compatta e liscia, formata da nanograni di circa 160 nm con una rugosità quadratica media (R_{rms}) di soli 29 nm. Al contrario, il film di $Cs_3Sb_2I_9$ mostra grani nettamente più grandi (~420 nm) ed una rugosità elevata ($R_{rms} \approx 100$ nm). Coerentemente composizioni intermedie presentano una transizione morfologica graduale. Le analisi SEM condotte sul film equimolare Cs_3BiSbI_9 hanno confermato la presenza di un rivestimento omogeneo, denso, continuo e completamente privo di crepe. Le microanalisi EDX hanno rivelato corrispondenza tra la stechiometria nominale dei target di partenza e la composizione effettiva dei film depositati (errori stechiometrici inferiori

al 4.7%), dimostrando coerenza del processo di sputtering nel trasferimento della stechiometria da target a substrato. Le mappe elementari hanno evidenziato una distribuzione spaziale uniforme di Cs, Bi, Sb e I senza alcuna segregazione di fase.

Nel complesso il lavoro svolto dimostra che la combinazione di sintesi meccanochimica e RF magnetron sputtering rappresenta una strategia efficace, scalabile e sostenibile per la produzione di materiali *perovskite-inspired* privi di piombo con proprietà ottiche modulabili. La possibilità di ridurre il band gap attraverso la formazione di soluzioni solide Bi/Sb apre nuove prospettive per l'impiego di questi materiali in dispositivi optoelettronici, fotovoltaici e fotodetettori, contribuendo allo sviluppo di tecnologie più sicure, stabili e rispettose dell'ambiente. In prospettiva futura ulteriori studi potranno concentrarsi sull'ottimizzazione dei parametri di deposizione, in particolare per il controllo della crescita dei grani e della rugosità superficiale, ma anche sull'eventuale utilizzo di trattamenti post-deposizione per migliorare ulteriormente la qualità dei film. L'integrazione delle composizioni otticamente più promettenti in dispositivi fotovoltaici o fotocatalitici costituirà inoltre un importante passo successivo per valutare concretamente il potenziale applicativo dei materiali sviluppati in questa tesi.

1 Introduction

1.1 Perovskites: general features

The study of perovskite materials began in 1839, when Prussian mineralogist Gustav Rose first discovered calcium titanate CaTiO_3 in a chlorite-rich skarn deposit. The mineral was subsequently named “perovskite” at the request of Russian mineral collector August Alexander Kämmerer, in honor of the Russian mineralogist Count Lev A. Perovskiy (1792–1856).

Later, the discovery of various inorganic metal oxides with the same crystal structure, including BaTiO_3 , PbTiO_3 , SrTiO_3 , and BiFeO_3 , led perovskite compounds to be recognized as metal oxides with the general formula ABO_3 .

More generally, perovskite refers to a specific crystal structure with the chemical formula ABX_3 , where A and B represent cations, and X denotes an anion. The ideal unit cell is cubic, where the B cation is coordinated by six X anions forming an octahedron at the face-centred positions, while the A cation occupies the cube corners in a 12-fold cuboctahedral coordination.¹

When the perovskite crystal lattice is defined as a network of corner-sharing BX_6 octahedra, the structure is called a 3D perovskite, as shown in **Figure 6**. If the octahedra share four, two, or zero corners, the structure is respectively a 2D, 1D, and 0D perovskite.²

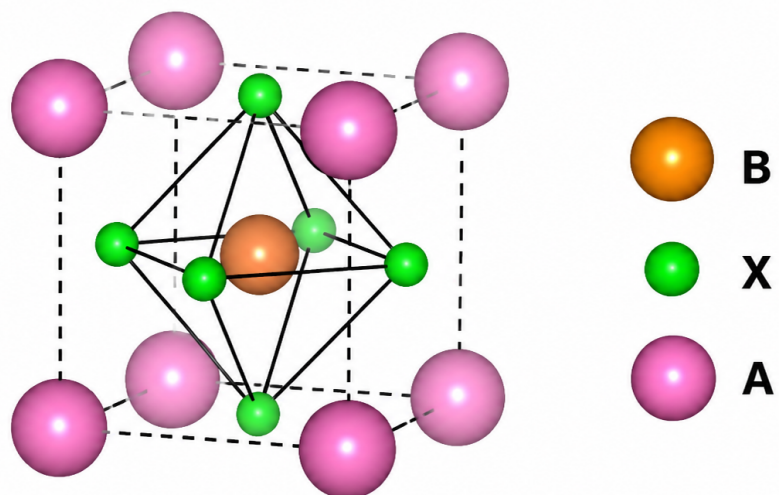


Figure 6: Crystal structure of a general perovskite

Structural deviations from ABX_3 stoichiometry can occur when the A and B cation sites become partially or fully vacant (resulting in vacancy-ordered perovskites), or when they are replaced

by a combination of alternative cations with different valences, maintaining overall charge neutrality to form double or quadruple perovskites.³

While oxide perovskites are extensively utilized in ferroelectric, piezoelectric, dielectric, and pyroelectric applications, most of these compositions lack the semiconducting properties required for photovoltaic (PV) technologies and photocatalysis.⁴ Conversely, halide perovskites, which differ by incorporating halide anions instead of oxide anions (ABX_3 , where A is a large monovalent cation, B is a divalent metal cation, and X is a halogen), exhibit these properties.¹

This is the most promising subgroup for optoelectronic devices, containing both fully inorganic and hybrid organic-inorganic materials.

1.2 Optoelectronic properties and application of perovskites

Although lead halide perovskites have a long history, their extraordinary optoelectronic properties remained largely unexplored for over a century. Interest in these materials was revived in the 1990s, beginning with the work of Era and co-workers, who investigated two-dimensional layered halide perovskites for electroluminescent devices in 1994. A few years later, Kagan et al. demonstrated the use of organic-inorganic hybrid perovskites as semiconducting channels in field-effect transistors. The real turning point, however, came in 2009, when Miyasaka and co-workers employed methylammonium lead iodide ($MAPbI_3$) as a sensitizer in dye-sensitized solar cells, achieving a power conversion efficiency (PCE) of 3.8%.⁵ Although modest, this result highlighted the enormous potential of perovskite materials. In 2012, the introduction of solid-state perovskite solar cells (PSCs) led to an immediate increase in PCE to 9.7%, marking the beginning of the rapid expansion of perovskite research worldwide.

The exceptional progress in PSC performance is largely attributed to the intrinsic defect tolerance of lead halide perovskites, which allows efficient charge transport even in solution-processed materials. As a result, certified power conversion efficiencies for single-junction, small-area PSCs increased from 25.5% at the end of 2020 to a record value of 26.7%, surpassing multicrystalline silicon and reaching efficiencies comparable to those of single-crystal silicon solar cells. Beyond conventional outdoor applications, perovskite solar cells have also shown

excellent performance under indoor illumination, where single-junction devices have achieved efficiencies as high as 35.2%.^{6,7}

The growing interest in metal halide perovskites (MHPs), especially those based on lead, tin, and germanium, arises from a distinctive combination of outstanding semiconductor properties. Their electronic and optical properties are primarily determined by the band gap, defined as the energy difference between the valence band maximum (VBM) and the conduction band minimum (CBM). The electronic states close to the band edges are predominantly derived from the inorganic component. In particular, the VBM and CBM are mainly associated with orbitals of the metal and halide ions, whereas the molecular orbitals of the organic cation generally lie energetically outside the band-gap region. Consequently, the fundamental electronic structure of these materials is largely governed by the connectivity, geometry, and chemical composition of the inorganic octahedral framework.⁸ In conventional semiconductors such as GaAs, the VBM and CBM are generally derived from bonding and antibonding orbitals, respectively. In contrast, the VBM of lead halide perovskites predominantly exhibits antibonding character, as shown in **Figure 7**.

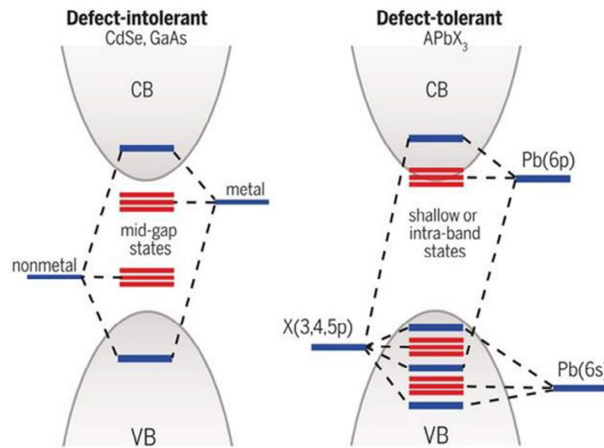


Figure 7: Band structures based on molecular orbital theory of classic semiconductors (GaAs or CdTe) and $APbX_3$ perovskites.⁷

This peculiar electronic configuration has important consequences for the formation and energetic position of defect states. Although structural defects can introduce electronic states near the band edges or within the bands, the resulting states are often relatively shallow rather than deep recombination centres. Moreover, the high dielectric constant of perovskite materials provides efficient dielectric screening of charged defects, reducing the interaction between

charge carriers and defect states and consequently limiting their capture probability. These features contribute to the remarkable defect tolerance characteristic of MHPs and help suppress non-radiative recombination losses.⁷ In addition, the band gap of MHPs can be tuned through compositional and structural modifications. In particular, halide substitution in the ABX₃ framework alters the orbital interactions within the inorganic network, modifying the band gap and, consequently, the optical and electronic properties can be tailored over a broad spectral range according to the requirements of a given application. Although the organic cation does not directly contribute to the band-edge states, its size, symmetry, and chemical nature can modify the geometry of the inorganic framework, affecting octahedral tilting, bond lengths, and bond angles, influencing the VBM and CBM. Furthermore, reducing the dimensionality of the inorganic framework enhances quantum confinement, generally resulting in an increase in the band-gap energy.⁹ This class of materials also presents other interesting characteristics like strong light absorption and high photoluminescence quantum yields (PLQYs), making MHPs particularly attractive for next-generation optoelectronic technologies.

From an industrial and manufacturing perspective, MHPs are highly appealing due to their solution-processability, flexibility, and low fabrication cost. Their compatibility with a wide range of low-temperature deposition techniques enables the preparation of high-quality crystalline films, facilitating systematic structure–property studies and the rapid development of new device architectures.^{5,10}

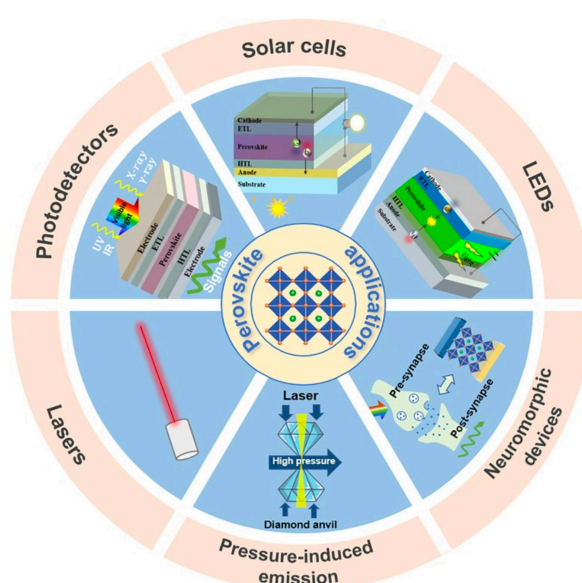


Figure 8: Different applications of perovskites.⁵

The physical properties and structural versatility that have driven the rapid development of perovskite photovoltaics have also enabled the application of these materials in a wide range of optoelectronic and electronic devices beyond solar energy conversion (**Figure 8**).

Among these, perovskite light-emitting diodes (LEDs) have shown particularly rapid progress. Since the first thin-film devices reported in 2014, advances in compositional design and interfacial engineering have increased the external quantum efficiency (EQE) beyond 20% for red, green, and near-infrared emitters, with green LEDs reaching a record EQE of 28.9%. Their high photoluminescence efficiency and narrow emission bandwidth also make halide perovskites attractive materials for next-generation full-color display technologies. The combination of high absorption coefficients, long carrier diffusion lengths and efficient charge transport has also established halide perovskites as promising active materials for photodetectors and imaging devices operating across the ultraviolet, visible, and near-infrared spectral regions, as well as for X-ray and γ -ray detection. In addition, their large optical gain enables low-threshold stimulated emission, making them suitable candidates for tunable laser applications.

In addition to their applications in optoelectronics, the ion migration and resistive switching properties of halide perovskites have generated increasing interest for their use in resistive memory devices (memristors) and artificial synapses in neuromorphic computing. Recently, advancements such as pressure-induced luminescence and other stimuli-responsive phenomena have created new possibilities in areas like mechanical sensing, anti-counterfeiting technologies, and information storage.^{5,10}

Despite these remarkable developments, the long-term operational stability of perovskite-based devices remains one of the major challenges limiting their practical implementation. In particular, defect formation and defect-assisted degradation continue to affect device performance under operating conditions, driving extensive research into defect passivation strategies and more robust device architectures.⁷

1.3 Perovskite-inspired materials

Despite the advantages of MHPs, issues such as the toxicity of lead (present in most MHPs) and the chemical instability of most of these materials under ambient conditions remain major problems for industrial scalability. Even with significant effort to address this, encapsulated MHPs solar cells used on the utility scale would ultimately need to achieve stability exceeding 25 years.⁶

The use of lead in electronics is restricted to <1000 ppm by the EU's Restriction of Hazardous Substances (RoHS) directive due to the toxicity of lead.¹¹

Even though only a low amount of Pb is implemented in solar cells, there is a potential risk of harm to humans and the environment.¹²

Perovskite-inspired materials (PIMs) have been suggested as alternatives to lead-based perovskite, preserving the advantages of traditional MHPs while addressing their limitations. However, their efficiencies remain much lower than those of lead-based, mainly due to inferior optoelectronic properties and processability.⁷

Chemical substitution of Pb^{2+} for alternative and less toxic B-site cations has been widely explored. However, the perovskite crystal structure can only be maintained if the cation has a +2 oxidation state and if the ionic radius fits within the structure. The latter is described by the Goldschmidt tolerance factor, as defined by the equation:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

Where r_A , r_B and r_X are respectively the ionic radii of the A , B and X site ions. Empirically, a perovskite is stable if the value of t is between 0.8 and 1.1, and this can be achieved only by a limited number of compositions.⁶

Substitution of Pb^{2+} with metal of group 14 with sufficiently large cations (Sn^{2+} and Ge^{2+}) can result in t values within the range, forming perovskite structures like ASnX_3 and AGeX_3 . Despite Sn- and Ge-based perovskites exhibit promising optoelectronic properties, their practical application is hindered by the instability of Sn^{2+} and Ge^{2+} , which readily oxidize to Sn^{4+} and Ge^{4+} under ambient conditions, leading to rapid degradation. An alternative is to form

double perovskites that combine a monovalent and a trivalent cation (Ag^+ and Bi^{3+}) that occupy alternating octahedra. Another approach to Pb substitution is to use trivalent cations, such as Bi^{3+} and Sb^{3+} , together with monovalent cations to maintain charge neutrality. Rather than keeping the conventional ABX_3 perovskite structure, this substitution leads to a different structural arrangement. This gives rise to a family of defect-ordered perovskite-related materials with general formula $\text{A}_3\text{B}_2\text{X}_9$, which have attracted considerable interest as lead-free perovskite-inspired materials due to their chemical stability and promising optoelectronic properties.^{6,13}

1.4 $\text{A}_3\text{B}_2\text{X}_9$ materials

Among these perovskites inspired materials, bismuth- and antimony-based compounds with the general formula $\text{A}_3\text{B}_2\text{X}_9$ ($\text{A} = \text{Cs}^+, \text{Rb}^+, \text{K}^+, \text{MA}^+$; $\text{B} = \text{Bi}^{3+}, \text{Sb}^{3+}$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) are particularly attractive. Bi^{3+} and Sb^{3+} are isoelectronic cations suitable for replacing Pb^{2+} in the B site because they share a similar electronic configuration with lead, but have low toxicity and improved chemical stability.⁶

In fact, Bi^{3+} and Sb^{3+} can react with organic iodides to form organic Bi- or Sb-halide materials, which have similar characteristics to lead halide perovskites due to comparable orbital overlaps between 6s (Bi^{3+}) and 5p (I^-) and 5s (Sb^{3+}) and 5p (I^-) orbitals.⁷

These materials can be viewed as defect-ordered perovskites, where only two-thirds of the B-site is occupied, requiring the chemical formula $\text{A}_3\text{B}_2\text{X}_9$ instead of ABX_3 to maintain chemical stability.

Some of these materials, like $\text{Cs}_3\text{Sb}_2\text{I}_9$, exhibit polymorphism: they can exist in a 0D dimer-phase structure, consisting of isolated bioctahedral clusters (specifically, two $[\text{BX}_6]^-$ octahedra share their faces to form a $[\text{B}_2\text{X}_9]^{3-}$ bi-octahedron) resulting in a hexagonal structure (S.G., $\text{P6}_3/\text{mmc}$) and in a 2D layered structure, which forms from a general ABX_3 arrangement with the removal of every third B layer along the crystal axis, the structure is made of corner-sharing $[\text{BX}_6]^{3-}$ octahedra that define the layers (**Figure 9**). These materials have the possibility to switch between a 0D and a 2D structure based on the composition and the processing method. Other materials have a fixed structure, like $\text{Cs}_3\text{Bi}_2\text{I}_9$, that can exist just in a 0D form.⁷

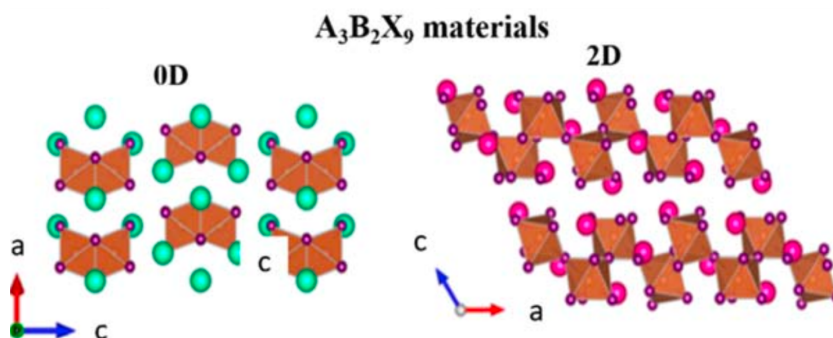


Figure 9: Polymorph crystal structure of $A_3B_2X_9$ material.⁶

Several $A_3B_2X_3$ materials have been investigated as potential absorber layers in future PV devices, these include the 0D $Cs_3Bi_2I_9$ and the 0D/2D $Cs_3Sb_2I_9$.⁶

Among Bi-containing perovskites, $Cs_3Bi_2Br_9$ and $Cs_3Bi_2I_9$ have been the object of several recent publications for their potential use in organic synthesis and photodetection.^{14–16}

The nature of the halide anion strongly influences the electronic structure and, consequently, the optical band gap of these materials. In general, bromide-based compounds exhibit larger band gaps than their iodide counterparts, while the replacement of Br^- with the larger and more polarizable I^- anion leads to a reduction in the band gap.

$Cs_3Bi_2Br_9$ showed good performance as an active layer in photodetectors and in photocatalytic applications. It was found to be effective in the direct selective photocatalyzed oxidation of hydrocarbons with high conversion rates and excellent selectivity, and in the ring-opening reaction of epoxides.

$Cs_3Bi_2I_9$ has been investigated for its possible use as an active layer in perovskite solar cells, due to its high absorption coefficient and a band gap of about 2.10 eV. There were some difficulties in optimizing the film morphology for PSCs due to the known dissolution problems of inorganic precursors in solution-based methods. The potential applications of $Cs_3Bi_2I_9$ have been further extended in the last few years to photodetection and photocatalysis for hydrogen evolution and organic pollutant degradation.¹⁷

Most of these materials can be synthesized via solution processing methods, as with MHPs, but various $A_3B_2X_9$ powders can also be prepared easily by solid-state synthesis, in which AX and BX_3 powders react to form the product under ball-milling. In general, $A_3Bi_2X_9$ materials could be prepared in ambient conditions and it was found that their properties are stable over time, differently from the Sn-based perovskites that require a specific working atmosphere in

nitrogen to avoid degradation. The Bi-based PIMs showed good stability for absorbing light after storage in the dark and in dry air after a month, too and also display, over time, just little variations in the spectrum. Solar cells with these materials have an efficiency that initially grows and then tends to stabilize without decreasing over a long period of time.¹⁸

1.5 Vapor phase deposition: RF magnetron sputtering

PIMs thin films for device applications are usually synthesized via solution processing, spin coating or vapor deposition. Producing high-quality thin films with large grains and few grain boundaries is difficult because film formation depends on multiple factors, such as precursor concentration, solvent, impurities, temperature and other process parameters. Optimizing them is essential to minimize defects such as traps, pinholes and surface roughness, which can negatively affect charge transport, device efficiency and long-term stability. The major issues are rapid crystallization and uneven crystal growth, which degrade thin film quality and yield an inhomogeneous surface.¹⁹ This problem is attributable to many factors, such as annealing conditions, solvent evaporation during deposition and surface properties. All these influence film morphology, thickness, crystallinity and, of course, have a negative effect on the performance of devices with these films. Another big problem is the production of sequential deposition: depositing subsequent layers is hardly achievable due to the requirement of solvents and heated substrates, which cause side reactions and alter the surface morphology of the preceding layers.^{20,21}

Furthermore, while solution processing is known as a low-cost manufacturing method, it often involves the use of toxic solvents that can compromise product quality and pose concerns for operators' health and environmental safety.

Solvent-free deposition techniques are a promising path to overcome these limitations.¹³

Vapor-based deposition techniques have attracted a lot of interest in the last few years since they provide purity of precursors and deposited films, due to the vacuum atmosphere and high control over deposition parameters. With these methods, it is easy to obtain perovskite thin films without the use of annealing steps, solvents and with high reproducibility, suited for scale-up preparation and large-area deposition. Unlike solution processing, with vapor-phase methods it is possible to have sequential deposition to create heterostructures and junctions.²⁰

Many different vapor-based deposition methods are available in depositing perovskite thin films and they belong to two big groups: CVD (Chemical Vapor Deposition) and PVD (Physical Vapor Deposition). The chemical techniques rely on one or more volatile precursors that undergo a chemical reaction at high temperature and create products that deposit on a substrate. The physical methods are always in vacuum, but in this case no chemical reaction occurs, the precursors pass from the solid state to the vapor phase and then deposit on the substrate. The main techniques that belong to this category are: vacuum evaporation, RF sputtering and pulsed laser deposition.

There are numerous advantages of using PVD processes, these allow the deposition of alloy compounds, multilayer compositions and special structures. However, PVD process exhibits greater energy consumption compared to the CVD process, which can be reduced, for example, by recycling target materials or otherwise interchange heat exchange modules in order to recover residual heat.²²

CVD has been explored to obtain $A_3B_3X_9$ thin films, but the different melting temperatures of the precursors require a multi-step process with elevated growth temperatures, which have direct consequences on the environment and can produce toxic gases.^{13,21}

These techniques applied to the synthesis of hybrid perovskites are generally based on vacuum evaporation processes and vapor-assisted solution processes (VASP).²⁰

The evaporation method operates at relatively low atomic energy and requires high-vacuum pressure, resulting in few adsorbed gases and highly directional deposition. It features high deposition rates and transfers large and oriented grains, though it typically offers low substrate adhesion. While crucible contaminants can sometimes migrate to the coating and reduce its purity, evaporation remains highly suitable for industrial applications and thick films where surface morphology is not a critical requirement.²²

Despite that, in many cases, target evaporation by heating is not suitable for the deposition of full inorganic thin films due to their low volatility, here, the sputtering process works more efficiently.²³ Sputtering deposition can be performed through various configurations, including Ion Beam, Diode, Triode, Reactive, and Magnetron sputtering, with Magnetron reactors experiencing the most significant development and recently giving rise to highly promising pulsed techniques. Magnetron systems traditionally rely on either Direct Current (DC) or Radio-Frequency (RF) power sources. DC power remains one of the most cost-effective and

easily controlled options, particularly for conductive targets, although its sputter yield can be lower. To overcome the charge accumulation that occurs when sputtering non-conductive or low-conductivity materials, RF sources utilize an alternating high-frequency signal to maintain the plasma. Regardless of the specific power source used, standard deposition systems share a foundational setup consisting of a high vacuum chamber with the substrates and targets, a pumping system, a DC, RF or pulsed power supply and a gas inlet to generate the plasma.²² Radio frequency (RF) magnetron sputtering is an emerging alternative to low-temperature deposition of perovskites, offering stoichiometric control and still largely unexplored, but an opportunity to develop scalable, high-performance lead-free optoelectronic materials.¹³ This technique allows fine-tuning of deposition conditions by adjusting parameters such as RF power, gas pressure, target-to-substrate distance and deposition duration, providing an excellent platform to optimize perovskite films.²⁰

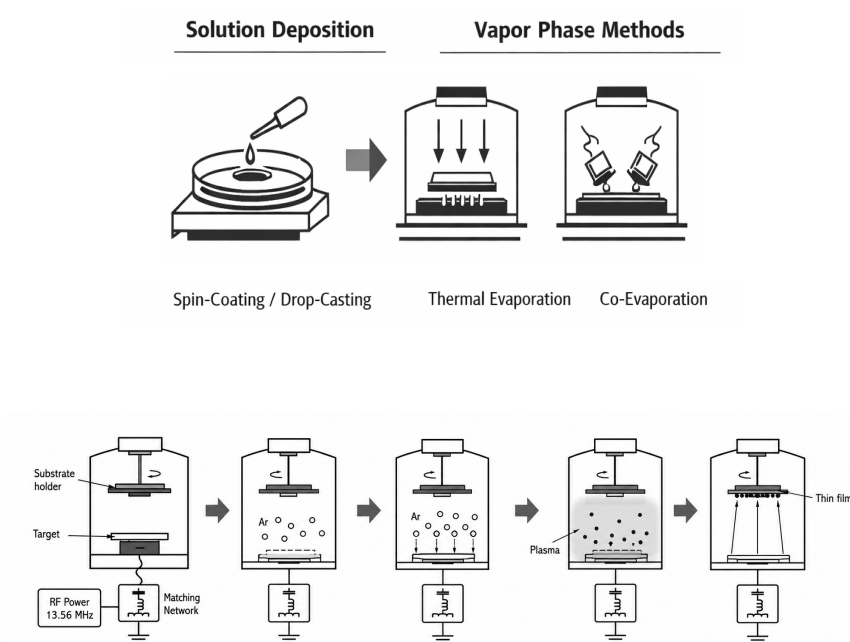


Figure 10: Evolution of perovskite thin film deposition methods.

Thin films of target materials with the desired morphology can be obtained in a single step and deposition can be performed directly on the substrate without using any binder chemicals or other routes.²¹

Sputtering offers control over the properties of deposited films, such as thickness, adhesion, and morphology, and the deposition parameters, including current density, gas type and flow,

bias, temperature, pressure, vacuum system configuration and the specific arrangement of substrates within the chamber, are subject to variations. These adjustments directly influence the resulting film thickness, grain size and substrate adhesion, determining film characteristics such as hardness, chemical composition, morphology, microstructure, and Young's modulus. Furthermore, operational conditions, such as the number of satellite holders, substrate and holder rotation, the area ratio between the global holder and satellites and the initial orientation of the substrate face, play a critical role in dictating the overall homogeneity of the coating. Post-deposition annealing or treatments remain a crucial point to observe for having defect-free films of high quality, too.²²

Therefore, radio frequency magnetron sputtering is a highly versatile technique for depositing thin films of both conductive (metallic) and non-conductive (ceramic) materials. This method enables the sequential growth of distinct layers with nanometric thickness control and minimized surface roughness. Key advantages include excellent film homogeneity, low contamination levels and straightforward doping processes.²⁴ This method is particularly vital for applications where overall film quality is more important than the deposition rate and is ideal for temperature-sensitive substrates, such as polymers with low melting points or materials prone to cooling stresses. Ultimately, because it is a cleaner process, it provides significantly better film densification and the ability to perform the deposition at room temperature significantly mitigates mechanical stress. This avoids the structural degradation and cracking typically caused by the large thermal expansion coefficient (CTE) mismatch between the perovskites and the substrate.^{22,24}

RF magnetron sputtering is very easy to implement even in industry and for this reason it could have an important role in producing large-scale coatings.²¹

1.6 Purpose of the research

In recent years, bismuth-based perovskite derivatives with the general formula $\text{Cs}_3\text{Bi}_2\text{X}_9$ (X= Br, I) have attracted significant attention from diverse scientific communities due to their remarkable technological potential, spanning from photovoltaics and photodetectors to photocatalysis and organic synthesis. The expansion of lead-free perovskite-inspired materials toward these novel applications is primarily driven by their excellent photocatalytic performance and their water stability, a property that remains critical for conventional lead-

based systems. Among these bismuth-containing candidates, $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{Br}_9$ have been the focus of numerous recent publications highlighting their promising photoactive properties.¹⁷

Despite their theoretical promise, the practical integration of these compounds into efficient optoelectronic devices is currently hindered by severe challenges related to film morphology and processability. Achieving continuous, pinhole-free, and highly crystalline thin films is a fundamental prerequisite for optimal device performance. Furthermore, a major intrinsic limitation restricting the widespread application of these PIMs is their relatively wide bandgap, which limits their optical absorption within the solar spectrum. Although halide alloying enables band-gap tuning, the minimum value reported to date is approximately 2.0 eV for $\text{Cs}_3\text{Sb}_2\text{I}_9$.²⁵

Motivated by these challenges, this thesis focuses on the mechanochemical fabrication and characterization of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x = 0; 0.5; 1; 1.5; 2$) solid solutions. Specifically, this work explores the deposition of high-quality thin films utilizing synthesized powder precursors as the starting material, aiming to develop reliable processing pathways that overcome the current limitations of lead-free perovskite-inspired thin films.

In order to address the wide bandgap issue, this work exploits the effect of metal alloying by mixing bismuth and antimony (Sb/Bi). Computational modeling on similar systems indicates that partial atomic substitution induces a staggered alignment of the valence and conduction bands of the pure endmembers.²⁶ This produces a unique, non-linear behavior characterized by a simultaneous upshift of the valence band maximum and a lowering of the conduction band minimum. Consequently, intermediate compositions exhibit lower absorption edge energies (a significant band-gap red-shift) compared to the pure compounds.²⁷ Specifically, the alloying strategy explored in this work enabled the isolation of the $\text{Cs}_3\text{BiSbI}_9$ composition, which exhibits an optical bandgap of approximately 1.70 eV, that is the lowest value reported to date for all-inorganic perovskite-related phases.

In order to bypass the morphological limitations inherent to traditional wet-chemical deposition, this thesis introduces an alternative, sustainable fabrication process based on physical vapor deposition. The proposed approach involves the mechanochemical synthesis of high-purity $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ powders via ball milling that are subsequently utilized as target materials for radio-frequency magnetron sputtering.

By transitioning from solution processing to vacuum-based RF magnetron sputtering, this research aims to exploit the deterministic control, high uniformity over large areas, and industrial scalability of PVD techniques. This innovative pathway has successfully yielded high-quality thin films across the entire compositional range while maintaining strict stoichiometric control over the Sb/Bi ratio, thereby establishing a reliable platform for the development of high-performance, stable, lead-free optoelectronic devices.

2. Experimental

2.1 Synthesis of powders

The powders of the perovskite-inspired materials, shown in **Figure 11**, were synthesized using a mechanochemical approach. This method is green, fast, economical, and easy to perform. It reduces to zero the use of solvents and acids, which can be toxic both for the environment and for the operator, and which can also be difficult to dispose of at the end of the process. With this method, it is also easy to obtain a 100% yield because the powders of the precursors are simply mixed to obtain the product powder.

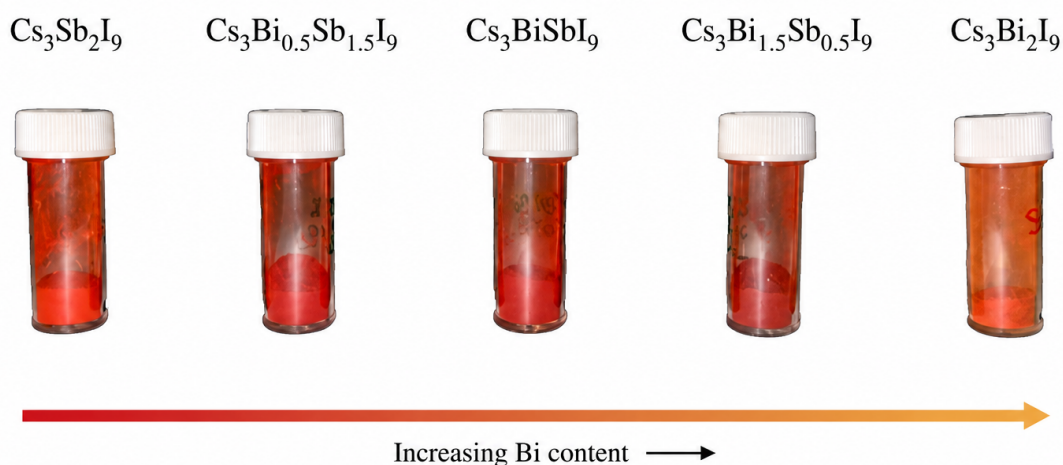


Figure 11: Photograph reporting the samples of $\text{Cs}_3\text{Sb}_{2-x}\text{Bi}_x\text{I}_9$ solid solution.

This synthesis process is used in many fields for the scalable production of metallic alloys as well as ionic compounds. The mixing takes place inside a vibratory ball miller. During the milling process, the balls shake at variable speed inside the jar, generating a large number of high-energy collisions over a period of time that depends on the materials being processed. These impacts transfer mechanical energy to the powder mixture, which is trapped between the balls and the walls of the jar. As a result, the powder undergoes severe plastic deformation together with a local increase in temperature, promoting the reaction between the precursors. At the same time, the particles are continuously flattened, fractured, and welded together. We have to pay attention to different factors during a mechanochemical synthesis: the material of the jar and the balls (which can be stainless steel, tungsten carbide, agate, or alumina) and their dimensions, the milling time, the milling speed, and the ball-to-powder ratio.²⁸

It is also possible to add a very small amount of solvent or surfactant during the synthesis to reduce the friction between the balls and the powders. The main disadvantages of this technique are the possible contamination of the product from the material of the jar and the balls, and the production of materials with a high concentration of defects caused by the impacts. This is not a problem in our case because perovskites are defect-tolerant.

Regarding the project of this thesis, a vibratory ball miller (Retsch MM 400), schematized in **Figure 12**, was used to produce the solid solutions. The powders were prepared by mixing stoichiometric amounts ($x = 0, 0.5, 1, 1.5, 2$) of the precursors CsI (99%, Alfa Aesar), BiI₃ (99.5%, Alfa Aesar), and SbI₃ (99%, Alfa Aesar) inside a 5 mL stainless steel jar using stainless steel balls with a diameter of 5 mm. The volume inside the jar was filled with one-third powder, one-third balls, while the remaining one-third was left empty to ensure efficient milling. To promote the reaction, 100 μ L of ethanol was added to each synthesis.

The mechanochemical synthesis involved four milling cycles, each consisting of 20 minutes of grinding at 15 Hz followed by a 10-minute pause. At the end of the process, powders of the perovskite with different colours were obtained, depending on their composition.



Figure 12: Picture of the vibratory ball mill used for the powder synthesis.

2.2 Deposition of thin films

Thin films of the perovskite-inspired materials were deposited by RF magnetron sputtering. This is a widely utilized physical vapour deposition technique used to fabricate films of desired materials with precise control over thickness and stoichiometry. The setup is constituted of a vacuum chamber and two electrodes connected to a high-voltage power source. In RF magnetron sputtering, the target material is situated on a magnetron cathode, to which a radio-frequency alternating voltage, typically of 13.56 MHz, is applied. This oscillating electric field sustains the plasma while preventing charge accumulation on the target surface, making the technique particularly suitable for the deposition of insulating materials, enabling a more stable sputtering process without arcing or uneven deposition.²¹ A schematic view of the entire setup is shown in **Figure 13**.

There are different steps to follow in order to have a successful deposition of thin films by sputtering. First of all is important that all the substrates go through a cleaning process, poor substrate handling and poor maintenance of the system could lead to contamination and the production of films of bad quality. The RF magnetron sputtering process can be divided into three main stages: *ramp-up*, *deposition*, and *ramp-down*.

The *ramp-up stage* involves preparing the vacuum chamber for the deposition process. Initially, the chamber is evacuated using a mechanical (roughing) pump to achieve a pressure of approximately 10^{-2} mbar. Subsequently, a high-vacuum pump, typically a turbomolecular pump, is activated to further reduce the chamber pressure to 10^{-5} - 10^{-6} mbar. During this stage, the substrate can be gradually heated, when required, with a temperature-controlled heating system to reach the desired deposition temperature.

Once high vacuum is reached, an inert gas (called the *working gas*), such as argon (Ar), is pumped into the chamber up to the desired pressure, known as *working pressure*, under which the sputtering is to take place. Finally, an RF power supply operating at 13.56 MHz is applied to the magnetron cathode, generating and stabilizing the plasma before film growth begins.

The *deposition stage* starts when the positively charged Ar ions (Ar^+), ionized by RF field, are accelerated towards the material target surface, which is maintained at a negative potential. The bombardment of Ar^+ onto the material surface ejects (sputters) the target atoms due to the transfer of momentum. Multiple such energetic ejected atoms get deposited on the surface of

the substrate, creating a thin film. The magnetron configuration creates a magnetic field parallel to the surface of the target, which increases the trapping of electrons near the surface, which consequently increases the ionization efficiency and plasma density. Therefore, the magnetrons effectively improve the efficiency of the sputtering process.

For reactive RF magnetron sputtering, reactive gases such as oxygen or nitrogen can be introduced together with argon to produce oxide or nitride coatings.

The *ramp-down stage* begins after the desired film thickness has been achieved. The RF power is switched off, the process gas flow is stopped, and the chamber is allowed to cool under vacuum to prevent oxidation and minimize thermal stresses in the deposited film. Once the system has reached a suitable temperature, the chamber is vented with dry gas or air until atmospheric pressure is restored, allowing the coated samples to be safely removed.^{21,22}

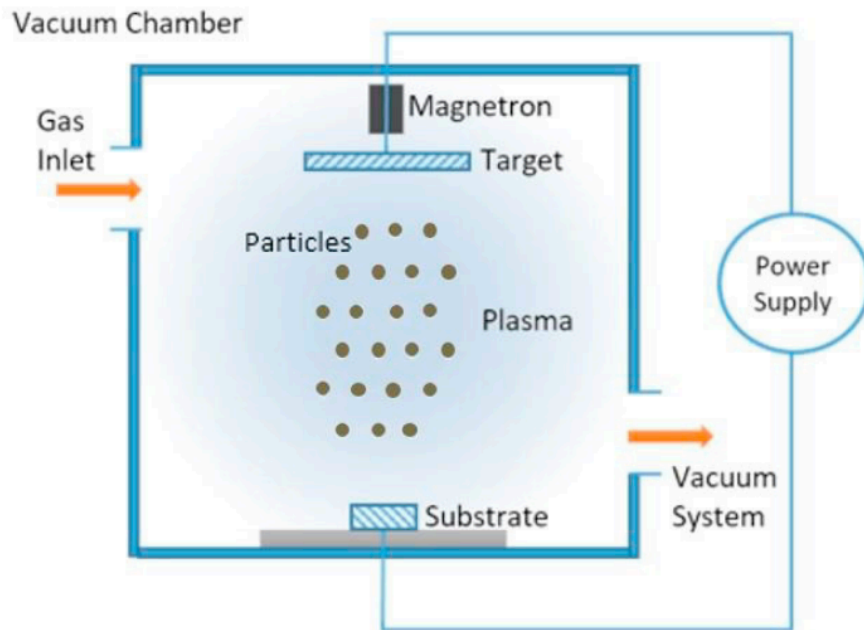


Figure 13: Schematic diagram of RF magnetron sputtering process.²²

In our case, the perovskite-inspired thin films were deposited with a Kenosistec KSE 500 CK confocal multitarget sputter and thermal evaporator. The substrates used for the deposition were 1×1 cm quartz glass. Before deposition, they were cleaned following this procedure: the surface was first rubbed with a cloth soaked in isopropanol, followed by three cleaning cycles in an ultrasonic bath: 20 minutes in distilled water, then 20 minutes in acetone, and finally 20 minutes in isopropanol. Just before deposition, the substrates underwent an additional cleaning

cycle in an *Ossila UV Ozone Cleaner* equipped with a mercury vapor lamp. The latter emits radiation in the 200 nm range, which is capable of breaking oxygen bonds, generating radicals and ozone that effectively remove any organic residues from the glass surface.

The target material used for the deposition process was prepared by placing approximately 4–5 g of the mechanosynthesized powder into a copper back plate and then pressing it to obtain a uniform surface, as shown in **Figure 14**.

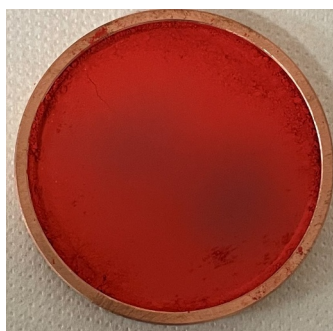


Figure 14: Target: pressed powders of precursors.

The thin films were deposited under the following operating conditions. A cathode power of 50 W was applied throughout the deposition process, while the working pressure inside the sputtering chamber was maintained at 2.3×10^{-2} mbar. Argon was used as the sputtering gas with a constant flow rate of 30 sccm to ensure stable plasma conditions during the deposition. The target-to-substrate distance was fixed at 10 cm for all depositions in order to guarantee reproducible growth conditions. All deposition parameters were kept constant throughout the process, allowing the investigation of the deposited film properties without introducing additional variables. At the end of the deposition process, uniform perovskite thin films with different colours were obtained, depending on their chemical composition, as shown in **Figure 15**.

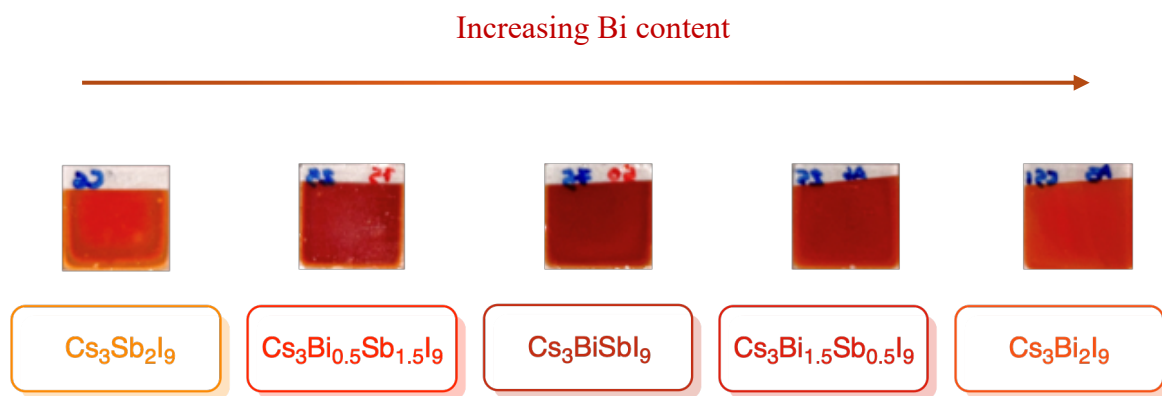


Figure 15: Photograph reporting the samples of $\text{Cs}_3\text{Sb}_{2-x}\text{Bi}_x\text{I}_9$ thin films.

2.3 Characterization Techniques

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) is a widely used and powerful material characterization technique that provides detailed information about atomic structures, including the position and arrangement of atoms within the unit cell and the spacing between atomic planes. As a non-destructive method, it is applicable to a wide range of materials, such as minerals, polymers, metals, and semiconductors, and is extensively used in both research and industry.²⁹ The main advantages of XRD are its speed, high precision and accuracy, the ability to probe a large sample volume, and the possibility of performing in situ measurements under non-ambient conditions. The technique provides information on crystalline phases, lattice parameters, degree of crystallinity, preferred crystallographic orientation (texture), crystallite size, and, indirectly, composition through lattice parameter analysis. Since the wavelength of X-rays (0.15–0.5 nm) is of the same order of magnitude as interatomic distances, XRD is ideally suited for investigating crystal structures.³⁰

When X-rays interact with a crystalline material, they are scattered by the electrons surrounding the atoms. The scattered waves interfere with one another, producing either constructive or destructive interference depending on their relative phase. Diffraction occurs when constructive interference is achieved, which is possible because of the periodic arrangement of atoms in a crystal lattice. Consequently, crystalline materials produce a series of sharp diffraction peaks, whereas amorphous materials, lacking long-range order, exhibit broad diffuse halos instead of

distinct reflections. In crystalline solids, the translational symmetry of the lattice gives rise to families of parallel and equally spaced crystallographic planes. According to Bragg's model, shown in **Figure 16**, these planes are considered infinitely extended and partially reflecting. X-rays are reflected by successive lattice planes separated by an interplanar distance d , giving rise to an optical path difference between the reflected beams. Constructive interference occurs when this path difference is an integer multiple of the X-ray wavelength, leading to the diffraction condition described by Bragg's law:

$$2d\sin\theta = n\lambda \quad (2)$$

where n is the order of diffraction, λ is the X-ray wavelength, d is the interplanar spacing, and θ is the beam angle.²⁹

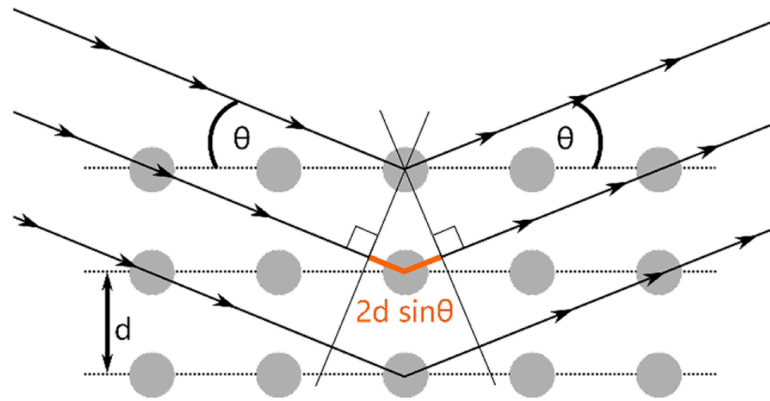


Figure 16: Schematic diagram of Bragg's diffraction model.³⁰

A more rigorous description of the constructive interference condition introduced by Bragg can be obtained through the construction of the Ewald sphere (shown in **Figure 17**). This model considers a sphere with radius equal to $1/\lambda$, where λ represents the wavelength of the incident beam passing through the diameter of the sphere. The origin of the reciprocal lattice is placed at the point where the incident wave vector emerges from the sphere (B). In this representation, any reciprocal lattice point ($B(hkl)$) that lies on the surface of the Ewald sphere satisfies the Bragg condition for the corresponding direct lattice:

$$OB = \frac{1}{d_{hkl}} = \frac{2}{\lambda} \sin\theta \quad (3)$$

where hkl are the components of a reciprocal lattice vector and correspond to the Miller indices of the family of crystallographic planes $\{hkl\}$ in the real space lattice. Therefore, to observe a diffraction signal, at least one reciprocal lattice point must intersect the surface of the Ewald sphere.²⁹

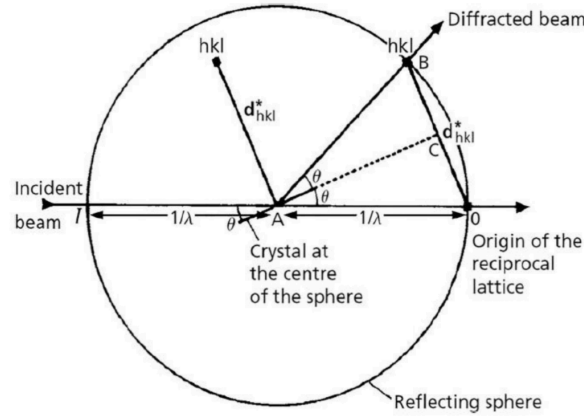


Figure 17: Schematic diagram of Ewald sphere.²⁹

Experimentally, there are three different ways to do diffraction:

1. Laue method, using polychromatic radiation on a fixed crystal;
2. Powder method, using a monochromatic beam on powder, with randomly orientated microcrystals;
3. Single crystal method, where a crystal is rotated under a monochromatic beam to satisfy Bragg conditions.

An X-ray diffractometer consists of five major components: The X-ray source, the detector, the incident (or primary beam) optics, the receiving (or diffracted beam) optics, and the goniometer. The diffractometer is contained within a radiation enclosure and controlled by a computer.³⁰ In the case of this thesis, for both powders and thin films, X-ray diffraction patterns were acquired by a Bruker D8 Advances diffractometer with a copper X-ray source ($\lambda = 1.5418\text{\AA}$), a crystal monochromator of SiO_2 and three different slits for beam control, in a Bragg-Brentano configuration. The measurement program used for the films scans from 5° to 70° , with a step of 0.02° and counting 12 seconds. The measurement program used for the powders scans from 5° to 70° , with a step of 0.02° and counting 2 seconds.

Diffraction experiments were carried out in flat-plate mode by using a null-background sample holder.

2.3.2 Rietveld refinement

In the characterization of crystalline materials, powder X-ray diffraction (PXRD) serves as an indispensable tool. To extract precise crystallographic information from polycrystalline samples, Hugo Rietveld introduced a whole-pattern fitting technique in the 1960s: the Rietveld method. Unlike traditional methodologies that extract individual peak intensities, the Rietveld method analyzes the entire diffraction profile as a continuous function. The refinement process begins with an initial theoretical model of the crystal structure, alongside parameters describing the instrument geometry. From this starting point, a simulated diffraction pattern is calculated and compared to the experimental data point-by-point. Using a non-linear least-squares minimization algorithm, the software systematically adjusts structural and instrumental variables to minimize the residual difference between the observed and calculated intensities, mathematically expressed as:

$$R_y = \sum_i w_i |y_i(\text{obs}) - y_i(\text{calc})|^2 \quad (4)$$

Here, $y_i(\text{obs})$ and $y_i(\text{calc})$ represent the observed and calculated intensities at each step i , while w_i is a statistical weighting factor. Throughout the refinement, the algorithm optimizes a lot of variables to achieve a physically realistic fit. These include structural parameters, such as unit cell dimensions, atomic fractional coordinates, thermal displacement parameters, and site occupancies, but also profile-specific parameters like background coefficients and peak shape functions. By fitting the entire profile rather than isolated peaks, the Rietveld method refines complex crystal structures without the need for single crystals, but also enables quantitative phase analysis of multiphase mixtures. Furthermore, by modeling peak broadening effects, the method can quantify microstructural properties of the sample, such as crystallite size and microstrain.³¹

In the case of this thesis, the Rietveld refinement was performed on powder samples diffraction data using the TOPASv6 software.

2.3.3. Raman Spectroscopy

Raman spectroscopy is a non-destructive technique based on the inelastic scattering of monochromatic light. It provides information about the molecular structure, chemical composition, and crystalline state of materials through the characteristic vibrations of their chemical bonds. The Raman effect arises from an energy exchange between the incident photons and the vibrational modes of a molecule, producing a shift in the wavelength of a small fraction of the scattered light. This shift, known as the *Raman shift* and typically expressed in cm^{-1} , depends on the chemical structure of the scattering molecules. When light interacts with a substance, three different scattering processes may occur, as illustrated in **Figure 18**. The most common is *Rayleigh scattering*, an elastic process in which no energy is exchanged and the scattered light retains the same frequency as the incident radiation. Alternatively, energy exchange between the photon and the molecule gives rise to Raman scattering. If the substance transfers vibrational energy to the scattered photon, this one gains energy and its frequency increases, producing *anti-Stokes Raman scattering*. Conversely, if the molecule absorbs energy from the incident photon, the scattered one loses energy and its frequency decreases, resulting in *Stokes Raman scattering*. Analysis of the Raman shift provides information on molecular vibrations, structure, symmetry, chemical bonding, and the electronic environment, enabling both qualitative and quantitative characterization of materials. The resulting Raman spectrum, which represents the distribution of Raman shifts, serves as a molecular fingerprint.³²

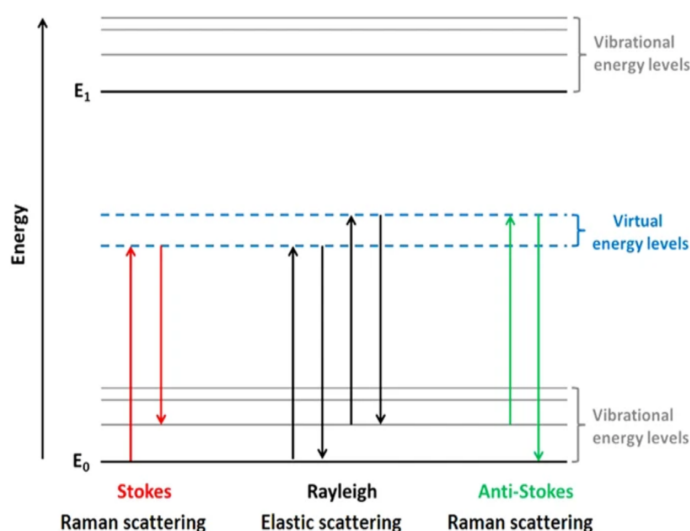
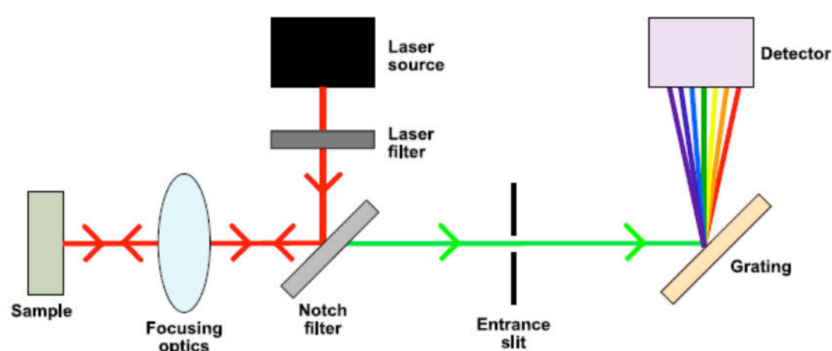


Figure 18: Jablonski diagram of energetic transitions involved in Raman scattering.³³

A Raman spectrometer consists of a light source (typically a monochromatic laser), a monochromator, a sample holder, and a detector. The laser beam is focused onto the sample through a high-magnification objective, allowing the acquisition of spectra with micrometric spatial resolution. A schematic diagram of a typical Raman spectrometer is shown in **Figure 19**. The quality of Raman analysis depends on several factors, including a high signal-to-noise ratio, instrument stability, and adequate spectral resolution. Acquisition parameters, such as the laser wavelength, incident laser power, integration time, number of accumulations, and spectral acquisition range, must be optimized according to the properties of the sample. Appropriate selection of these parameters maximizes the signal-to-noise ratio while minimizing the risk of local heating or laser-induced degradation of the sample. Two main technologies are commonly used to acquire Raman spectra: dispersive Raman spectroscopy and Fourier transform (FT)-Raman spectroscopy. These techniques differ in the type of laser source and in the method used to detect and analyze the Raman-scattered light. Each approach offers specific advantages, and the most suitable technique should be selected according to the characteristics of the sample.³²



*Figure 19: Schematic diagram of Raman spectroscopy setup.*³⁴

In the case of this thesis, Micro-Raman measurements were performed at room temperature using an integrated confocal XploRA Plus spectrometer (HORIBA Scientific) coupled to an Olympus BX43 microscope. The incident laser power can be adjusted by the use of neutral density filters with different optical densities in order to optimize the incident laser power. The spectrometer is equipped with a motorized x - y stage for precise sample positioning and provides a spectral resolution of approximately 2 cm^{-1} . Raman signals are collected using an open-electrode CCD detector cooled by a multistage Peltier air-cooling system. All measurements were done using the 638 nm (100 mW) laser light source. The laser beam

was focused onto the sample through a 100× magnification objective, providing a spot size of approximately 0.7 μm^2 . The incident laser power at the sample surface was kept at $3 \times 10^4 \text{ W cm}^{-2}$ to avoid laser-induced transformations.

2.3.4. UV-Vis spectroscopy

UV–Visible (UV–Vis) spectroscopy is a non-destructive analytical technique widely employed to investigate the optical properties and electronic structure of materials. Thanks to its simplicity, relatively low cost, and ease of implementation, it is one of the most commonly used characterization methods for semiconductors, thin films, and powdered materials. The technique uses the interaction between electromagnetic radiation and matter, providing information on light absorption and electronic transitions, allowing the estimation of the optical band gap of a material. UV–Vis spectroscopy operates in the wavelength range between 200 and 800 nm, covering both the ultraviolet (200–400 nm) and visible (400–800 nm) regions of the electromagnetic spectrum. Consequently, it can be used to characterize both colourless materials, which mainly absorb in the UV region, and coloured compounds exhibiting absorption features in the visible range. The operating principle is based on the absorption of photons whose energy is similar to the energy difference between occupied and unoccupied electronic states. When photons with sufficient energy interact with the material, electrons are promoted from lower-energy occupied states to higher-energy unoccupied states. In semiconductors this process mainly corresponds to electronic transitions from the valence band to the conduction band, whereas in molecular systems or materials containing transition-metal ions additional electronic transitions may occur. The position, intensity, and shape of the absorption bands are highly related to the chemical composition, crystal structure, defect concentration, and electronic structure of the investigated material. A typical UV–Vis spectrophotometer consists of a light source, a monochromator, a sample holder, and a detector (**Figure 20**). The light source usually combines a deuterium lamp for the ultraviolet region and a tungsten-halogen lamp for the visible and near-infrared regions. The monochromator, typically based on a diffraction grating, isolates a wavelength interval from the incident polychromatic radiation. After interacting with the sample, the transmitted or reflected light is collected by a detector, which converts the optical signal into an electrical one. Depending on

the instrument configuration, detectors may include silicon photodiodes, charge-coupled devices (CCD), charge-injection devices (CID), or photomultiplier tubes (PMTs). Among these, PMTs provide the highest sensitivity because of the multiplication of photoelectrons generated by the photoelectric effect through a cascade of dynodes maintained at progressively higher electric potentials.^{35,36}

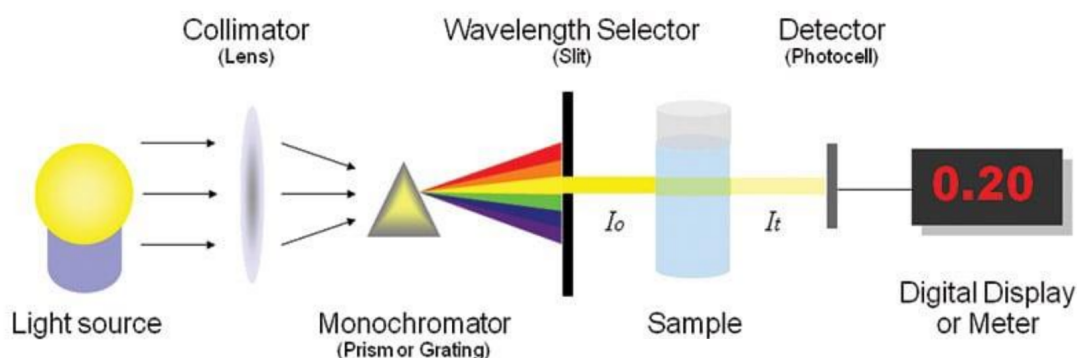


Figure 20: Schematic diagram of UV-Vis setup.³⁵

Depending on the sample, UV–Vis measurements are performed in either transmittance or diffuse reflectance mode. Thin films deposited on transparent substrates are characterized by measuring the transmitted light, whereas powders are analysed by diffuse reflectance spectroscopy (DRS). In DRS measurements, the diffusely reflected radiation is collected using an integrating sphere (**Figure 21**), allowing efficient collection of scattered light.

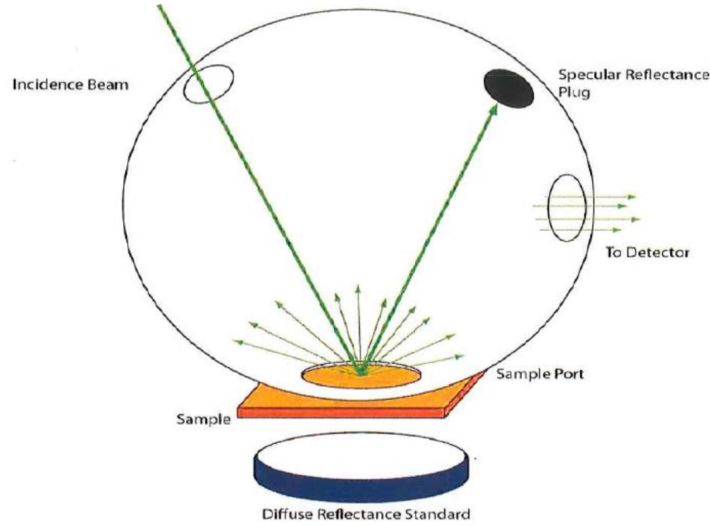


Figure 21: Schematic diagram of integrating sphere.

The acquired spectra are subsequently processed to extract optical parameters. For the transmittance measurements, the optical band gaps were extracted using the following method. The measured transmittance (T) was converted into absorbance (A) according to:

$$A = -\log_{10}(T) \quad (5)$$

where T is expressed as a fraction of the incident radiation. The absorption coefficient α was subsequently calculated from the absorbance and the film thickness d according to:

$$\alpha = \frac{2.303 \cdot A}{d} \quad (6)$$

where the factor 2.303 arises from the conversion between base 10 logarithmic absorbance and the natural logarithm commonly used in the definition of the absorption coefficient. The optical band gap (E_g) was estimated using the Tauc method, whose relation is expressed as:

$$(\alpha h\nu)^n = B(h\nu - E_g) \quad (7)$$

where $h\nu$ is the photon energy, B is a proportionality constant, and n depends on the nature of the electronic transition. Assuming an allowed indirect transition ($n=1/2$), $(\alpha h\nu)^{\frac{1}{2}}$ was plotted as a function of the photon energy $h\nu$. The optical band gap was determined by linearly fitting

the approximately linear region of the absorption edge and extrapolating the fitted line to $(\alpha h\nu)^{\frac{1}{2}} = 0$. The intercept with the energy axis provides an estimate of the optical band gap. For diffuse reflectance measurements, the reflectance data are converted using the Kubelka–Munk function,

$$F(R) = \frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (8)$$

where R is the diffuse reflectance, K is the absorption coefficient, and S is the scattering coefficient. Assuming that the scattering coefficient remains approximately constant over the investigated spectral range, the Kubelka–Munk function is proportional to the absorption coefficient. The Tauc relation was therefore applied by replacing α with $F(R)$:

$$(F(R) \times h\nu)^n = B(h\nu - E_g) \quad (9)$$

For an allowed indirect transition ($n=1/2$), the Tauc plot was obtained by plotting $[F(R)h\nu]^{1/2}$ as a function of $h\nu$. The optical band gap was estimated by linearly fitting the absorption-edge region and extrapolating the fit to the $h\nu$ axis.

For the powder samples investigated in this work, diffuse reflectance spectra were acquired directly on the powders using a Jasco V-750 UV–Vis spectrophotometer equipped with an integrating sphere (Jasco ISV-922). The instrument has a deuterium lamp and a tungsten-halogen lamp as radiation sources, a single monochromator based on a diffraction grating, and a photomultiplier tube (PMT) detector. Measurements were carried out over the wavelength range of 300–850 nm using solid-state sample holders with an optical path length of 1 mm. A white reflectance standard was used as the reference for all measurements. For the thin-film samples, transmittance spectra were recorded using a Cary Varian 6000i spectrophotometer in the wavelength range between 200 and 1800 nm.

2.3.5. Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a non-destructive surface characterization technique belonging to the family of Scanning Probe Microscopy (SPM) methods. These techniques enable the investigation of surface morphology, roughness, local variations in material properties, and other nanoscale features, providing three-dimensional images with nanometer resolution. Unlike conventional electron microscopy, which relies on an electron beam, AFM uses a sharp mechanical probe to directly scan the specimen. This approach allows the characterization of both conductive and insulating materials without the need for conductive coatings or complex sample preparation. The operating principle of all SPM techniques is based on the measurement of a local interaction between a probe and the sample surface during a scan along parallel lines. The probe geometry and mechanical properties determine the spatial resolution. Generally, SPM instruments are compact, relatively simple to operate and suitable for a wide range of applications. In AFM specifically, this interaction consists of interatomic forces, including van der Waals, electrostatic, capillary, and short-range repulsive forces. The probe is composed of a sharp tip mounted on a highly flexible cantilever that acts as the force transducer. As the tip interacts with the surface, the cantilever bends or twists proportionally to the applied force according to Hooke's law. This deflection is monitored by an optical detection system consisting of a laser beam focused on the back side of the cantilever and reflected onto a position-sensitive photodiode. This setup is sensitive enough to register sub-nanometer movements, enabling the measurement of weak interaction forces typically ranging from 10^{-12} to 10^{-7} N. AFM cantilevers are commonly made of silicon or silicon nitride, existing in a variety of geometries, with micrometric dimensions and with spring constants between 0.01 and 100 N/m depending on the application. More recently, carbon nanotube-based probes have also been developed, with enhanced resolution due to their extremely small tip diameter and high mechanical robustness. During measurement, the sample is mounted on a piezoelectric stage, which performs the scan over the x–y plane while simultaneously adjusting its vertical position along the z-axis. As the tip encounters surface protrusions or depressions, the interaction force changes. A feedback control system continuously adjusts the relative tip–sample distance to maintain a constant interaction force (or oscillation amplitude in dynamic operating modes). The corresponding z displacement required to preserve this constant interaction is recorded for

every x–y coordinate, allowing the reconstruction of a high-resolution three-dimensional topographic map of the sample surface.³⁷ A schematic diagram of a typical AFM setup is shown in **Figure 22**.

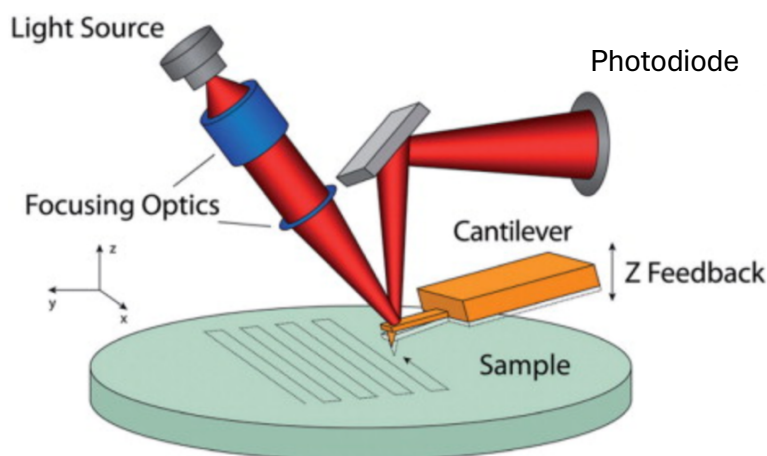


Figure 22: Schematic diagram of AFM setup.³⁸

AFM can operate in *contact*, *non-contact*, and *tapping mode* (**Figure 23**). In the conventional *contact mode*, the cantilever remains only a few angstroms from the sample surface and the interaction is dominated by short-range repulsive forces. In *non-contact mode*, the tip is maintained at a greater distance from the surface, typically between 10 and 100 Å, where long-range attractive forces, such as van der Waals interactions, predominate. Although this mode minimizes mechanical interaction with the sample, it is generally more sensitive to environmental conditions and often provides lower spatial resolution. In *tapping mode*, the cantilever is driven to oscillate close to its resonance frequency with a predefined oscillation amplitude. As the oscillating tip periodically approaches and lightly contacts the sample surface, the tip–sample interaction modifies the oscillation amplitude, phase, and frequency. These variations are continuously monitored by the feedback system and are used to reconstruct the surface topography with nanometer-scale resolution. Compared with *contact mode*, *tapping mode* significantly reduces the lateral forces on the sample surface and the risk of damaging either delicate samples or the probe itself. For this reason, it is particularly suitable for the characterization of soft materials, polymers, biological specimens, and thin films. According to the characteristics of the investigated sample is important to select appropriate experimental

parameters, these include the scan area, scan rate, cantilever resonance frequency, spring constant, oscillation amplitude, and working setpoint, all of which must be optimized to ensure stable imaging and high-resolution data acquisition.

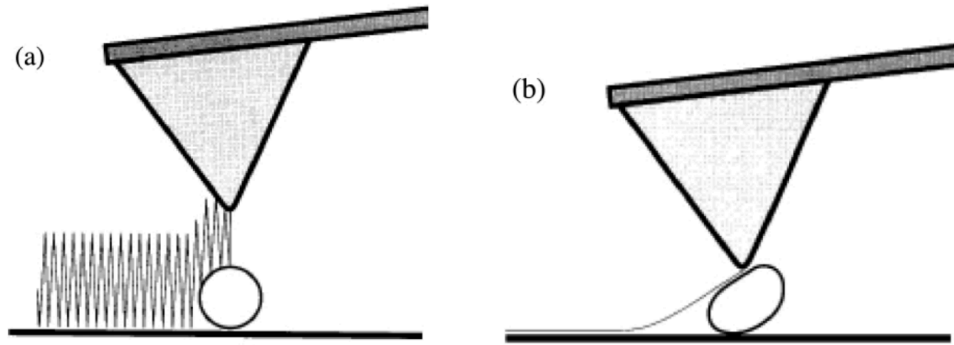


Figure 23: Comparison between the two AFM scanning types: tapping mode (a) and contact mode (b).³⁷

In this thesis, the surface morphology of the thin-film samples was investigated with an Atomic Force Microscopy using a Smart SPM scanning probe microscope (Horiba Scientific). The topographic characterization was performed in *tapping mode* using MikroMash NSC14 silicon cantilevers, characterized by a resonance frequency of 170 kHz and a force constant of 5 N/m. During the measurements the oscillation amplitude was maintained in the range of 100–120 nm, providing stable tip–sample interaction throughout the scanning process. Depending on the scan size and the surface characteristics of the samples, the scan rate was adjusted between 1.0 and 0.7 Hz to optimize image quality and resolution while maintaining measurement stability

2.3.6. Scanning Electron Microscopy and Energy Dispersive X-ray analysis

Scanning Electron Microscopy (SEM) is a high-resolution imaging technique used to analyze the surface topography and microstructure of materials. The sample is irradiated with a high-energy electron beam, generated by an electron source and focused by electromagnetic lenses. A schematic view of the setup is shown in **Figure 24**. The signals produced when the beam

interacts with the specimen surface include secondary electrons (SE), backscattered electrons (BSE), Auger electrons, X-rays, and photons of different energies. Secondary electrons originate from the most superficial layer of the sample, providing detailed information about surface morphology and roughness. Backscattered electrons highlight compositional differences across the sample, their intensity correlates with the atomic number of the elements and it is possible to produce high-resolution images down to 1 nm. Additionally, X-rays can be used to investigate the elemental composition of the sample. Compared to conventional light microscopy, SEM has a superior resolution of three-dimensional structures, a greater depth of field and it is able to achieve a higher magnification.³⁹ During analysis it is possible to adjust instrumental parameters, such as accelerating voltage, working distance, beam current, and magnification, depending on the characteristics of the material and the required level of detail. The choice of accelerating voltage is a critical parameter, as it directly influences electron penetration depth, interaction volume, and image contrast.⁴⁰

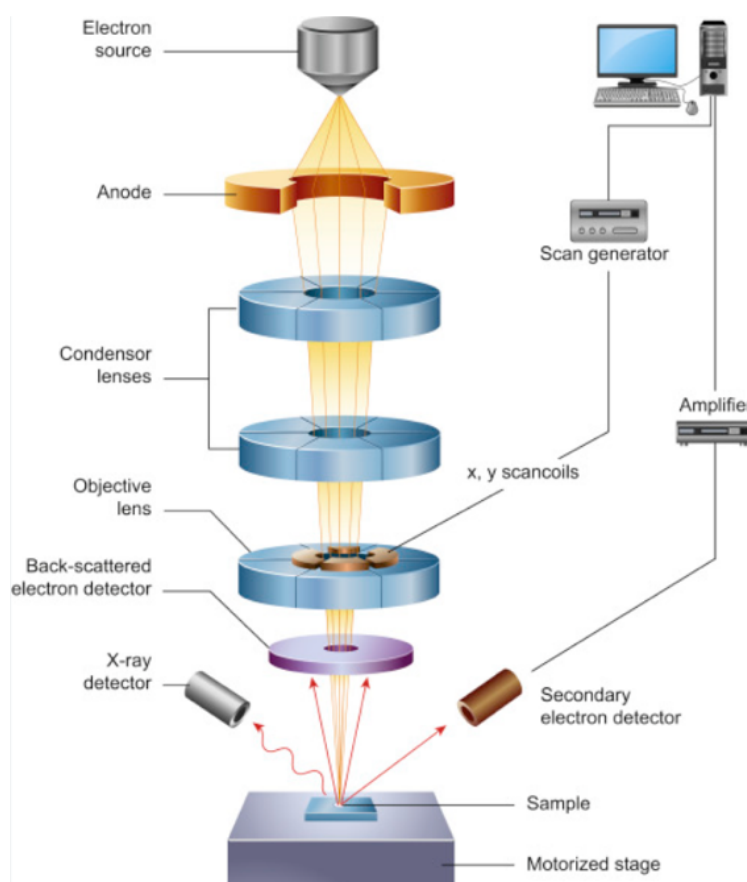


Figure 24: Schematic diagram of SEM.⁴¹

Energy-dispersive X-ray spectroscopy (EDX) is a non-destructive microanalytical technique used to identify and quantify the elemental composition of a sample, as well as to map the spatial distribution of these elements. This technique relies on the generation of characteristic X-rays resulting from the interaction of a primary electron beam with the atoms of the target material. Electron probe microanalysis is generally divided into two main methods: Wavelength-Dispersive Spectrometry (WDS) and Energy-Dispersive Spectrometry (EDS). WDS operates sequentially based on Bragg's law of diffraction, utilizing specialized crystals with varying interplanar spacings to isolate and measure specific X-ray wavelengths. While WDS offers superior spectral resolution and lower detection limits, the instrument is larger, more complex, and requires longer acquisition times. In contrast, EDS detects X-rays of all energies simultaneously, generating a spectrum of X-ray intensity versus photon energy. Although EDS is a powerful tool for rapid, semi-quantitative elemental mapping and point analysis, its detection limit for most elements is typically restricted to concentration levels above 0.1 wt.% to 1.0 wt.% under standard operating conditions, making it less suitable for trace element analysis compared to bulk techniques.⁴⁰

In the case of this thesis, the surface morphology and microstructural features of the samples were investigated using a Zeiss EVO MA10 scanning electron microscope (Carl Zeiss, Oberkochen, Germany). To prevent electrostatic charging under the electron beam and to ensure optimal surface conductivity, the specimens intended for morphological investigation were mounted onto aluminum stubs using conductive double-sided carbon tape. Subsequently, they were coated with a thin, uniform nanometric layer of gold via sputter coating. SEM images were acquired in high-vacuum mode using a Secondary Electron (SE) detector. To achieve a balance between spatial resolution, signal-to-noise ratio, and sample stability, the instrumental parameters were optimized with an accelerating voltage of 20kV and a working distance of 8.5mm, maintained throughout the imaging sessions. In addition, qualitative and semi-quantitative elemental analysis, along with elemental spatial distribution mapping, was performed using an Energy-Dispersive X-ray (EDX) spectrometer integrated within the same microscope assembly. To avoid any spectral interference and to prevent the masking of the sample's elemental composition by foreign conductive media, the EDX analyses and compositional mappings were performed on uncoated samples.

3. Results

The central objective of this thesis was to evaluate the effect of metal-alloying (Bi/Sb) on the structural, morphological, and optical properties of lead-free perovskite-inspired hybrid materials ($\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$). The idea behind the project was to synthesize a series of innovative materials capable of combining high chemical stability with a narrow optical band gap, and to characterize them using various techniques to demonstrate the effectiveness of metal-alloying and the validity of vapor deposition for obtaining thin films with controlled stoichiometry.

The starting point was the pure $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Sb}_2\text{I}_9$, already known in the literature for their promising optoelectronic properties but limited by a relatively wide band gap ($\approx 2.1\text{--}2.3$ eV).^{42,43} For my thesis, I chose to explore the entire solid solution of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x = 0, 0.5, 1, 1.5, 2$), first synthesizing the powdered samples using a highly sustainable and scalable solvent-free mechanochemical approach. This permits to analyze the structural and optical evolution as the Bi/Sb ratio varies. Comparison of the different compositions allowed to investigate the band gap bowing phenomenon along the series (related to the staggered alignment of the valence and conduction bands of the two pure members), which led to the identification of the equimolar composition $\text{Cs}_3\text{BiSbI}_9$ with a minimum band gap of approximately 1.71 eV in the powders.

From the mechanosynthesized powders used as targets, thin films were produced by RF magnetron sputtering, demonstrating the ability of this vapor-phase physics method to faithfully transfer the target stoichiometry to the film.

Structural analyses were conducted on each powder sample using Rietveld-refined X-ray powder diffraction (PXRD) and optical characterizations using UV-Vis diffuse reflectance spectroscopy (with analysis of the Kubelka-Munk function and Tauc plot).

The resulting thin films were structurally analysed by XRD, revealing a strong preferential orientation along the crystallographic (001) direction. They were investigated by Raman spectroscopy, scanning electron microscopy (SEM-EDX), and atomic force microscopy (AFM) to assess their effective stoichiometry, continuity, and surface morphology. Finally, the optical properties of the films were evaluated by UV-Vis transmittance measurements, confirming the retention of the band gap bowing even in the thin layer, with a minimum value of 1.76 eV for the $\text{Cs}_3\text{BiSbI}_9$ phase.

3.1 Structural characterization

3.1.1. X-ray Diffraction and Rietveld Refinement

Powder samples of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ solid-solution series ($x = 0, 0.5, 1, 1.5, \text{ and } 2$) were characterized by X-ray diffraction (XRD) to investigate their crystal structure and determine the lattice parameters by Rietveld refinement using TOPAS v6 software. The crystal structures of the two end members, $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Sb}_2\text{I}_9$, are well established in the literature, and their crystallographic information files (CIFs) are available in the ICSD database. Both compounds crystallize in the hexagonal $P6_3/mmc$ space group and consist of isolated face-sharing bioctahedral $[\text{M}_2\text{I}_9]^{3-}$ units ($\text{M} = \text{Bi}^{3+}$ or Sb^{3+}).^{42,43} Their crystal structure is shown in **Figure 25**.

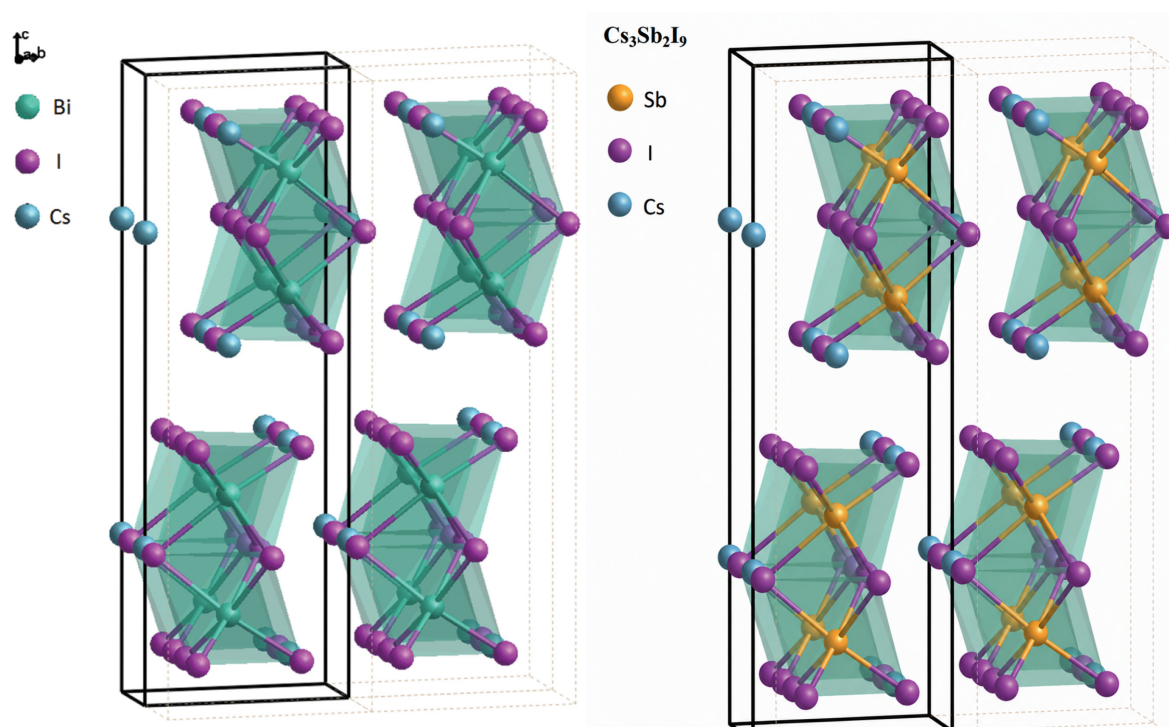


Figure 25: Schematic picture of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Sb}_2\text{I}_9$ crystalline structure.¹⁸

The experimental diffraction patterns of the two end members are in excellent agreement with the corresponding reference reported in the literature. Moreover, all intermediate compositions

exhibit single-phase diffraction patterns, demonstrating that the mechanochemical synthesis performed using stoichiometric amounts of precursors successfully produced phase-pure $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ solid solutions over the entire compositional range. The powder patterns systematically change with composition, showing a shift of the peak positions toward higher 2θ , this is due to the gradual substitution of Bi^{3+} by Sb^{3+} at the B site of the perovskite-derived structure. The XRD patterns of the entire compositional series are reported in **Figure 26**.

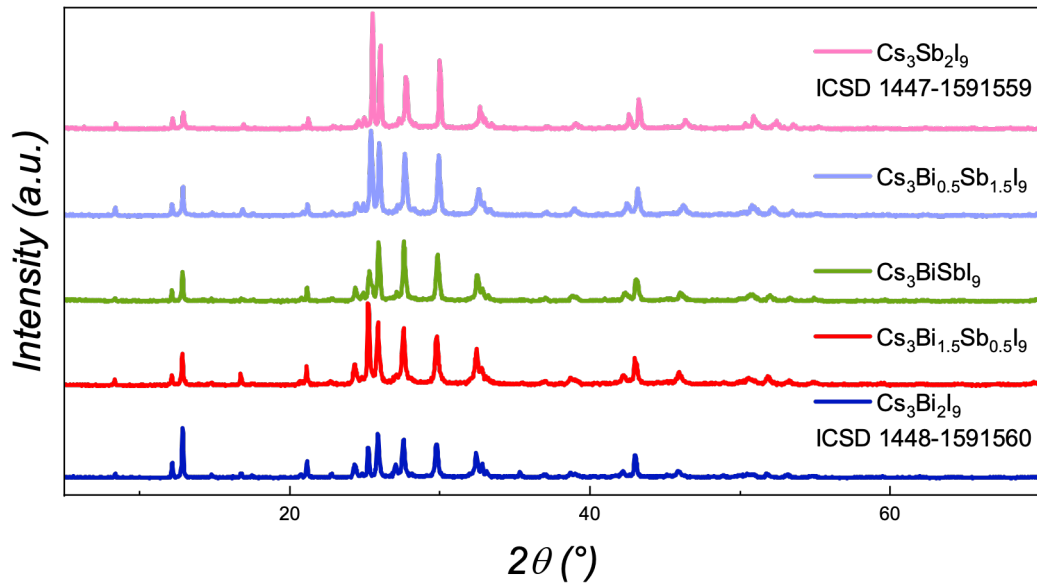


Figure 26: Powder X-ray diffraction patterns of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$) solid solutions.

Rietveld refinement was used to investigate the evolution of the lattice parameters and unit cell volume as a function of Sb content. A progressive decrease in both the lattice parameters (a and c) and the unit cell volume is observed with increasing Sb concentration, indicating a continuous contraction of the crystal lattice across the solid-solution series. The compositional dependence of these parameters is shown in **Figure 27**.

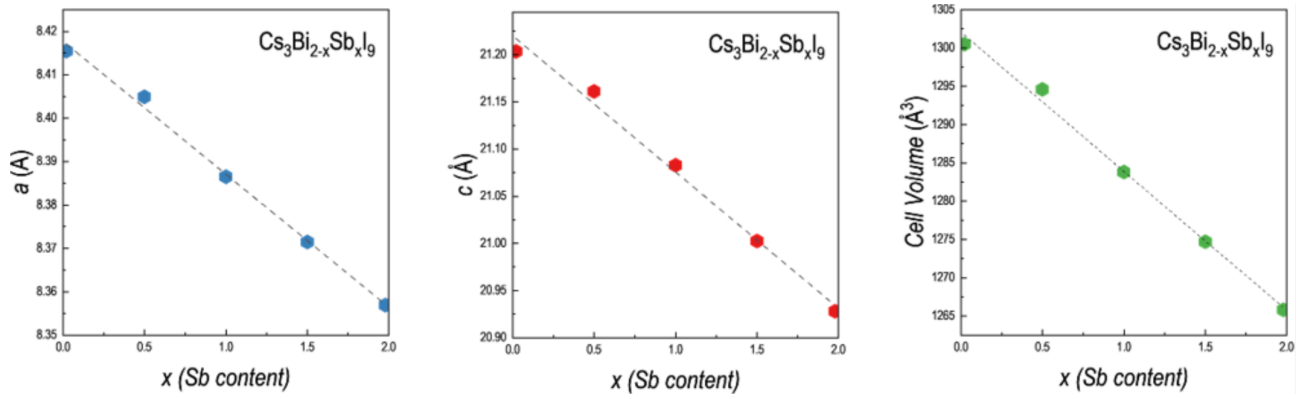


Figure 27: Lattice parameters and cell volumes as a function of the sample composition determined from Rietveld refinement.

The refined structural parameters exhibit an approximately linear decrease with increasing Sb content, consistent with Vegard's law. According to this empirical relationship, the lattice parameter of a substitutional solid solution varies linearly with composition and can be expressed for a binary system $A_{1-x}B_x$ as:

$$a = (1 - x) \cdot a_A + x \cdot a_B \quad (10)$$

where a_A and a_B are the lattice parameters of the two end-member compounds.⁴⁴ The observed evolution of the lattice parameters confirms the formation of a continuous isostructural solid solution throughout the investigated compositional range. The lattice contraction is also consistent with the smaller ionic radius of Sb^{3+} (0.76 Å) compared with Bi^{3+} (1.03 Å), leading to a gradual reduction of the unit cell dimensions as Bi is replaced by Sb. The refined lattice parameters as a function of Sb content are summarized in **Table 2**.

x	$a = b$ (Å)	c (Å)	Volume (Å ³)
0	8.416 (9)	21.203 (3)	1300.5 (4)
0.5	8.405 (1)	21.161 (3)	1294.6 (4)
1	8.386 (1)	21.080 (4)	1283.8 (5)
1.5	8.371 (1)	21.002 (4)	1274.7 (5)
2	8.356 (1)	20.927 (3)	1265.8 (4)

Table 2: Lattice parameters and unit cell volume as a function of the powder sample's compositions.

Thin films of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x = 0, 0.5, 1, 1.5$, and 2) were investigated by X-ray diffraction and compared with those of the corresponding powder samples to evaluate the structural evolution after deposition by RF magnetron sputtering. The thin films were deposited onto $1 \times 1 \text{ cm}^2$ fused silica (quartz) substrates by RF magnetron sputtering under the optimized deposition conditions described in the Experimental section. Film thickness was measured by stylus profilometry and was found to be approximately 400 nm for all compositions, confirming the good reproducibility of the deposition process. The XRD patterns of the thin films are reported in **Figure 28**.

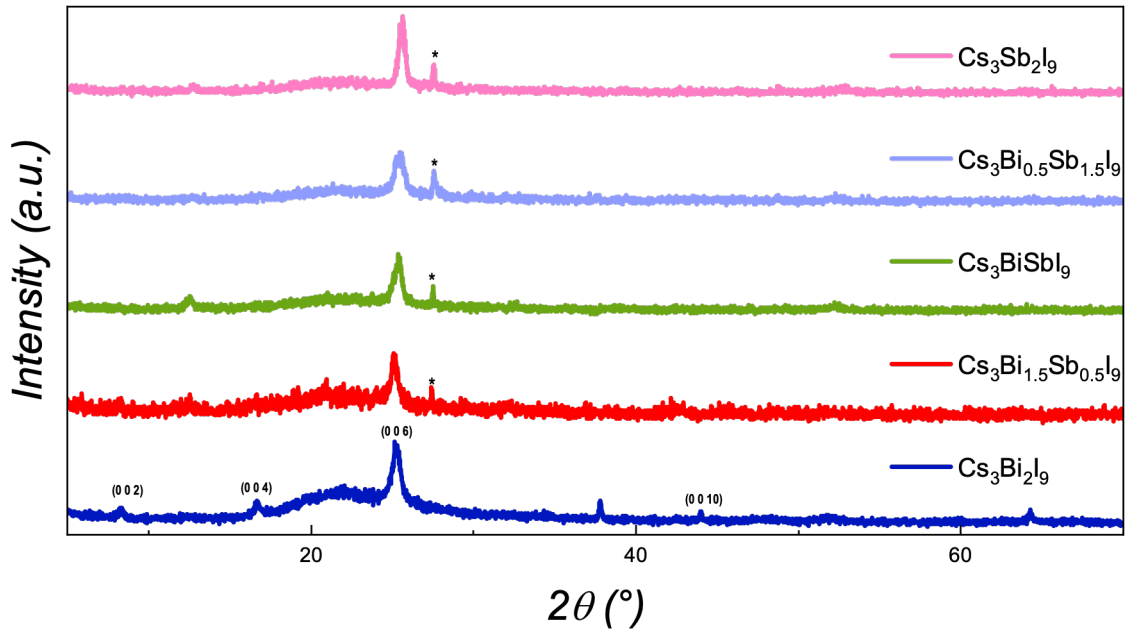


Figure 28: Thin films X-ray diffraction patterns of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$).

The diffraction data confirm that the deposited layers retain the same crystal structure as the corresponding powder targets, indicating that the RF magnetron sputtering process preserves the crystalline phase of the source material. Furthermore, all samples exhibit a pronounced preferential orientation along the (00 l) crystallographic direction, as evidenced by the dominant intensity of the corresponding diffraction peaks. This suggests that crystal growth during deposition is strongly favored along the c -axis. For the Sb-containing compositions, an additional weak diffraction peak is observed at approximately $2\theta = 28^\circ$, marked with an asterisk (*). This reflection is attributed to a minor SbI_3 secondary phase, likely originating from local

segregation during film growth. A close-up view of the main (006) diffraction peak is presented in **Figure 29**. A gradual shift of the peak position toward higher 2θ values is clearly observed with increasing Sb content. According to Bragg's law, this shift corresponds to a decrease in the interplanar spacing and therefore to a progressive contraction of the crystal lattice. This behavior is fully consistent with the Rietveld refinement results obtained for the powder samples and provides further evidence for the successful incorporation of Sb into the crystal structure, leading to the formation of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ mixed solid-solution system in thin-film form.

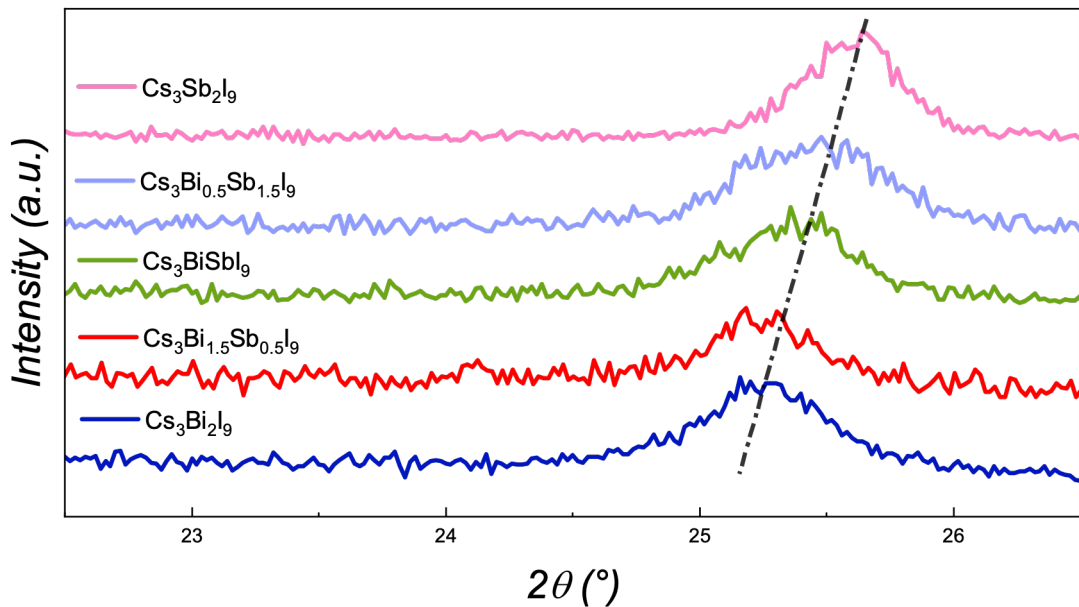


Figure 29: Close-up on the main diffraction peak of thin films X-ray diffraction patterns.

3.1.2. Raman Spectroscopy

Raman spectroscopy was performed on both powder and thin-film samples to obtain information about the structural characterization and investigate the local bonding environment of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ solid-solution series. As a vibrational spectroscopy technique, Raman analysis gives information on the lattice dynamics and the vibrational modes associated with the metal–halide framework and allows the study of the local structure of the face-sharing $[\text{M}_2\text{I}_9]^{3-}$ bioctahedral units ($\text{M} = \text{Bi}, \text{Sb}$). All measurements were carried out using a 638 nm

excitation laser coupled with a 100× objective. To avoid laser-induced degradation of the samples, the laser power was limited to 1%. Preliminary measurements performed at higher power revealed progressive changes in the spectra during acquisition. The Raman spectra of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ series collected for powders over the 40–300 cm^{-1} spectral range are reported in **Figure 30**.

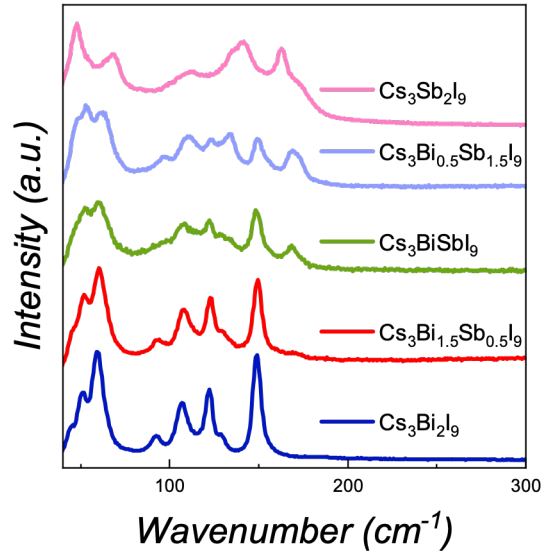


Figure 30: Powder Raman spectra of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$) solid solutions.

The reported Raman spectra correspond to the average of measurements collected at different locations on each sample, ensuring that the acquired data are representative of the overall sample homogeneity. The spectra of the two end-member compounds are in good agreement with those previously reported in the literature, confirming the successful synthesis of the desired crystal structures. In particular, the spectral region between approximately 40 and 180 cm^{-1} is characterized by well-defined bands associated with the Bi–I and Sb–I stretching vibrations within the isolated face-sharing $[\text{M}_2\text{I}_9]^{3-}$ ($\text{M} = \text{Bi}, \text{Sb}$) bioctahedra. At lower Raman shifts, the spectra are mainly dominated by bending modes involving the same structural units.⁴⁵ As the Sb content increases, the Raman spectra evolve progressively from $\text{Cs}_3\text{Bi}_2\text{I}_9$ to $\text{Cs}_3\text{Sb}_2\text{I}_9$. The gradual shift in peak positions and the continuous evolution of the spectral profile indicate that the local coordination environment changes systematically with composition. The absence of additional features attributable to secondary crystalline phases supports the formation of

homogeneous solid solutions throughout the investigated compositional range, in agreement with the XRD and Rietveld refinement results. All these considerations are valid for the thin films Raman spectra, too, shown in **Figure 31**.

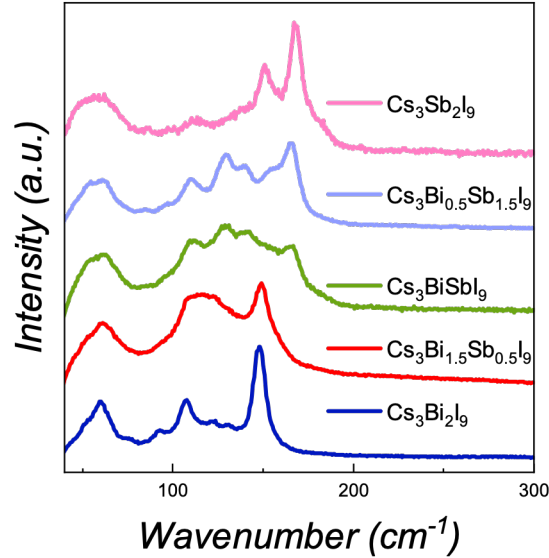


Figure 31: Thin films Raman spectra of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$).

As expected, the Raman signal collected from the thin films is considerably weaker than that obtained from the corresponding powder samples because of the significantly smaller scattering volume associated with the film geometry. Nevertheless, the main vibrational features remain detectable, confirming that the deposited films preserve the characteristic local structure of the corresponding compounds. Compared with the powders, however, several Raman bands exhibit markedly lower intensity or disappear almost completely. This behavior is attributed primarily to the strong preferential orientation of the crystallites along the $(00l)$ direction, as previously evidenced by X-ray diffraction, which alters the Raman selection rules and therefore the relative intensity of the vibrational modes. In addition, differences in crystallite size, film texture, and microstructure between the sputtered thin films and the bulk powders may further contribute to the observed spectral differences.^{45,46}

3.2 Optical characterization

3.2.1. UV-Vis Spectroscopy

The optical properties of both powder and thin-film samples belonging to the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x = 0, 0.5, 1, 1.5, \text{ and } 2$) compositional series were investigated by UV–Vis spectroscopy. The optical response of the powders was evaluated from diffuse reflectance measurements, whereas the optical properties of the thin films were investigated through their transmittance spectra. The results obtained for the two forms of the material were subsequently compared in order to assess the effect of the deposition process and microstructure on the optical properties of the solid-solution system.

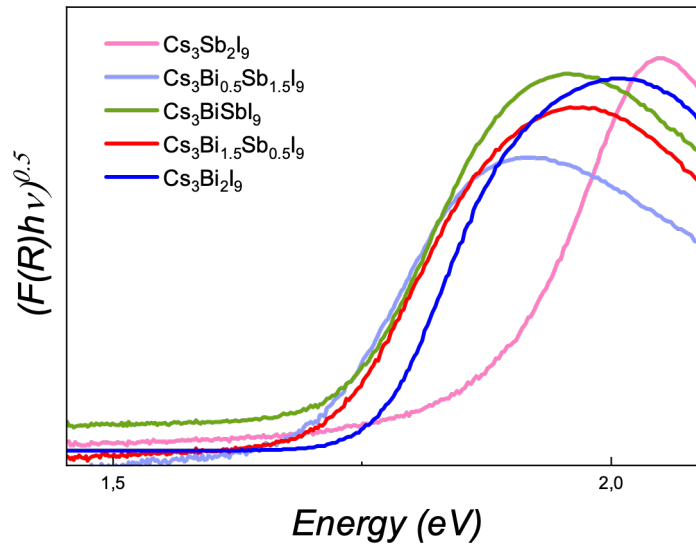


Figure 32: Kubelka–Munk analysis of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$) powdered samples.

Figure 32 reports the Kubelka–Munk function obtained from the diffuse reflectance spectra of the powder samples. The optical band-gap energies were estimated from the corresponding Tauc plots by considering an indirect electronic transition, consistent with the behavior previously reported for the $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Sb}_2\text{I}_9$ end members and related compounds.^{17,43} As described in the Experimental section, the diffuse reflectance data were converted into the Kubelka–Munk function and subsequently used as a measure proportional to the absorption coefficient for the construction of the Tauc plots. The linear region of the corresponding Tauc

plot was extrapolated to the energy axis, and the intercept was taken as the effective optical absorption-edge energy. The resulting plots show a clear evolution of the optical absorption as a function of composition, indicating that the progressive substitution of Bi with Sb significantly affects the electronic structure of the material. In particular, the position of the absorption edge changes systematically across the compositional series, providing the first indication of the non-linear evolution of the optical gap discussed below.

The optical properties of the thin films were investigated by UV–Vis transmittance measurements, as shown in **Figure 33**. The spectra exhibit well-defined interference fringes, which originate from multiple reflections occurring at the film/substrate interfaces and are characteristic of relatively uniform and optically transparent thin layers. The optical absorption-edge energies were determined from the transmittance spectra following the methodology described in the Experimental section. Briefly, the measured transmittance was converted into the corresponding absorbance, which was subsequently used to construct the Tauc plots. Considering an indirect allowed transition, the optical absorption-edge energy was obtained by extrapolating the linear region of the Tauc plot to the energy axis.

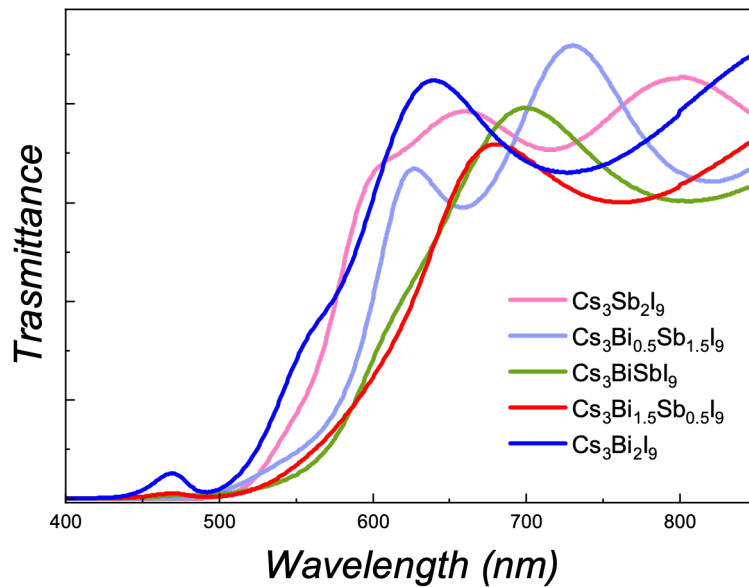


Figure 33: Transmittance spectra of $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0, 0.5, 1, 1.5, 2$) thin films.

The band-gap energies extracted from both powder and thin-film measurements are summarized in **Table 3** and plotted as a function of composition in **Figure 34**.

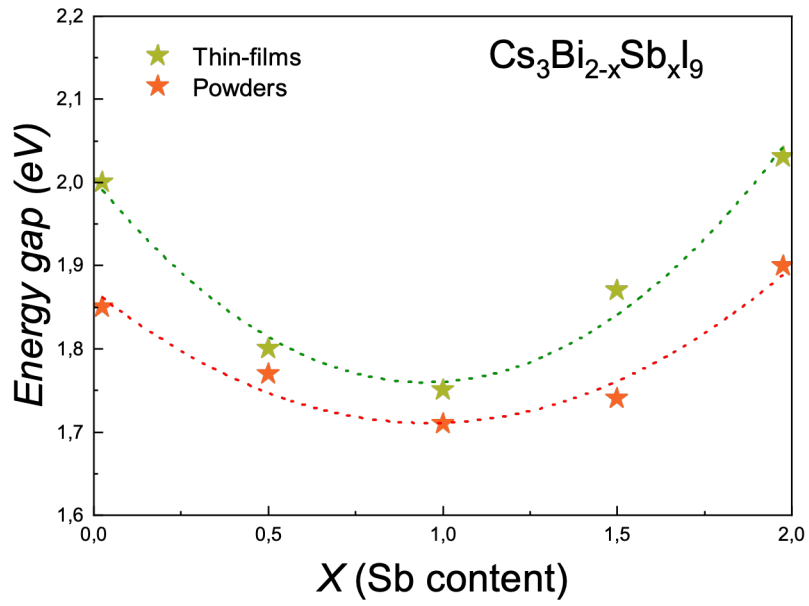


Figure 34: Band-gap energies as a function of Sb content (x).

A pronounced non-linear dependence of the optical gap on the Sb content is observed for both sample types. In particular, the band gap does not evolve linearly between the two end members but exhibits a clear bowing behavior, with the intermediate compositions characterized by lower absorption-edge energies than either of the two end members.

Absorbtion edge (eV)

x	Thin films	Powders
0	1.87	1.85
0.5	1.83	1.77
1	1.76	1.71
1.5	1.77	1.74
2	1.91	1.89

Table 3: Extrapolated band-gap values as a function of the sample's compositions.

For the powder samples, the absorption-edge energy increases slightly from approximately 1.85 eV for $\text{Cs}_3\text{Bi}_2\text{I}_9$ to 1.89 eV for $\text{Cs}_3\text{Sb}_2\text{I}_9$. In contrast, the intermediate compositions exhibit a substantial reduction in the optical gap, reaching a minimum value of approximately 1.71 eV

for the $\text{Cs}_3\text{BiSbI}_9$ composition. A similar trend is observed for the thin films. The absorption-edge energies of the end members are approximately 1.87 eV for $\text{Cs}_3\text{BiI}_2\text{I}_9$ and 1.91 eV for $\text{Cs}_3\text{SbI}_2\text{I}_9$, while the minimum value, approximately 1.76 eV, is again obtained for the intermediate $\text{Cs}_3\text{BiSbI}_9$ composition. Despite the small differences between the absolute values obtained for powders and thin films, the same evolution is observed in both cases.

The evolution of the optical gap is also consistent with the systematic change in color observed across the compositional series, as previously shown in **Figure 11** and in **Figure 15** for the powder and for the films, respectively. While the two end members display a more orange appearance, the intermediate solid solutions become progressively darker. This trend reflects the gradual compositional variation and indicates that the sputtering process successfully preserves the chemical composition of the starting targets. This behavior can also be correlated with the non-linear variation of the optical band gap. A material with a relatively larger band gap absorbs photons only above a higher energy threshold, corresponding mainly to the higher-energy region of the visible spectrum. Consequently, a larger fraction of the lower-energy visible light is reflected or scattered, contributing to a brighter coloration. Conversely, the reduction of the optical gap observed for the intermediate compositions extends the absorption onset toward lower photon energies, allowing a larger portion of the visible spectrum to be absorbed. The resulting reduction in reflected light can explain the darker appearance observed for the intermediate compositions. The observed band-gap bowing is consistent with previous observations reported for related mixed Bi/Sb halide systems, including the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{Br}_9$ defect-perovskite system.²⁶ In this related system, electronic-structure calculations have shown that the non-linear evolution of the band gap can be related to the different electronic structures of the Bi- and Sb-containing end members. In particular, the mismatch between the conduction- and valence-band edges of the two parent compounds can lead to a staggered band alignment and to a non-linear mixing of their electronic states upon alloying. As a consequence, the introduction of the second metal cation can simultaneously lower the conduction-band minimum and raise the valence-band maximum, resulting in a reduction of the overall band-gap energy for intermediate compositions. A schematic representation of the proposed evolution of the electronic structure upon Bi/Sb alloying is reported in **Figure 35**.

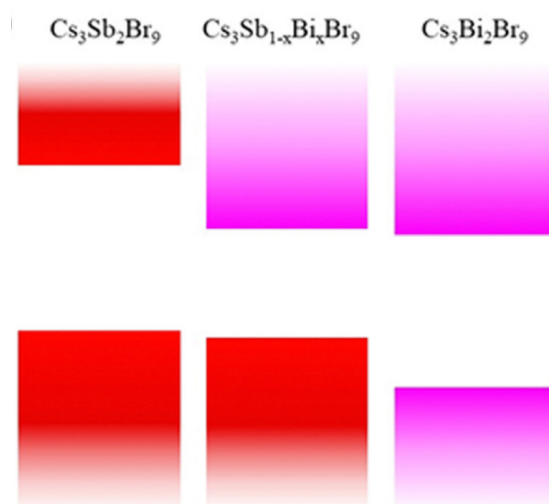


Figure 35: Schematics of the band contributions in $\text{Cs}_3(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{Br}_9$ system.²⁶

When Bi and Sb are progressively mixed within the same crystallographic site, the corresponding electronic states interact and undergo an energetic rearrangement, effectively reducing the energy separation between the two band edges. The largest reduction is therefore expected for intermediate compositions, where the electronic states of the two end members are most strongly mixed, providing a microscopic interpretation of the experimentally observed band-gap bowing.

The pronounced bowing observed across the entire compositional series therefore represents a key result of this work. In particular, the minimum absorption-edge energy of approximately 1.7 eV obtained for the intermediate composition demonstrates that Bi/Sb alloying provides an effective strategy for tuning the optical absorption toward lower energies in all-inorganic, lead-free perovskite-inspired materials. The ability to achieve a lower optical gap while maintaining the same crystal structure across the whole solid-solution series highlights the potential of this approach for the development of lead-free perovskite-inspired materials with tailored optical properties. The slight differences observed between the optical gap values extracted from powders and thin films can be attributed to their different microstructural characteristics. The sputtered thin films exhibit a relatively uniform and continuous morphology, whereas the mechanochemically synthesized powders are characterized by irregular particles and a higher density of structural imperfections arising from the milling process. Such defects and local structural disorder may contribute to sub-band-gap absorption and broaden the absorption

onset, thereby affecting the precise determination of the optical gap from experimental spectra. In addition, the gradual nature of the absorption onset expected for an indirect-band-gap semiconductor introduces an intrinsic uncertainty in the extrapolation of the absorption edge.⁴⁷ The values reported in this thesis should be regarded as effective optical absorption-edge energies rather than as absolute fundamental band-gap values. Nevertheless, the excellent agreement in the overall compositional trend observed for powders and thin films demonstrates that the band-gap bowing is not just a consequence of the specific sample morphology or deposition process, but rather represents an intrinsic feature of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ system.

3.3 Morphological characterization

3.3.1. Atomic Force Microscopy

The surface morphology of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ thin-film series ($x = 0, 0.5, 1, 1.5$, and 2) was investigated by atomic force microscopy to evaluate the influence of composition on the microstructure of the sputtered layers. Representative AFM topographic images of the samples, acquired over a $20 \times 20 \mu\text{m}^2$ scan area, are presented in **Figure 36**. All deposited films appear continuous, homogeneous, and highly reflective over the entire substrate surface, without visible defects or macroscopic inhomogeneities, suggesting good quality.

The AFM analysis reveals a pronounced effect of the Bi/Sb ratio on the surface morphology of the deposited films. The $\text{Cs}_3\text{Bi}_2\text{I}_9$ exhibits a compact and relatively smooth surface composed of densely packed nanograins with an average lateral size of approximately 160(80) nm. The grains are uniformly distributed over the scanned area, resulting in a homogeneous morphology and a relatively low root-mean-square roughness (R_{rms}) of about 29 nm. These observations indicate a continuous film with limited surface irregularities, suggesting that the deposition conditions promote uniform nucleation and grain growth for the Bi-rich composition. In contrast, the $\text{Cs}_3\text{Sb}_2\text{I}_9$ film displays a markedly different morphology. The surface is characterized by significantly larger crystallites, with an average grain size of approximately 420(260) nm, and a much higher surface roughness ($R_{\text{rms}} \approx 100$ nm). The film exhibits a granular texture, with more pronounced height variations and a less compact microstructure compared with the Bi-rich sample, indicating that Sb incorporation strongly

affects the crystallization process during film growth. The intermediate compositions exhibit a gradual morphological evolution between these two limiting cases. As the Sb content increases, the initially compact nanogranular morphology progressively transforms into a more heterogeneous surface characterized by grain coalescence, the formation of island-like features, and the appearance of larger aggregates. This continuous evolution suggests that the relative Bi/Sb ratio plays a key role in controlling nucleation density and crystal growth kinetics during RF magnetron sputtering. Consequently, the observed increase in grain size and surface roughness with increasing Sb content reflects a progressive modification of the thin-film growth mechanism across the solid-solution series. Overall, the AFM results demonstrate that compositional tuning not only influences the crystal structure of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ system, as evidenced by XRD analysis, but also has a significant impact on the morphology and surface topography of the deposited thin films.

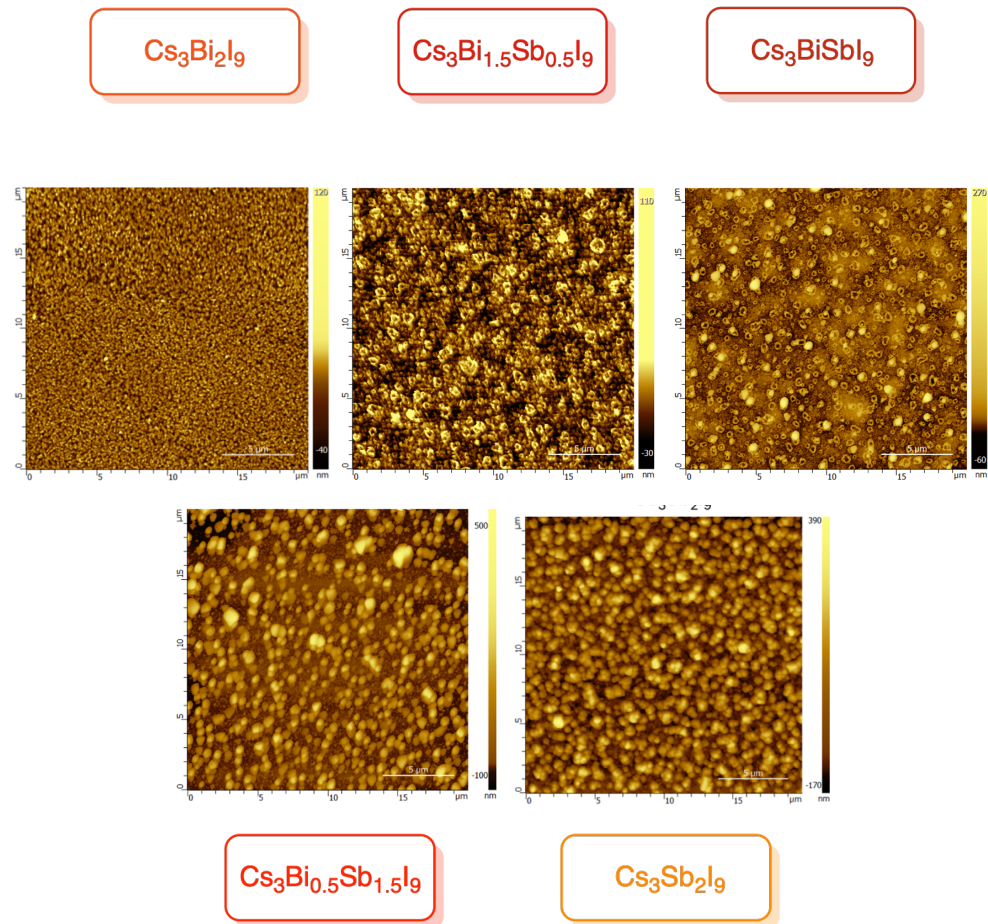


Figure 36: AFM topography images of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x=0.5, 1, 1.5$) thin films.

3.3.2. Scanning Electron Microscopy and Energy Dispersive X-ray analysis

The morphology and chemical composition of the deposited $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ thin films were further investigated by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). These techniques provide valuable information on the surface microstructure of the films as well as on their elemental composition. SEM images of the $\text{Cs}_3\text{BiSbI}_9$ thin film are presented in **Figure 37**. The pics reveal a homogeneous, compact, and continuous coating over the entire substrate surface, without the presence of cracks, pinholes, or other macroscopic defects. The deposited layer appears to uniformly cover the substrate, confirming that the RF magnetron sputtering process yields high-quality films with good surface continuity. These observations are consistent with the AFM results, which also indicate the formation of continuous films with a morphology strongly influenced by the Bi/Sb ratio.

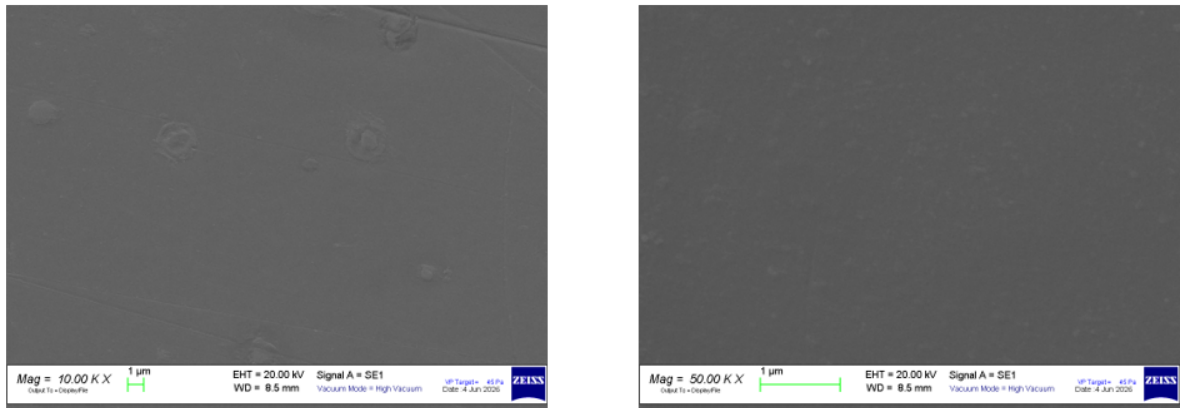


Figure 37: SEM surface images of the $\text{Cs}_3\text{BiSbI}_9$ thin film.

The elemental composition of all deposited thin films was determined by EDX analysis, and the resulting compositions are summarized in **Table 4** together with the corresponding calculated error percentage and the film thicknesses measured by stylus profilometry. The measured Bi/Sb ratios are in good agreement with the nominal compositions of the corresponding sputtering targets throughout the entire compositional series. This result demonstrates that the RF magnetron sputtering process effectively preserves the stoichiometry of the starting target materials during deposition, despite the multicomponent nature of the $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ system. The excellent agreement between the nominal and experimental

compositions further confirms the reliability of this deposition technique for producing compositionally controlled all-inorganic mixed-metal halide thin films.

Nominal x	Effective x	Error %	Thickness (nm)
0	0		391
0.5	0.49	3.21	357
1	0.90	4.70	401
1.5	1.43	2.52	335
2	2		460

Table 4: Nominal and effective composition of thin films from EDX analysis and corrispective thickness.

For comparison, a representative SEM image of the mechanochemically synthesized $\text{Cs}_3\text{BiSbI}_9$ powder sample is shown in **Figure 38**. The powders consist of irregularly shaped particles with a broad size distribution and no well-defined morphology. This irregular appearance is typical of mechanochemical synthesis, where repeated fracture and cold welding events occurring during the milling process generate particles with non-uniform shapes and dimensions.

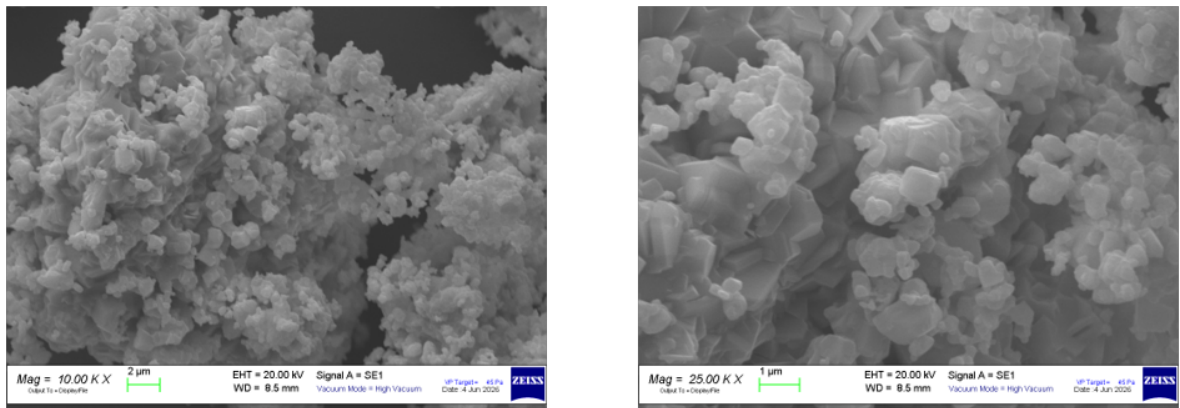


Figure 38: SEM image of the $\text{Cs}_3\text{BiSbI}_9$ powder sample.

To further evaluate the chemical homogeneity of the deposited layers, SEM–EDX elemental mapping was carried out on the thin films. The corresponding elemental distribution maps are presented in **Figure 39** and reveal a homogeneous spatial distribution of Cs, Bi, Sb, and I over the investigated area, with no evidence of elemental segregation or significant compositional fluctuations. These results further confirm the high compositional uniformity of the sputtered films and demonstrate that the deposited layer uniformly covers the substrate, in agreement with the observations obtained from SEM, AFM, and EDX quantitative analysis.

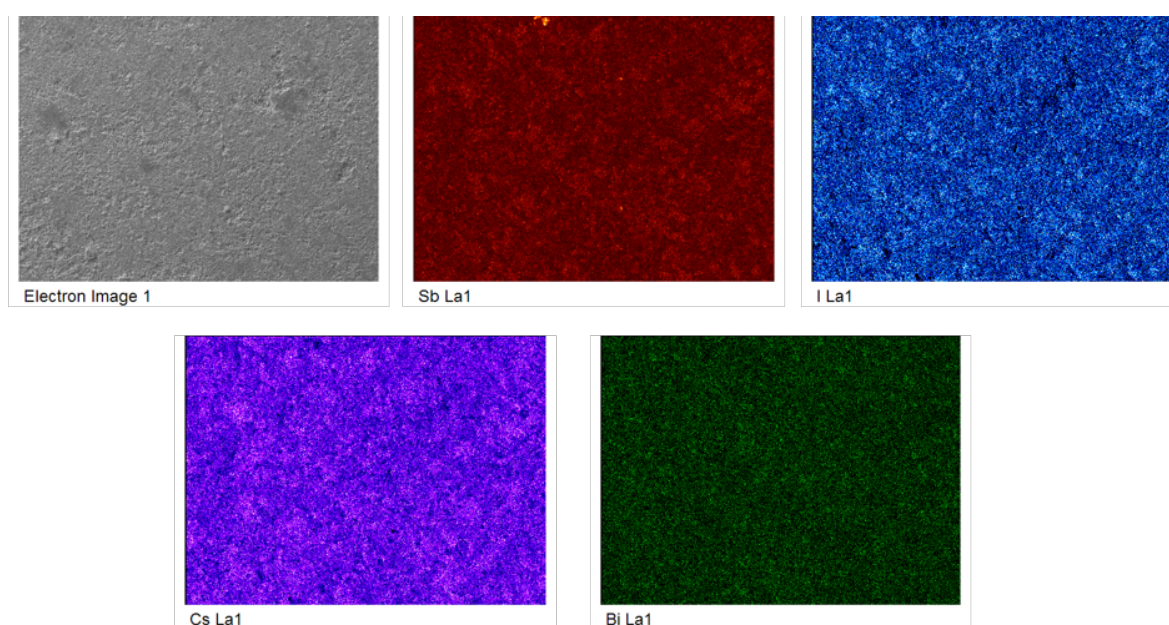


Figure 39: SEM–EDX elemental maps of Sb, I, Cs and Bi of the $\text{Cs}_3\text{BiSbI}_9$ powder sample.

4. Conclusion

This thesis aimed to investigate the structural, optical, and morphological properties of the lead-free perovskite-inspired solid-solution system $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ ($x = 0, 0.5, 1, 1.5, \text{ and } 2$), and to develop a reliable approach for the fabrication of thin films through radio-frequency magnetron sputtering. The work addressed two of the main limitations of Bi- and Sb-based perovskite-inspired materials: their relatively wide optical band gaps and the poor film morphology and reproducibility typically associated with conventional wet-chemical solution processing.

First, the entire $\text{Cs}_3\text{Bi}_{2-x}\text{Sb}_x\text{I}_9$ compositional series was successfully synthesized using a vibratory ball miller. The mechanochemical approach proved to be an efficient, solvent-free, and environmentally friendly route for obtaining phase-pure powders and represents a simple and potentially scalable route for the fabrication of lead-free perovskite-inspired materials. X-ray powder diffraction (PXRD) paired with Rietveld refinement demonstrated that all synthesized compositions crystallize in the zero-dimensional (0D) hexagonal dimer structure (space group $P6_3/mmc$), consisting of isolated face-sharing bioctahedral $[\text{M}_2\text{I}_9]^{3-}$ ($\text{M} = \text{Bi}^{3+}, \text{Sb}^{3+}$) units. A continuous, linear contraction of both the lattice parameters (a and c) and unit cell volume was observed as a function of increasing antimony content, strictly following Vegard's law. This linear evolution confirms the formation of a homogeneous substitutional solid solution driven by the smaller ionic radius of Sb^{3+} compared to Bi^{3+} . Raman spectroscopy further validated the preservation of the characteristic local structure of the face-sharing $[\text{M}_2\text{I}_9]^{3-}$ ($\text{M} = \text{Bi}, \text{Sb}$) bioctahedra.

To surpass the morphological and solubility problems of solution processing, physical vapor deposition via Radio-Frequency (RF) magnetron sputtering was successfully introduced. Using the pressed mechanosynthesized powders as target materials, uniform, highly compact, and pinhole-free thin films with a nominal thickness of ~ 400 nm were deposited onto quartz substrates at room temperature. Structural analysis via XRD revealed that the sputtered thin films not only retained the hexagonal crystal phase of the target materials, indicating that the sputtering process does not induce a structural transformation, but also exhibited a pronounced uniaxial preferential orientation along the $(00l)$ crystallographic direction, indicating strong anisotropic grain growth along the c -axis.

RF magnetron sputtering successfully transferred the stoichiometry of the powder targets to the thin films, as confirmed by EDX analysis. SEM-EDX elemental mapping demonstrated a homogeneous spatial distribution of Cs, Bi, Sb, and I, without any macroscopic or microscopic phase segregation. AFM further highlighted a smooth, continuous surface morphology, where increasing the Sb content induces a gradual shift from small, tightly packed to larger crystallite aggregates.

Most importantly, UV-Vis spectroscopy revealed a pronounced band-gap bowing across the solid-solution series. Both diffuse reflectance measurements on powders and transmittance measurements on thin films showed a non-linear evolution of the optical absorption edge, with a minimum band gap of 1.71 eV in bulk powders and 1.76 eV in sputtered thin films for the equimolar composition $\text{Cs}_3\text{BiSbI}_9$. This value represents the lowest optical gap reported to date for fully inorganic $\text{A}_3\text{B}_2\text{X}_9$ perovskite-inspired materials. The bowing behavior is attributed to the staggered alignment of the band edges of the Bi- and Sb-rich end members, which simultaneously lowers the conduction band minimum and raises the valence band maximum in intermediate compositions.

Overall, this thesis provides a complete and coherent framework for the development of lead-free perovskite-inspired materials with tunable optical properties. The combination of mechanochemical synthesis and physical vapor deposition offers a promising route for producing stable, scalable, and compositionally controlled thin films suitable for optoelectronic applications. The achieved combination of low toxicity, high ambient stability, highly oriented pinhole-free film morphology, and a narrow optical band gap opens new opportunities for designing environmentally sustainable materials for photovoltaics, photodetectors, and other emerging technologies. Future work could focus on further optimization of the sputtering parameters to control grain growth and surface roughness, investigation of post-deposition treatments, and integration of the optimized compositions into functional optoelectronic devices.

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