



Cite this: *Dalton Trans.*, 2025, **54**, 11006

Solvent-free mechanochemical access to phase-pure Cs–Co–Cl halometalates with tuneable electronic properties for energy applications†

Pablo Garrido,^a Darío Espinoza,^b ^a Karem Gallardo,^b Rosa M. González-Gil^c and Rodrigo Castillo *^d

We report a solvent-free mechanochemical route for the selectively synthesis of three different caesium cobalt chlorides: CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, by simply tuning the CsCl:CoCl₂ precursor ratio. This is the first comprehensive comparative study of these phases synthesized in pure form, enabling a clear correlation between composition, crystal structure, and optoelectronic properties. Each phase exhibits a unique Co²⁺ coordination geometry: octahedral in CsCoCl₃ and tetrahedral in Cs₂CoCl₄ and Cs₃CoCl₅, as revealed by XRD, SEM-EDS, Raman, and XPS, with several features reported here for the first time. All phases display high thermal stability and narrow optical bandgaps (1.65–1.70 eV), supported by ligand field analysis and CIE colorimetry. Valence and conduction band energies determined by VB-XPS and cyclic voltammetry reveal a systematic, composition-driven tuning of energy levels across the series. Importantly, the band edge alignment are suitable for visible-light-driven hydrogen evolution and photovoltaic applications. SCAPS-1D simulations predict power conversion efficiencies up to 17.1%, positioning these halocobaltates as promising absorbers. Altogether, this work introduces a scalable synthesis route and demonstrates the potential of cobalt-based halide frameworks as modular systems for solar energy conversion and photocatalysis.

Received 10th June 2025,
Accepted 24th June 2025

DOI: 10.1039/d5dt01355k

rsc.li/dalton

Introduction

There has been a renewed and growing interest in metal halide perovskites, both hybrid and fully inorganic, driven by their remarkable optoelectronic properties and wide range of potential applications. This resurgence was undoubtedly triggered by the success of the hybrid perovskite CH₃NH₃PbI₃,^{1,2} whose outstanding semiconducting behavior and light-harvesting capability in solar cells have led to an unprecedented increase in power conversion efficiencies, reaching over 30% within a decade.^{3,4} This breakthrough not only underscored the potential of metal halide frameworks for photovoltaics, but also catalyzed intensive research into lead-free alternatives with

improved stability and compositional flexibility.^{5–13} In particular, the pursuit of non-toxic, thermally stable, and compositionally tunable alternatives has turned attention to new families of halide perovskites and perovskitoids, aiming to preserve the desirable optical and structural features while expanding chemical diversity.^{14–16}

This exploration has naturally extended to transition metal-based halide systems, where replacing lead with other metals introduces opportunities to modulate structural, magnetic, and optical properties.^{17–26} Cobalt-based halides are especially intriguing due to the flexible coordination chemistry of Co²⁺, and its characteristic d–d electronic transition within the visible and near-infrared range. These features make cobalt halides attractive candidates for light-absorbing and photoactive materials, with potential applications beyond conventional photovoltaics. Within this family, the CsCl–CoCl₂ system contains three well-defined stoichiometric phases: CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, each featuring distinct structural motifs and cobalt coordination environments. However, despite their compositional simplicity and structural richness, these compounds have remained synthetically challenging to isolate as pure phases *via* conventional methods, and as a result, there is a limited body of work reporting their

^aDepartamento de Química, Universidad Católica del Norte, Antofagasta, Chile^bInstituto de Ciencias Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile, San Miguel, Santiago, Chile^cNovel Energy-Oriented Materials Group at Catalan Institute of Nanoscience and Nanotechnology (ICN2) CSIC and BIST, Campus UAB, Barcelona, Spain^dFacultad de Química y de Farmacia, Pontificia Universidad Católica de Chile, Macul, Santiago, Chile. E-mail: rodrigo.castillo@uc.cl†Electronic supplementary information (ESI) available: SEM-EDS, crystallographic tables. See DOI: <https://doi.org/10.1039/d5dt01355k>

properties, and many of their fundamental characteristics as well as potential applications, remain poorly understood. Among the well-established characteristics of these phases is their magnetic behavior. CsCoCl₃ exhibits Ising-like antiferromagnetic ordering with frustrated interchain interactions at low temperatures.^{27,28} Cs₂CoCl₄ behaves as a quasi-one-dimensional antiferromagnet with Co²⁺ ($S = \frac{1}{2}$) chains and XY-type interactions, showing long-range order below 22 K.^{29,30} Cs₃CoCl₅ displays magnetic anisotropy due to spin-orbit coupling and crystal field effects, and can be described by an effective $S = 1$ spin Hamiltonian.³¹

The crystallization behavior of CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅ has been studied using both melt- and solution-based approaches, revealing significant differences in phase stability, compositional constraints, and synthesis times. Among the three, Cs₂CoCl₄ is the most synthetically accessible, readily forming from stoichiometric mixtures *via* slow evaporation over several days.^{32,33} CsCoCl₃, by contrast, has only been obtained from melts using a slight excess of CoCl₂,^{34,35} or from aqueous solution under narrowly controlled evaporation conditions and with a large excess of CoCl₂.³⁶ Cs₃CoCl₅ requires an excess of CsCl and similarly tight compositional windows, whether synthesized from melt or in solution, typically over long evaporation periods.^{32,37–39}

In this context, mechanochemical synthesis has emerged as a powerful alternative for the preparation of inorganic compounds, particularly in systems where conventional methods are limited by solubility, volatility, or selectivity.^{40,41} This solvent-free approach enables the direct formation of crystalline materials under ambient conditions, often with superior control of stoichiometry and without requiring prolonged thermal treatments.⁴² Notably, mechanochemistry has proven especially effective for accessing metastable phases, complex halide and oxyhalide systems, and compounds that are otherwise inaccessible or unstable in melt or solution routes.^{43–47}

In the present work, we report the solvent-free mechanochemical synthesis of the halocobaltate phases CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, as phase-pure products obtained by direct reaction of stoichiometric amounts of CsCl and CoCl₂ under ambient conditions. A comprehensive characterization of the materials is presented, including structural analysis by powder X-ray diffraction (XRD), morphological inspection by scanning electron microscopy (SEM), and vibrational analysis through Raman spectroscopy. The thermal behavior was assessed using simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA-DSC). Furthermore, optical absorption was investigated *via* UV-Vis-NIR spectroscopy and diffuse reflectance, and the electronic structure of each compound was probed using valence-band XPS, cyclic voltammetry (CV), and solar cell simulations performed with the SCAPS-1D software. These results not only demonstrate the efficacy of mechanochemistry for accessing halide phases with controlled stoichiometry but also provide new insights into the structure–property relationships and highlight their potential in optoelectronic and photovoltaic applications.

Experimental

Materials and synthesis

All sample handling was performed under an Ar atmosphere. Caesium chloride (CsCl, ≥98%, Sigma-Aldrich) and cobalt(II) chloride (CoCl₂, 97%, Sigma-Aldrich) were weighed in molar ratios of 1 : 1, 2 : 1, and 3 : 1, to synthesize CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, respectively. The mixtures were loaded into 50 mL stainless steel jars along with 8 mm stainless steel balls, maintaining a ball-to-sample mass ratio of 100 : 1. The jars were mounted in a TMAX-XQM planetary ball mill and operated at 500 rpm for 60 minutes.

Characterization

X-ray powder diffraction (XRD) was carried out using a Malvern PANalytical diffractometer equipped with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and a linear X'Celerator detector, covering the angular range $5^\circ < 2\theta < 70^\circ$. Full-profile refinements were performed by the Rietveld method as implemented in the Jana2020 software.⁴⁸

Scanning electron microscopy (SEM) images were acquired on a FEI Quanta 650 FEG, operated at 30 kV in high-vacuum mode. Elemental analysis was carried out using an Inca 250 SSD XMax20 detector. Quantification was performed using ZAF correction procedures and calibrated against appropriated standards: KCl for Cl, and Co metal for Co.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a STAIB Instrument Surface Analysis Station 1 RQ300/2, with Al K α radiation ($\lambda = 1486.6 \text{ eV}$) as the excitation source.

Raman spectroscopy was conducted using a Jasco NRS-4500 confocal Raman microscope, equipped with a Peltier-cooled CCD detector and a 532 nm laser. Spectra were collected over the 50–3600 cm⁻¹ range with a 2 cm⁻¹. Each spectrum was acquired by accumulating six 50 seconds scans at a laser power of 1.8 mW with 10% attenuation to minimize sample degradation.

Thermal analysis was carried out using a Netzsch Jupiter STA 449 instrument for simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Heating and cooling rates were 10 °C min⁻¹ under nitrogen flow (50 mL min⁻¹), in the temperature range of 20 °C–700 °C.

UV-Vis-NIR spectroscopy was performed using a Jasco V-770 spectrophotometer equipped with an integrating sphere to account for diffuse reflectance. Spectra were collected from 200 to 2500 nm on polycrystalline powders at room temperature, using BaSO₄ as a non-absorbing reference. The reflectance data were converted using the Kubelka–Munk transformation, $F(R) = ((1 - R)^2/2R)$, and optical bandgaps were estimated by extrapolating the linear region of the Tauc plots. Additionally, CIE Lab* color coordinates were extracted from the reflectance spectra using the Color Analysis module in JASCO Spectra Manager (D65 standard illuminant, 10° observer, 380–780 nm), providing quantitative assessment of the perceived sample color.



Electrochemical measurements were performed on a BioLogic VMP3 potentiostat using a conventional three-electrode configuration. The working electrode consisted of a glassy carbon disk (0.0707 cm²) modified with a drop-cast ink prepared by dispersing 10 mg of the sample in 1 mL of methanol and 10 μ L of Nafion. A platinum wire and silver wire were used as the counter and reference electrodes, respectively, the latter connected *via* a salt bridge containing 0.1 M tetraethylammonium tetrafluoroborate (TEABF₄, 99%, Acros Organics) in dichloromethane (CH₂Cl₂, \geq 99.5%, Sigma-Aldrich). Measurements were carried out in an inert atmosphere using the same electrolyte. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple (50 mM ferrocene, Sigma-Aldrich) dissolved in 0.1 M TEABF₄/CH₂Cl₂ was employed as an internal pseudoreference for potential calibration. The onset of oxidation and reduction processes were used to estimate the valence and conduction band edge positions.

Solar cell simulations were performed using SCAPS-1D (version 3.3.12, University of Ghent).^{49,50} A planar n-i-p device structure was modeled with the architecture FTO/TiO₂/absorber/Spiro-OMeTAD, employing layer thicknesses of 100, 30, 200, and 90 nm, respectively. Standard parameters for FTO, TiO₂, and Spiro-OMeTAD were taken from literature and SCAPS databases,⁵¹ while absorber parameters such as bandgap, electron affinity and energy levels were experimentally derived. The absorbers were modeled as lightly n-doped semiconductors (donor concentration 1×10^{15} cm⁻³), with carrier mobilities set to 5 cm² V⁻¹ s⁻¹, effective density of states (N_c and N_v) of 2×10^{18} cm⁻³, and a dielectric constant of 9.0. A mid-gap trap with a density of 1×10^{15} cm⁻³ was also included. Simulations were conducted under AM1.5G illumina-

tion (100 mW cm⁻², 300 K), yielding key photovoltaic parameters such as J - V curves, short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE).

Results and discussion

The three caesium cobalt chloride phases synthesized *via* direct mechanochemical milling are readily distinguishable by their characteristic colours, which reflect differences in cobalt coordination geometry. CsCoCl₃ exhibits a turquoise hue, consistent with high-spin Co²⁺ in octahedral environment, while Cs₂CoCl₄ and Cs₃CoCl₅ appear cyan-blue, indicating tetrahedral coordination. All samples are highly sensitive to moisture and air, gradually turning purple upon exposure due to hydration and the formation of Co²⁺-aquo species. The structural identity and crystallinity of the mechanothesized products were confirmed by powder X-ray diffraction and Rietveld refinements (Fig. 1 top). The experimental patterns match closely the calculated models, and the low residuals support the phase purity and structural fidelity of the synthesized materials (Table S1†). CsCoCl₃ and Cs₂CoCl₄ were refined as single-phase products, whereas the Cs₃CoCl₅ sample displays a minor impurity attributed to CsCl, evidenced by a weak reflection near $2\theta \approx 21.6^\circ$. The slightly elevated background observed in all patterns is attributed to diffuse scattering from adsorbed moisture, a common feature in air-sensitive chlorides. These results demonstrate the successful and selective formation of each target phase under solvent-free conditions. Structurally, the three compounds exhibit distinct Co²⁺ coordi-

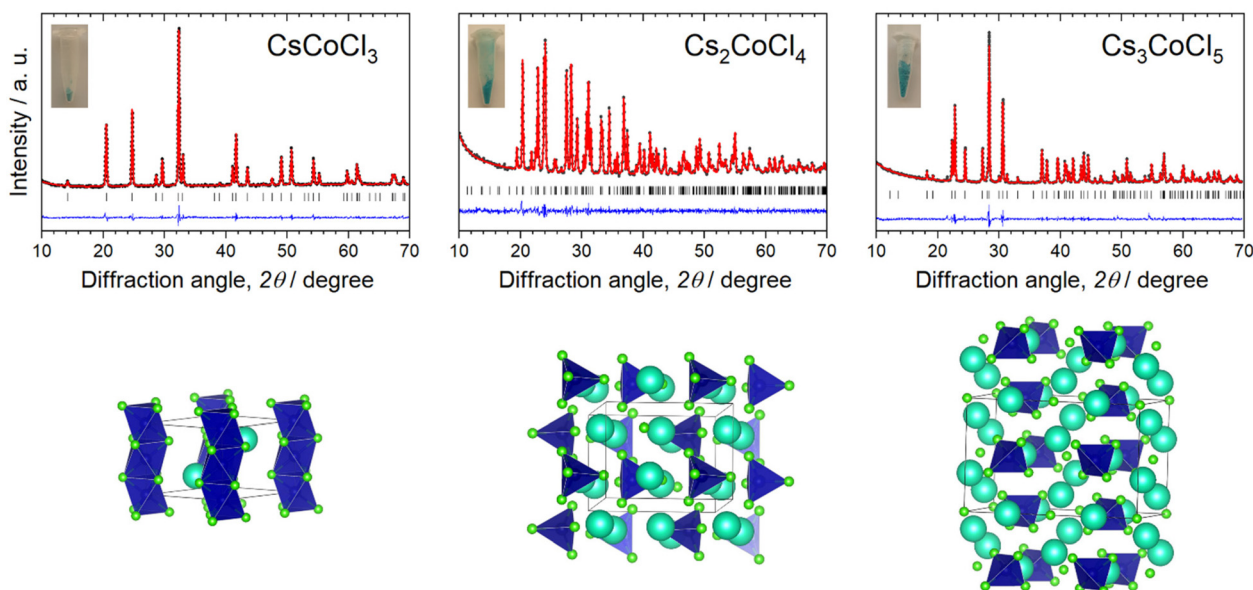


Fig. 1 (Top) Rietveld-refined X-ray diffraction patterns (black points: observed; red line: calculated; blue line: difference; black ticks: reflections position) of mechanochemically synthesized samples. Inset show the visual appearance of each sample. (bottom) Crystal structures illustrating the progression from infinite columns of face-sharing CoCl₆ octahedra to isolated tetrahedra. Green, purple-blue, and cyan spheres represent Cl, Co, and Cs atoms, respectively.



nation environments that evolve with increasing Cs:Co ratio. CsCoCl₃ crystallizes in a hexagonal structure featuring infinite columns of face-sharing CoCl₆ octahedra aligned along the [001] axis. In contrast, Cs₂CoCl₄ adopts an orthorhombic structure with isolated CoCl₄ tetrahedra distributed throughout the lattice. Cs₃CoCl₅ also contains discrete CoCl₄ tetrahedra embedded in a three-dimensional array where Cs⁺ cations bridge and stabilize isolated CoCl₄²⁻ tetrahedra. The refined crystallographic parameters for each phase are summarized in Table S1.†

The morphology and elemental homogeneity of the CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅ samples were examined by SEM and EDS. As shown in Fig. S1,† all three phases exhibit compact polycrystalline aggregates, with particle sizes in the range of 1–10 μm. CsCoCl₃ displays larger faceted domains with angular edges, while Cs₂CoCl₄ and Cs₃CoCl₅ reveal more granular morphologies composed of rounded, densely packed particles. Elemental mapping (Fig. S2–S4†) confirms that Cs, Co, and Cl are homogeneously distributed throughout the selected crystallites for all three compositions. Quantitative EDS analysis, calibrated using external standards, further supports the expected stoichiometries, with atomic ratios in excellent agreement with the nominal Cs:Co:Cl values of 1:1:3, 2:1:4, and 3:1:5, respectively. These results validate the compositional uniformity and phase purity of the mechanochemically synthesized samples.

X-ray photoelectron spectroscopy was used to assess the oxidation state and local chemical environment of cobalt in the three synthesized samples (Fig. 2a). The Co 2p core-level

spectra of all three samples display two principal peaks corresponding to Co 2p_{3/2} and Co 2p_{1/2} centered at ~781 and ~796 eV, respectively. The observed spin-orbit splitting (15.44–15.91 eV) and the presence of characteristic shake-up satellites confirm the Co²⁺ state.⁵² Although the binding energies differ only slightly among the samples, notable variations are observed in the full width at half maximum (FWHM) of the 2p_{3/2} peak: CsCoCl₃ exhibits the narrowest signal (3.28 eV), followed by Cs₃CoCl₅ (3.31 eV) and Cs₂CoCl₄ (3.591 eV). These differences likely reflect variations in local symmetry and electronic delocalization, with the sharper signal in CsCoCl₃ indicative of greater structural order, consistent with its octahedral coordination of Co²⁺, while broader peaks in Cs₂CoCl₄ and Cs₃CoCl₅ align with more distorted tetrahedral environments.^{53–55} These results corroborate the phase-dependent structural motifs and confirm the uniform +2 oxidation state of cobalt across the series.

The low-frequency Raman spectra (< 400 cm⁻¹) of the samples reveal distinct vibrational signatures consistent with their respective cobalt coordination environments and crystallographic symmetries (Fig. 2b). In CsCoCl₃, the spectrum resolves five well-defined modes corresponding to the expected A_{1g} + E_{1g} + 3E_{2g} representations of the P6₃/mmc space group.^{56,57} For the orthorhombic lattice of Cs₂CoCl₄, the spectrum exhibits broad overlapping bands characteristic of its rich vibrational manifold (42 Raman-active modes). Three regions can be discerned: lattice modes (< 100 cm⁻¹), Cl–Co–Cl bending modes (100–140 cm⁻¹), and Co–Cl stretching modes (> 280 cm⁻¹).^{58,59} Cs₃CoCl₅ also shows distinct tetra-

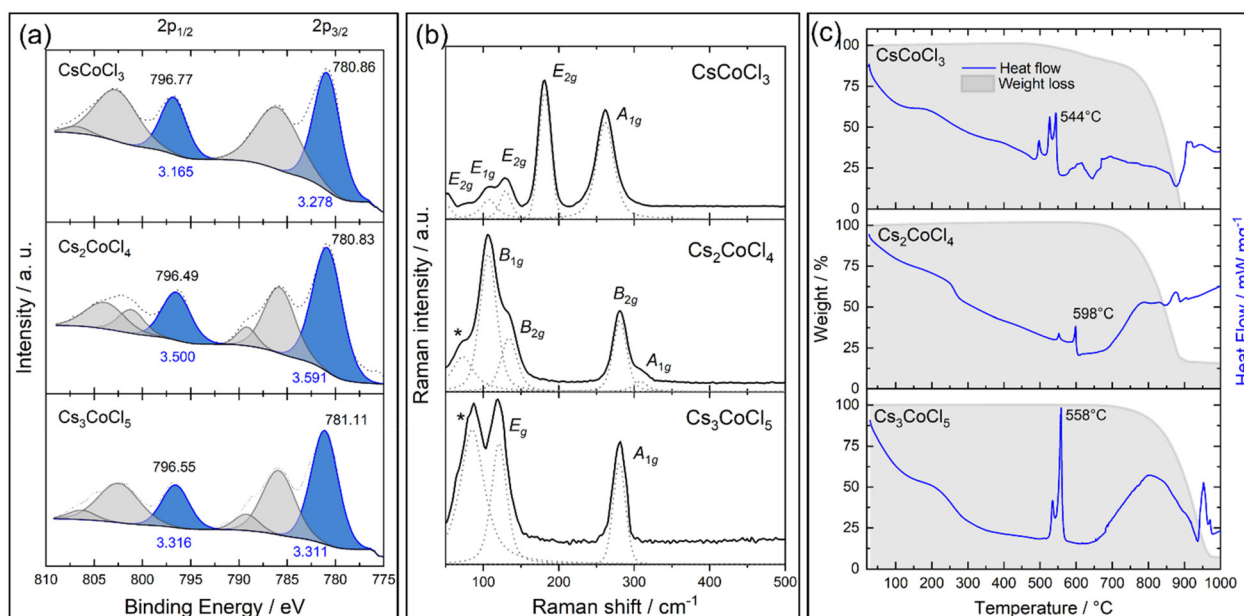


Fig. 2 (a) High-resolution Co 2p XPS spectra of CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, showing characteristic Co²⁺ 2p_{3/2} and 2p_{1/2} peak and satellite features; full width at half maximum (FWHM, in eV) values are indicated. (b) Raman spectra of the three phases, highlighting vibrational fingerprints corresponding to octahedral and tetrahedral Co–Cl coordination environments, as well as lattice modes indicated by *. (c) Thermogravimetric and differential scanning calorimetry (TGA-DSC) profiles showing thermal stability and endothermic transitions up to the melting points of each compound.



hedral CoCl_4 vibrational signatures with three main bands at 87, 120, and 282 cm^{-1} , assigned respectively to external lattice, bending (E_g), and symmetric stretching (A_{1g}) modes. These assignments are in good agreement with reports on structurally analogous Cs_3MCl_5 compounds ($M = \text{Fe}, \text{Cd}, \text{Mg}$).^{60–62}

The thermal behaviour evaluated by TGA-DSC shows different features for each phase (Fig. 2b). CsCoCl_3 displays three endothermic transitions, with the most intense event at $544\text{ }^\circ\text{C}$ attributed to congruent melting. Lower-temperature peaks at $497\text{ }^\circ\text{C}$ and $527\text{ }^\circ\text{C}$ are assigned to eutectic equilibria involving Cs_2CoCl_4 and CoCl_2 . Cs_2CoCl_4 shows thermal events at $522\text{ }^\circ\text{C}$ and $598\text{ }^\circ\text{C}$, the latter corresponding to its congruent melting. Cs_3CoCl_5 exhibits transitions at $534\text{ }^\circ\text{C}$ and $558\text{ }^\circ\text{C}$, also consistent with eutectic and melting processes.⁶³ These results confirm the thermal stability of all three compounds well above room temperature and establish their feasibility for integration into functional devices processed at moderated to high temperatures.

Optical absorption measurements reveal distinct spectral signatures consistent with the Co^{2+} coordination environment in each phase (Fig. 3a). CsCoCl_3 exhibits three well-defined spin-allowed transitions at approximately 1646, 826, and 600 nm, corresponding to the ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$, ${}^4\text{A}_2(\text{F})$, and ${}^4\text{T}_1(\text{P})$ excitations, respectively.⁶⁴ On the other hand, Cs_2CoCl_4

and Cs_3CoCl_5 show nearly identical spectra characterized by two spin-allowed transitions at 1942 and 670 nm, assigned to the ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ and ${}^4\text{T}_1(\text{P})$ transitions. Analysis of these transitions using Tanabe–Sugano diagrams allowed the extraction of ligand field parameters (Table S2†), which corroborate the structural assignments: octahedral Co^{2+} in CsCoCl_3 exhibits a larger ligand field splitting (Δ), while the slightly lower Racah (B) and nephelauxetic (β) parameters observed in the tetrahedral Co^{2+} phases suggest more localized and covalent Co–Cl interactions in Cs_2CoCl_4 and Cs_3CoCl_5 . Additionally, colorimetric analysis based on the measured spectra further supports these distinctions, yielding CIE Lab coordinates (Table S1†) that differentiate the samples by hue: turquoise for CsCoCl_3 and cyan-blue for Cs_2CoCl_4 and Cs_3CoCl_5 (Fig. 3a, inset).

Building on these ligand field characteristics, the optical bandgaps energies were evaluated by diffuse reflectance spectroscopy using the Kubelka–Munk transformation (Fig. 3b). All three compounds exhibit absorption edges in the near infrared to visible region, confirming their nature as narrow bandgap semiconductors. For Cs_2CoCl_4 and Cs_3CoCl_5 , a sharp absorption was observed at 1.66 and 1.65 eV, respectively. In contrast, CsCoCl_3 displays a more complex spectrum consisting of two main features: a subtle absorption at 1.50 eV associated with

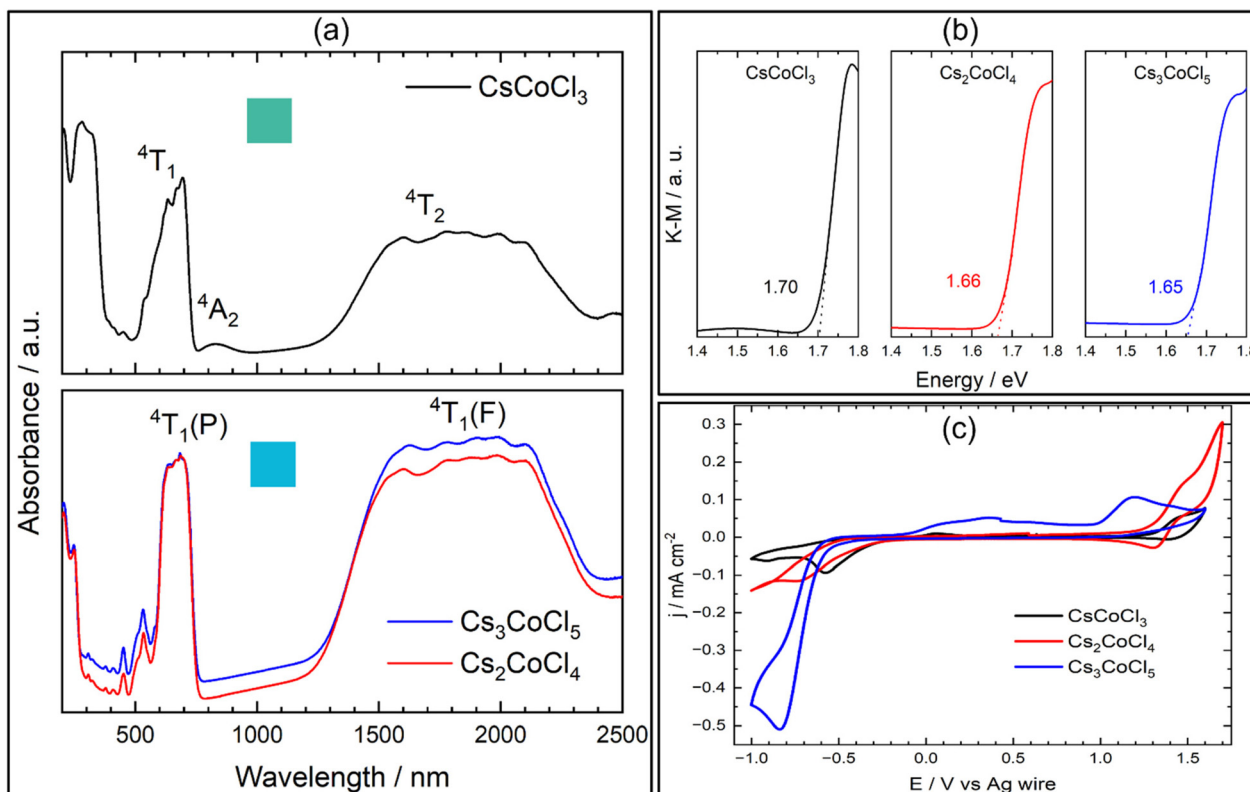


Fig. 3 (a) Optical absorption spectra showing Co^{2+} d-d transitions in CsCoCl_3 (octahedral) and $\text{Cs}_2\text{CoCl}_4/\text{Cs}_3\text{CoCl}_5$ (tetrahedral). Forbidden transitions are not indicated. (b) Tauc plots derived from diffuse reflectance (Kubelka–Munk function), used to estimate the optical bandgaps: 1.70 eV (CsCoCl_3), 1.66 eV (Cs_2CoCl_4), and 1.65 eV (Cs_3CoCl_5). (c) Cyclic voltammetry profiles used to extract onset oxidation and reduction potentials for estimation of valence and conduction band positions.



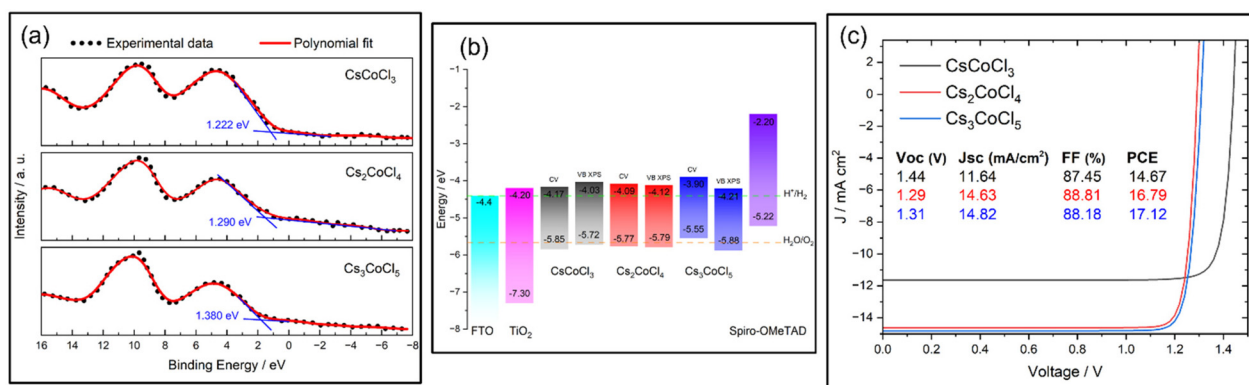


Fig. 4 (a) Valence band spectra obtained by XPS, showing extrapolated onsets used to determine EVB values. (b) Absolute energy level diagrams of CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅ determined by CV and VB-XPS, compared with common charge transport layers (FTO, TiO₂, Spiro-OMeTAD) and redox potentials of water (H⁺/H₂ and H₂O/O₂). (c) Simulated J–V curves for planar heterojunction solar cells using each compound as the absorber layer (FTO/TiO₂/absorber/Spiro-OMeTAD), highlighting the predicted performance metrics: open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE).

internal d-d transition, and a stronger onset around 1.70 eV attributed to the optical bandgap. These results reinforce the electronic distinctions between octahedral and tetrahedral Co²⁺ environments and support the potential of these compounds for low-bandgap optoelectronic applications.

To further explore the electronic properties, cyclic voltammetry was employed to estimate the frontier energy levels of the three compounds (Fig. 3c).⁶⁵ The valence band (EVB) and conduction band (ECB) energies were calculated from the oxidation and reduction onset potentials, using the ferrocene/ferrocenium (Fc/Fc⁺) couple as an internal reference (−4.80 eV vs. vacuum, Fig. S5†).^{66–68} For CsCoCl₃, EVB and ECB were determined to be −5.85 eV and −4.17 eV, respectively, yielding an electrochemical bandgap of 1.68 eV. Similarly, Cs₂CoCl₄ and Cs₃CoCl₅ exhibit EVB/ECB values of −5.78/−4.11 eV and −5.55/−3.90 eV, respectively, with corresponding bandgaps of 1.67 and 1.65 eV. These values are in excellent agreement with the optical bandgaps derived from diffuse reflectance, confirming the reliability of the methods and reinforcing the intrinsic semiconducting character of the phases.

To corroborate the electrochemical data and further probe the electronic structure, valence band XPS was performed. The EVB values were extracted from the extrapolated leading edges of the spectral and referenced to the vacuum level (Fig. 4a). For CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, the EVB positions were determined to be −5.72, −5.79, and −5.88, respectively. By subtracting the optical bandgaps determined from diffuse reflectance spectroscopy, the corresponding ECB were estimated as −4.03, −4.12, and −4.21 eV. These values are consistent with those obtained by CV, validating the internal consistency between spectroscopic and electrochemical methods. The progressive downshift of both EVB and ECB across the CsCoCl₃–Cs₂CoCl₄–Cs₃CoCl₅ series (Fig. 4b) reflects the effect of compositional variation on band edges positions. Altogether, these findings confirm the narrow bandgap semiconducting nature of these materials and reveal the potential for fine-tuning their

electronic structure through structural and chemical modification.

The absolute energy level diagrams derived from VB XPS, CV, and optical spectroscopy suggest that CsCoCl₃, Cs₂CoCl₄, and Cs₃CoCl₅, are promising candidates for optoelectronic and photocatalytic applications. All three compounds exhibit conduction band minima above the H⁺/H₂ reduction potential (−4.44 eV) and valence band maxima below the H₂O/O₂ oxidation potential (−5.67 eV), indicating their thermodynamic suitability for overall water splitting under visible light irradiation (Fig. 4b).^{69,70} Additionally, their band edge alignment is compatible with common charge transport materials used in photovoltaic devices: electron extraction by TiO₂ (ECB = −4.0 eV) or SnO₂ (ECB = −4.2 eV), and hole extraction by NiO_x (EVB = −5.4 eV) or Spiro-OMeTAD (EVB = −5.2 eV) would be energetically favorable.^{71–73}

Given this energetic compatibility, the photovoltaic potential of these materials was further evaluated through SCAPS-1D simulations. Planar heterojunction solar cells with a standard FTO/TiO₂/absorber/Spiro-OMeTAD architecture were modeled for each compound. The predicted power conversion efficiencies (PCE) reached 14.7% for CsCoCl₃, 16.8% for Cs₂CoCl₄, and 17.1% for Cs₃CoCl₅, driven by high open-circuit voltages and fill factors above 87% (Fig. 4c). The higher PCEs of the tetrahedral phases reflect their narrower bandgaps and improved alignment within the devices stack. While these simulations represent idealized conditions, they underscore the potential of Cs–Co–Cl halometalates as compositionally tunable absorbers for low-bandgap photovoltaics and integrated solar-driven systems.

Conclusions

In this work, we have conducted the first comprehensive comparative study of the cobalt chloride phases CsCoCl₃,



Cs_2CoCl_4 , and Cs_3CoCl_5 , synthesized as phase-pure materials *via* a rapid and solvent-free mechanochemical approach. By tuning the $\text{CsCl}:\text{CoCl}_2$ ratio, each phase was selectively obtained within one hour, highlighting the efficiency and precision of this method. Detailed structural, spectroscopic, and electronic characterizations, including SEM-EDS mapping, CV, and VB XPS, are presented here for the first time for this family of halide cobaltates. The compounds feature distinct structural motifs, octahedral Co^{2+} in CsCoCl_3 and tetrahedral Co^{2+} in Cs_2CoCl_4 and Cs_3CoCl_5 , which result in well-defined differences in their vibrational, optical, and electronic properties. This clear structure–property correlation is evidenced by their unique Raman fingerprints, d–d transitions, ligand field parameters, and colorimetric profiles. Bandgaps in the narrow 1.65–1.70 eV range were confirmed by both optical and electrochemical methods, and absolute band edge positions obtained by VB XPS reveal systematic shifts in EVB and ECB with increasing Cs content, highlighting the tunability of their electronic structure *via* coordination and compositional control. Thermal analysis confirms the robustness of all three phases up to their melting points, and their band alignments are well-positioned for both photocatalytic water splitting and photovoltaic applications. SCAPS-1D simulations further support this, predicting PCEs exceeding 17% under ideal conditions, placing these materials among promising candidates for low bandgap solar absorbers.

Overall, this study introduces an efficient synthetic strategy and reveals key structure–property relationships, establishing cobalt-based halide frameworks as a versatile platform for future optoelectronic and solar energy technologies.

Author contributions

Rodrigo Castillo contributed to supervision, project administration, and writing – review & editing. Pablo Garrido was responsible for investigation, methodology, and writing – original draft. Darío Espinoza contributed to supervision, data curation, and validation. Karem Gallardo was involved in funding acquisition, provision of resources, and validation. Rosa M. González-Gil contributed to data curation, formal analysis, and provision of resources.

Conflicts of interest

There are no conflicts to declare.

Data availability

Necessary datasets supporting this article have been included in the ESI.† Additional raw data, including crystallographic information files (CIFs), Rietveld refinement input/output files, and spectroscopic data, are available from the corresponding author upon reasonable request.

Acknowledgements

R. C. thanks to Fondecyt Iniciación (11230732). P. G. thanks to Beca UCN and ICN2. K. G. thanks to Fondecyt Iniciación (11230831). Authors thank to Unidad de Equipamiento Científico MAINI-UCN, and to FONDEQUIP EQM 210078. Authors acknowledge Prof. Pedro Gómez for valuable discussion.

References

- 1 C. C. Stoumpos and M. G. Kanatzidis, The renaissance of halide perovskites and their evolution as emerging semiconductors, *Acc. Chem. Res.*, 2015, **48**, 2791–2802.
- 2 L. Mao, J. Chen, P. Vishnoi and A. K. Cheetham, The renaissance of functional hybrid transition-metal halides, *Acc. Mater. Res.*, 2022, **3**, 439–448.
- 3 S. Kim, T. T. Trinh, J. Park, D. P. Pham, S. Lee, H. B. Do, N. N. Dang, V. A. Dao, J. Kim and J. Yi, Over 30% efficiency bifacial 4-terminal perovskite-heterojunction silicon tandem solar cells with spectral albedo, *Sci. Rep.*, 2021, **11**, 15524.
- 4 A. Harter, K. Artuk, F. Mathies, O. Karalis, H. Hempel, A. Al-Ashouri, S. Albrecht, R. Schlatmann, C. Ballif, B. Stannowski and C. M. Wolff, Perovskite/silicon tandem solar cells above 30% conversion efficiency on submicron-sized textured Czochralski-silicon bottom cells with improved hole-transport layers, *ACS Appl. Mater. Interfaces*, 2024, **16**, 62817–62826.
- 5 R. L. Z. Hoyer, R. E. Brandt, A. Osherov, V. Stevanovic, S. D. Stranks, M. W. B. Wilson, H. Kim, A. J. Akey, J. D. Perkins, R. C. Kurchin, J. R. Poindexter, E. N. Wang, M. G. Bawendi, V. Bulovic and T. Buonassisi, Methylammonium bismuth iodide as a lead-free, stable hybrid organic-inorganic solar absorber, *Chem. – Eur. J.*, 2016, **22**, 2605–2610.
- 6 M. Lyu, J. H. Yun, M. Cai, Y. Jiao, P. V. Bernhardt, M. Zhang, Q. Wang, A. Du, H. Wang, G. Liu and L. Wang, Organic-inorganic bismuth(III)-based material: a lead-free, air stable and solution-processable light-absorber beyond organolead perovskites, *Nano Res.*, 2016, **9**, 692–702.
- 7 M. Wang, W. Wang, B. Ma, W. Shen, L. Liu, K. Cao, S. Chen and W. Huang, Lead-free perovskite materials for solar cells, *Nano-Micro Lett.*, 2021, **13**, 62.
- 8 N. K. Tailor, S. Kar, P. Mishra, A. These, C. Kupfer, H. Hu, M. Awais, M. Saidaminov, M. I. Dar, C. Brabec and S. Satpathi, Advances in lead-free perovskite single crystals: fundamentals and applications, *ACS Mater. Lett.*, 2021, **3**, 1025–1080.
- 9 X. Li, J. Wu, S. Wang and Y. Qi, Progress of all-inorganic cesium lead-free perovskite solar cells, *Chem. Lett.*, 2019, **48**, 989–1005.
- 10 G. Volonakis, M. R. Filip, A. A. Haghghirad, N. Sakai, B. Wenger, H. J. Snaith and F. Giustino, Lead-free halide



- double perovskites via heterovalent substitution of noble metals, *J. Phys. Chem. Lett.*, 2016, **7**, 1254–1259.
- 11 N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A. A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, A. Petrozza, L. M. Herz and H. J. Snaith, Lead-free organic-inorganic tin halide perovskites for photovoltaic applications, *Energy Environ. Sci.*, 2014, **7**, 3061–3068.
 - 12 R. Nie, A. Mehta, B. W. Park, H. W. Kwon, J. Im and S. I. Seok, Mixed sulfur and iodide-based lead-free perovskite solar cells, *J. Am. Chem. Soc.*, 2018, **140**, 872–875.
 - 13 R. Nie, R. R. Sumukam, S. H. Reddy, M. Banavoth and S. I. Seok, Lead-free perovskite solar cells enabled by hetero-valent substitutes, *Energy Environ. Sci.*, 2020, **13**, 2363–2385.
 - 14 X. Li, Y. He, M. Kepenekian, P. Guo, W. Ke, J. Even, C. Katan, C. C. Stoumpos, R. D. Schaller and M. G. Kanatzidis, Three-dimensional lead iodide perovskitoid hybrids with high X-ray photoresponse, *J. Am. Chem. Soc.*, 2020, **142**, 6625–6637.
 - 15 Q. Sun, Y. Xu, H. Zhang, B. Xiao, X. Liu, J. Dong, Y. Cheng, B. Zhang, W. Jie and M. G. Kanatzidis, Optical and electronic anisotropies in perovskitoid crystals of Cs₃Bi₂I₉ studies of nuclear radiation detection, *J. Mater. Chem. A*, 2018, **6**, 23388–23395.
 - 16 T. Kong, H. Xie, Y. Zhang, J. Song, Y. Li, E. L. Lim, A. Hagfeldt and D. Bi, Perovskitoid-templated formation of a 1D@3D perovskite structure toward highly efficient and stable perovskite solar cells, *Adv. Energy Mater.*, 2021, **11**, 2101018.
 - 17 H. Shankar, A. Jha and P. Kar, Water-assisted synthesis of lead-free Cu based fluorescent halide perovskite nanostructures, *Mater. Adv.*, 2022, **3**, 658–664.
 - 18 J. Qu, S. Xu, H. Shao, P. Xia, C. Lu, C. Wang and D. Ban, Recent progress of copper halide perovskites: properties, synthesis and applications, *J. Mater. Chem. C*, 2023, **11**, 6260–6275.
 - 19 N. Navarro, R. Nelson, K. Gallardo and R. Castillo, Exploring the influence of cation and halide substitution in the structure and optical properties of CH₃NH₃NiCl₃ perovskite, *Molecules*, 2024, **29**, 2141.
 - 20 N. Navarro, C. Núñez, D. Espinoza, K. Gallardo, I. Brito and R. Castillo, Synthesis, characterization, and photoelectric and electrochemical behavior of (CH₃NH₃)₂Zn_{1-x}Co_xBr₄ perovskites, *Inorg. Chem.*, 2023, **62**, 17046–17051.
 - 21 H. Zhou, X. Cui, C. Yuan, J. Cui, S. Shi, G. He, Y. Wang, J. Wei, X. Pu, W. Li, D. Zhang, J. Wang, X. Ren, H. Ma, X. Shao, X. Wei, J. Zhao, X. Zhang and J. Yin, Band-gap tuning of organic-inorganic hybrid palladium perovskite materials for a near-infrared optoelectronics response, *ACS Omega*, 2018, **3**, 13960–13966.
 - 22 X. Cheng, L. Jing, Y. Yuan, S. Du, Q. Yao, J. Zhang, J. Ding and T. Zhou, Centimeter-size square 2D layered Pb-free hybrid perovskite single crystal (CH₃NH₃)₂MnCl₄ for red photoluminescence, *CrystEngComm*, 2019, **21**, 4085–4091.
 - 23 J. Yin, X. Liu, L. Fan, J. Wei, G. He, S. Shi, J. Guo, C. Yuan, N. Chai, C. Wang, J. Cui, X. Wang, H. Zhou and D. Tian, Synthesis, crystal structure, absorption properties, photoelectric behavior of organic-inorganic hybrid (CH₃NH₃)₂CoCl₄, *Appl. Organomet. Chem.*, 2019, **33**, e4795.
 - 24 T. Lee, D. B. Straus, X. Xu, W. Xie and R. J. Cava, Tunable magnetic transition temperatures in organic-inorganic hybrid cobalt chloride hexagonal perovskites, *Chem. Mater.*, 2023, **35**, 1745–1751.
 - 25 J. B. Abdallah, C. J. Gómez-García and H. Boughzala, Synthesis, crystal structure, optical, thermal and magnetic studies of a new organic-inorganic hybrid based on tetrachloroferrate(III), *J. Solid State Chem.*, 2021, **303**, 122504.
 - 26 R. Babu, A. K. Vardhaman, V. M. Dhavale, L. Giribabu and S. P. Singh, MA₂CoBr₄: lead-free cobalt-based perovskite for electrochemical conversion of water to oxygen, *Chem. Commun.*, 2019, **55**, 6779–6782.
 - 27 W. B. Yelon, D. E. Cox and M. Eibschütz, Magnetic ordering in CsCoBr₃, *Phys. Rev. B*, 1975, **12**, 5007–5015.
 - 28 F. Matsubara, S. Inawashiro and H. Ohhara, On the Raman scattering in CsCoCl₃, CsCoBr₃ and RbCoCl₃, *J. Phys.: Condens. Matter*, 1991, **3**, 1815–1826.
 - 29 O. Breunig, M. Garst, A. Rosch, E. Sela, B. Buldmann, P. Becker, L. Bohatý, R. Müller and T. Lorenz, Low-temperature ordered phases of the spin-1/2 XXZ chain system in Cs₂CoCl₄, *Phys. Rev. B:Condens. Matter Mater. Phys.*, 2015, **91**, 024423.
 - 30 K. Hirakawa, H. Yoshizawa, G. Shirane and H. Shiba, Neutron scattering study of Cs₂CoCl₄: A system of 1D, S = 1/2 XY antiferromagnetic chains with spin frustration, *J. Magn. Magn. Mater.*, 1983, **31–34**, 1137–1138.
 - 31 W. Fang, H. J. Chen and J. W. Zhang, Theoretical studies of optical spectra and spin-Hamiltonian parameters for Co²⁺ in Cs₃CoCl₅ with first-principles calculations and ligand field theory, *Opt. Mater.*, 2025, **158**, 116428.
 - 32 V. A. Komornikov, A. V. Gudymenko, I. S. Timakov and A. A. Kulishov, Phase equilibria, growth, and properties of crystals in the CsCl-CoCl₂-H₂O system, *Inorg. Mater. Appl. Res.*, 2023, **14**, 286–292.
 - 33 L. Nataf, F. Aguado, I. Hernández, R. Valiente, J. González, M. N. Sanz-Ortiz, H. Wilhelm, A. P. Jephcoat, F. Baudelet and F. Rodríguez, Volume and pressure dependences of the electronic, vibrational, and crystal structures of Cs₂CoCl₄: identification of a pressure-induced piezochromic phase at high pressure, *Phys. Rev. B*, 2017, **95**, 014110.
 - 34 AtH. Trutia and M. Lébl, Optical spectrum of Co(II) in CsCoCl₃ single crystals, *Krist. Tech.*, 1969, **4**, 129–133.
 - 35 J. Makovsky, A. Horowitz and D. Gazit, Single crystal growth of CsCoCl₃, Cs₂CoCl₄, Cs₃CoCl₅, RbCoCl₃, Rb₂CoCl₄, and Rb₃CoCl₅, *J. Cryst. Growth*, 1974, **22**, 241–243.
 - 36 H. Soling, G. Johansson, F. Sandberg and T. Norin, The crystal structure and magnetic susceptibility of CsCoCl₃, *Acta Chem. Scand.*, 1968, **22**, 2793–2802.
 - 37 J. C. Rivoal, C. Grisolia, J. P. Torre and M. Vala, Magneto-optical evidence of magnon sidebands in Cs₃CoCl₅, *J. Phys.*, 1985, **46**, 1709–1716.



- 38 B. N. Figgis and A. N. Sobolev, Cs_3CoCl_5 at 10 K, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2001, **57**, 139–140.
- 39 B. N. Figgis, E. S. Kucharski and P. A. Reynolds, Electron density distribution in Cs_3CoCl_5 , *Acta Crystallogr., Sect. B: Struct. Sci.*, 1989, **45**, 232–240.
- 40 L. E. Wenger and T. P. Hanusa, Synthesis without solvent: consequences for mechanochemical reactivity, *Chem. Commun.*, 2023, **59**, 14210–14222.
- 41 J. D. Loya, S. J. Li, D. K. Unruh and K. M. Hutchins, Mechanochemistry as a tool for crystallizing inaccessible solids from viscous liquid components, *Cryst. Growth Des.*, 2022, **22**, 285–292.
- 42 F. Cuccu, L. De Luca, F. Delogu, E. Colacino, N. Solin, R. Mocci and A. Porcheddu, Mechanochemistry: new tools to navigate the uncharted territory of “impossible” reactions, *ChemSusChem*, 2022, **15**, e202200362.
- 43 K. Kanazawa, S. Yubuchi, C. Hotehama, M. Otoyama, S. Shimono, H. Ishibashi, Y. Kubota, A. Sakuda, A. Hayashi and M. Tatsumisago, Mechanochemical synthesis and characterization of metastable hexagonal Li_4SnS_4 solid electrolyte, *Inorg. Chem.*, 2018, **57**, 9925–9930.
- 44 T. Jardiel, D. G. Calatayud, M. Rodríguez, D. Fernández-Hevia and A. C. Caballero, Synthesis of metastable $\text{Bi}_6\text{Ti}_5\text{WO}_{22}$ phase by the mechanochemical method, *Mater. Lett.*, 2013, **94**, 58–60.
- 45 T. F. Grigor'eva, S. V. Tsybulya, S. V. Cherepanova, G. N. Kryukova, A. P. Barinova, V. D. Belykh and V. V. Boldyrev, Mechanochemical synthesis of metastable solid solutions: phase composition and microstructure evolution, *Inorg. Mater.*, 2000, **36**, 143–149.
- 46 E. M. Heppke, A. Koldemir, R. Pöttgen, T. Bredow and M. Lerch, Mechanochemical synthesis and structural evaluation of a metastable polymorph of Ti_3Sn , *Z. Naturforsch., B: J. Chem. Sci.*, 2023, **78**, 209–214.
- 47 Yu. A. Skakov, Formation and stability of metastable phases in mechanochemical synthesis, *Met. Sci. Heat Treat.*, 2005, **47**, 296–304.
- 48 V. Petříček, L. Palatinus, J. Plášil and M. Dušek, Jana2020 – a new version of the crystallographic computing system Jana, *Z. Kristallogr. - Cryst. Mater.*, 2023, **238**, 271–282.
- 49 M. Burgelman, P. Nollet and S. Degraeve, Modelling polycrystalline semiconductor solar cells, *Thin Solid Films*, 2000, **361–362**, 527–532.
- 50 M. Burgelman, K. Decock, S. Khelifi and A. Abass, Advanced electrical simulation of thin film solar cells, *Thin Solid Films*, 2013, **535**, 296–301.
- 51 A. Usman and T. Bovornratanaraks, Modeling and optimization of modified TiO_2 with aluminum and magnesium as ETL in MAPbI_3 perovskite solar cells: SCAPS 1D frameworks, *ACS Omega*, 2024, **9**, 39663–39672.
- 52 M. Fantauzzi, F. Secci, M. Sanna Angotzi, C. Passiu, C. Cannas and A. Rossi, Nanostructured spinel cobalt ferrites: Fe and Co chemical state, cation distribution and size effects by X-ray photoelectron spectroscopy, *RSC Adv.*, 2019, **9**, 19171–19179.
- 53 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. St. C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, *Appl. Surf. Sci.*, 2011, **257**, 2717–2730.
- 54 J. Baltrusaitis, B. Mendoza-Sanchez, V. Fernandez, R. Veenstra, N. Dukstiene, A. Roberts and N. Fairley, Generalized molybdenum oxide surface chemical state XPS determination via informed amorphous sample model, *Appl. Surf. Sci.*, 2015, **326**, 151–161.
- 55 A. Cano, J. Rodríguez-Hernández, L. Reguera, E. Rodríguez-Castellón and E. Reguera, On the scope of XPS as sensor in coordination chemistry of transition metal hexacyanometallates, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1724–1732.
- 56 W. Breitling, W. Lehmann, T. P. Srinivasan and R. Weber, One phonon Raman scattering of hexagonal ABX_3 -compounds, *Solid State Commun.*, 1976, **20**, 525–526.
- 57 W. Breitling, W. Lehmann, T. P. Srinivasan and R. Weber, Raman scattering on the electronic states of Co^{2+} in the 1D Ising antiferromagnet CsCoCl_3 , *J. Magn. Magn. Mater.*, 1977, **6**, 116–119.
- 58 O. P. Lamba and S. K. Sinha, Polarized Raman scattering from oriented single crystals of A_2BX_4 halides ($\text{A} = \text{Cs}$, $\text{B} = \text{Zn}$, $\text{X} = \text{Cl}$, Br , I), *Solid State Commun.*, 1986, **57**, 365–371.
- 59 O. P. Lamba, M. B. Patel, S. Ram, P. Chand and H. D. Bist, Raman scattering study of the phase sequence in A_2BX_4 halides, *Solid State Commun.*, 1984, **50**, 321–325.
- 60 B. Briat and J. C. Canit, Polarized absorption and magnetic circular dichroism of the FeCl_4^{2-} ion in a tetragonally distorted tetrahedral site the crystal spectra of Cs_3FeCl_5 , *Mol. Phys.*, 1983, **48**, 33–61.
- 61 M. H. Brooker and C.-H. Huang, Raman spectroscopic investigations on the structures of CsMgCl_3 and Cs_3MgCl_5 , *Mater. Res. Bull.*, 1980, **15**, 9–16.
- 62 M. H. Brooker and J. Wang, Raman studies on the structures and properties of the compounds formed in the CdCl_2 - CsCl binary system, *J. Raman Spectrosc.*, 1992, **23**, 471–478.
- 63 H. Seifert, Über die systeme alkalimetallchlorid/Kobalt(II)-chlorid, *Z. Anorg. Allg. Chem.*, 1961, **307**, 137–144.
- 64 C. F. Putnik and S. L. Holt, 7. Magnon sidebands in the electronic absorption spectra of cesium trichlorocobaltate and rubidium trichlorocobaltate, *Inorg. Chem.*, 1977, **16**, 1010–1016.
- 65 Y. Xu and M. A. A. Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, *Am. Mineral.*, 2000, **85**, 543–556.
- 66 S. N. S. Nasir, N. A. Mohamed, M. A. Tukimon, M. F. M. Noh, N. A. Arzaee and M. A. M. Teridi, Direct extrapolation techniques on the energy band diagram of BiVO_4 thin films, *Physica. B. Condens. Matter.*, 2021, **604**, 412719.
- 67 R. E. Aderne, B. G. A. L. Borges, H. C. Ávila, F. Von Kieseritzky, J. Hellberg, M. Koehler, M. Cremona, L. S. Roman, C. M. Araujo, M. L. M. Rocco and C. F. N. Marchiori, On the energy gap determination of



- organic optoelectronic materials: the case of porphyrin derivatives, *Mater. Adv.*, 2022, 3, 1791–1803.
- 68 A. Shafiee and M. Yahaya, Determination of HOMO and LUMO of [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester and Poly (3-octyl-thiophene-2, 5-diyl) through Voltametry Characterization, *Sains Malays.*, 2011, 40, 173–176.
- 69 X. Yang, D. Singh and R. Ahuja, Recent advancements and future prospects in ultrathin 2d semiconductor-based photocatalysts for water splitting, *Catalysts*, 2020, 10, 1–50.
- 70 F. A. Chowdhury, Recent advances and demonstrated potentials for clean hydrogen via overall solar water splitting, *MRS Adv.*, 2019, 4, 2771–2785.
- 71 M. K. Hossain, G. F. I. Toki, A. Kuddus, M. H. K. Rubel, M. M. Hossain, H. Bencherif, M. F. Rahman, M. R. Islam and M. Mushtaq, An extensive study on multiple ETL and HTL layers to design and simulation of high-performance lead-free CsSnCl₃-based perovskite solar cells, *Sci. Rep.*, 2023, 13, 2521.
- 72 A. Alsalmeh and H. Alsaedi, Twenty-two percent efficient Pb-free all-perovskite tandem solar cells using SCAPS-1D, *Nanomaterials*, 2022, 13, 96.
- 73 M. Elawad, K. I. John, A. M. Idris, L. Yang and Y. Gao, An organic hole-transporting material spiro-OMeTAD doped with a Mn complex for efficient perovskite solar cells with high conversion efficiency, *RSC Adv.*, 2021, 11, 32730–32739.

