Solid-State Growth of CsPbI₃ Perovskites: Phases Formation and Stability

Jessica Satta

University of Cagliari

Alberto Casu

King Abdullah University of Science and Technology

Daniele Chiriu

University of Cagliari

Carlo Carbonaro

University of Cagliari

Luigi Stagi

University of Sassari

Pier Carlo Ricci (✉ carlo.ricci@dsf.unica.it)

University of Cagliari

Research Article

Keywords: CsPbI₃, Inorganic lead halide perovskites, Solid-State synthesis, Phase stability

Posted Date: May 14th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-515136/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Solid-State growth of CsPbI₃ perovskites: phases formation and stability

Jessica Satta^a, Alberto Casu^b, Daniele Chiriu^a, Carlo Maria Carbonaro^a, Luigi Stagi^c and Pier Carlo Ricci^{a*}

^a Department of Physics, University of Cagliari, Campus of Monserrato, sp n.8, km 0.700, Monserrato, 09042, Italy

^b King Abdullah University of Science and Technology (KAUST), Biological and Environmental Sciences and Engineering (BESE) Division, Nabla Lab, Thuwal, 23955-6900, Saudi Arabia

^c Laboratory of Materials Science and Nanotechnology, CR-INSTM, Department of Chemistry and Pharmacy, University of Sassari, Via Vienna 2, Sassari, 07100, Italy

* Corresponding author: carlo.ricci@dsf.unica.it

Abstract

Totally inorganic perovskites are playing an increasingly important role for their potential applications in optoelectronics devices. However, a big problem to be solved is the role of the different phases, the presence of which is closely linked to the growth method and to the role of impurities. In this article, we propose a solvent-free, solid-state growth method, which allows to obtain samples free of any organic residues. The analysis of structural (XRD and Raman measurements), optical (absorption, steady-time and time-resolved luminescence) and morphological (HRTEM imaging), permitted to understand the phase evolution during the synthesis as a function of the temporal duration. The dynamic equilibrium process at high temperature between the CsPbI₃ and the starting precursors, CsI and PbI₂, plays a fundamental role in the final phase. If, from one side, the α and δ phases are related to the exact stoichiometry, on the other hand an excess of CsI permits the formation of room temperature stable perovskite γ -phase and, with a further excess, the secondary Cs₄PbI₆ phase is obtained.

Keywords

CsPbI₃; Inorganic lead halide perovskites; Solid-State synthesis; Phase stability

1. Introduction

Since the 1990s organic-inorganic hybrid halide perovskites have received increasing attention in the optoelectronic context [1] for their intrinsic properties such as ambipolarity, high charge-carrier mobilities, great diffusion lengths and high absorption coefficients [2][3][4][5]. As a consequence, they found potential application in many different sectors and devices, from efficient light harvesters to photovoltaics, photodetectors and solar fuels [6][7][8][9]. Also, due to their very high photoluminescence quantum yield and narrow-band emission in the whole visible region [10], they are promising materials to exploit for lighting and display applications.

Perovskites are a class of crystalline compounds described by the generic chemical formula AMX_3 , with A being a large cation, M a smaller metal cation and X an anion, like oxygen or one from the halide series. In the hybrid halides perovskites, the organic cations are small and are typically restricted to methylammonium, ethylammonium and formamidinium; in the all-inorganic halides perovskites the A cation is Caesium or Rubidium. The metal cations are typically divalent metal ions such as Pb^{2+} , Ge^{2+} , Sn^{2+} while the halide anions are I^- , Cl^- and Br^- .

One of the most fascinating characteristics of perovskites is the possibility to tune their optical and electronic properties by varying the composition of halide ion constituents. On the other hand, their application in commercial devices is strongly hampered by low phase stability. The requirements of resistance to various environmental stresses, such as humidity, illumination and high temperatures, being thermodynamically stable under operative conditions should be fully satisfied. Replacing the organic part of perovskites by an inorganic one currently represents a promising way to increase the long-term stability in operating conditions[11][12]. Indeed, the absence of organic part facilitates the resistance to high temperature and to the interaction with solvents and surrounding atmosphere.

As a general rule, the structural stability of perovskites AMX_3 is determined by the Goldschmidt tolerance factor

$$t = \frac{r_A + r_X}{\sqrt{2}(r_M + r_X)}$$

and by the octahedral factor $\mu = r_M/r_X$, with r_A , r_M , r_X being the different ionic radii. The ideal cubic structure is not very common and usually occurs in the ranges $0.8 < t < 1$ and $0.4 < \mu < 0.9$ ranges [13]. All the members of the group of lead trihalides undergo phase transitions by varying the temperature, but with the high temperature phase being the cubic perovskite. Indeed, for inorganic for lead-based $CsPbX_3$ ($X=Cl, Br, I$) four phases are expected: a cubic (α), a tetragonal (β) and two orthorhombic

phases (a black γ and a non-perovskite yellow δ phase). The α -phase has a lower band gap as compared to the δ phase (in particular, 1.7 eV vs 2.8 eV in CsPbI₃, respectively) and displays a different luminescence emission peak (700 nm vs. 550 nm in CsPbI₃) and lower emission efficiency. Since the spherical Cs⁺ ion is not large enough to preserve the PbI₆ octahedra, CsPbI₃ has relatively smaller t value compared to the hybrid organic-inorganic perovskites. So the cubic phase, which is desirable for optoelectronic applications, is stable only at high temperature and undergoes a phase transition to the thermodynamically favoured orthorhombic δ phase when the samples are cooled down to room temperature [14][15].

Different synthesis techniques were applied to obtain high quality samples, the solution deposition techniques being the most widely utilized, because of their low-cost and easy processing. There are mainly two approaches, based on a one-step or a two-step procedure [16][17]. In the latter, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are used as solvents followed by high temperature annealing process. Solvent properties affect the quality of the film and for this reason, antisolvents engineering or solvent evaporation control are used to promote the crystallization process [18][19]. Surface passivation strategies are common, the use of hydriodic acid or the so-called hydrogen lead iodide precursor [20][21][22]. In the former approach, cubic phase is achieved in solution by co-precipitation of monodisperse colloidal nanocrystals, the stability being due to the large contribution of surface energy [23]. These methods require the use of long chain organic capping agents and high boiling point solvents. It was reported that the use of solvents and specific precursors can affect the synthesis, creating organic inclusions in a full inorganic perovskite [24]. Alternatively, other methods allow producing lead halide perovskites without the exploitation of capping ligands or solvents: gas phase deposition, mechanochemical synthesis or synthesis of single crystals [25][26][27][28]. In this work, we focalized our studies on CsPbI₃ obtained by one step solid-state reaction. This kind of synthesis is relatively simple and, mainly, doesn't need the use of any solvent or ligand. This point is fundamental for clearly assessing the structural parameters that define the stable phase and to define how it is possible to achieve room temperature stable γ -phase CsPbI₃. Recently it has been proposed that many of the reported fully inorganic perovskite are stabilized by the organic part of the organic precursor utilized during the synthesis (*i.e.*, hydrogen lead iodide), increasing the uncertainty about the real structure of the samples.

On this basis, we investigated the formation of secondary phases by means of XRD, HRTEM, micro-luminescence and micro-Raman, imaging spectroscopy, time resolved luminescence and optical measurements, pointing out the fundamental role of balancing the stoichiometry between the cations to define which phase will be formed.

2. Material and methods

2.1 Materials

Caesium iodide (CsI, 50 ppm alkali metals, 99,9%) was purchased from Alfa Aesar, Lead iodide (PbI₂, 99%) was purchased from Sigma Aldrich. All chemicals were used without any further purification.

2.1 Synthesis

CsPbI₃ and Cs₄PbI₆ samples were synthesized by a solid-state reaction of CsI and PbI₂. Stoichiometric raw materials were weighed, ground in an agate mortar, and then sintered in a furnace.

Different synthesis processes were performed.

First, the samples were slowly heated at 10 °C/min, up to 400 °C and treated at constant temperature for 10 minutes. Then, the samples were slowly cooled to room temperature.

The same process was carried out multiple times treating the samples at 400 °C for 1 hour, 5 and 10 hours, 17 hours and 24 hours, respectively, to study the effect of the synthesis duration on the final products. Hereinafter, the samples are called CPI3-10m, CPI3-1h, CPI3-5h, CPI3-10h, CPI3-17h, CPI3-24h. In order to discriminate the features of CsPbI₃ from those of secondary phases, we synthesized pure Cs₄PbI₆. We repeated the previous procedure, treating the sample at 400 °C for 5 hours. The resulting sample will be indicated as C4PI6 in the following. As stated above, the stability is affected by oxygen and moisture, so the syntheses were performed in continuous vacuum ($\sim 8 \cdot 10^{-5}$ mbar).

2.2 Characterization

X-ray patterns were collected at room temperature by using a Rigaku Miniflex II diffractometer with θ -2 θ Bragg-Brentano geometry with Cu K α ($\lambda = 1.54059$ Å) radiation. The powder patterns were recorded in the $5^\circ \leq 2\theta \leq 45^\circ$ range. High temperature measurements were performed with a Bruker D8 Advance diffractometer operating at 30 kV and 20 mA, equipped with a Cu tube ($\lambda = 1.5418$ Å), a Vantec-1 PSD detector, and an Anton Parr HTK2000 high-temperature furnace. The powder patterns were recorded in the $21^\circ \leq 2\theta \leq 45^\circ$ range. To avoid the evaporation of the powder at high temperature, the sample was sealed in Kapton.

Micro-photoluminescence and micro-Raman imaging spectroscopy were collected using MS750 spectrograph (sol-instruments) equipped with different gratings (150 gr/mm and 1200 gr/mm for luminescence and Raman measurements, respectively). The laser beam (405 nm and 785 nm, for luminescence and Raman, respectively) was focalized through an Olympus objective (100x), with a

laser power about 0.75 mW. The measurements were acquired with 100 ms time window in a 300–800 nm spectral range.

The micro PL-Raman measurements were carried out in backscattering geometry coupled with a Reflecting Bragg Grating (Optigrate-Braggrade 405 and 785, respectively). Measurements were performed at room temperature, with a spectral resolution for the Raman measurements of 1 cm^{-1} .

Time-resolved photoluminescence (TR-PL) measurements were recorded by exciting the samples with 200 fs pulses sourced from an optical parametric amplifier (Light Conversion TOPAS-C) pumped by a regenerative Ti:Sapphire amplifier (Coherent Libra-HE). The repetition frequency was 1 kHz and the TR-PL signal was recorded by a streak camera (Hamamatsu C10910) equipped with a grating spectrometer (Princeton Instruments Acton Spectra Pro SP-2300). All the measurements were collected in the front-face configuration to reduce inner filter effects. Proper emission filters were applied to remove the reflected contribution of the excitation light.

Excitation-Emission Fluorescence maps were recorded by a NanoLog spectrofluorometer (Horiba Jobin Yvon). Absolute quantum yields (QYs) were obtained by a quanta- ϕ integrating sphere accessory with a 450 W Xenon lamp as the excitation source.

The absorption measurements were obtained by diffuse reflectance spectroscopy utilizing a UV-Vis-NIR Agilent Technologies Cary 5000. Measurements were performed by using a PbS solid state photodetector using KBr as reference. The reflection configuration measures the diffuse reflection of sample respect to a reference sample which is considered to have a 100% reflectivity. The Kubelka-Munk equation was applied to define the absorption properties.

HR-TEM measurements were performed using a HRTEM JEOL 2010 UHR equipped with a Gatan imaging filter (GIF) with a 15 eV window and a 794 slow scan CCD camera. The structural characterization was conducted by 2-Dimensional Fast Fourier Transform (2D-FFT) analysis, calculating planar and angular relationships between diffraction spots and comparing them with the diffraction cards previously adopted for X-ray diffraction analysis.

3. Results and discussion

3.1 X-ray diffraction measurements

The phase stability of CPI3 samples at different temperatures is underlined in Figure 1. CPI3-10m sample was obtained by solid state reaction with the correct stoichiometric amount of the precursors. Figure 1A reports the XRD pattern obtained at 400 °C in continuous vacuum, confirming the presence

of α -CsPbI₃, with lattice parameter $a = 6.218(1) \text{ \AA}$ (ICSD 161481). The sample was kept at 400 °C degree for 10 minutes and cooled down to RT, hence the XRD pattern was collected again (Figure 1B). The sample turns in color from black to yellow and the Rietveld refinement on the X-ray diffraction pattern confirms the formation of the δ -CsPbI₃ structure: the peaks are relatives to the orthorhombic δ -CsPbI₃ (ICSD 27979), with crystal structure Pmnb (space group N. 62) and lattice parameters $a=4.7993(2) \text{ \AA}$, $b=10.4521(6) \text{ \AA}$, $c=17.7456(9) \text{ \AA}$, with $R_{wp}=10.5 \%$ and $R_B=8 \%$.

Figure 1: Rietveld refinement of the sample CPI3-10m at 400 °C a) and at room temperature b).

This result shows the possibility of rapidly synthesizing lead halide perovskites by solid state reaction in the δ -CsPbI₃ phase, which only at high temperature converts to α -phase, as already reported in previous study [29].

The XRD patterns of samples obtained by prolonged synthesis at 400°C (CPI3-1h, CPI3-5h, CPI3-10h, CPI3-17h, CPI3-24h) were collected once the samples were brought back to RT (Figure 2). Comparing these patterns with the one from CPI3-10m, the secondary phase Cs₄PbI₆ with crystal structure R-3c:H (Space group N. 167) is clearly observable in addition to the δ -CsPbI₃ phase. The percentages of these two phases have been calculated by Rietveld refinement using the software MAUD [30] and highlighting that the percentage of Cs₄PbI₆ increases proportionally to the synthesis duration (Table 1).

Figure 2: Rietveld refinement of CPI3 samples at different times: a) 1h, b) 5h, c) 10h, d) 17h, e) 24h.

Additionally, Figure 3 reports the Rietveld refinement of the C4PI6 sample, obtained from the synthesis of $4\text{CsI} + \text{PbI}_2$. The pattern reveals the presence of Cs_4PbI_6 up to 74% by weight, with a residual contribution of CsI precursor (20%) and 6% by weight of $\delta\text{-CsPbI}_3$. The lattice parameters of Cs_4PbI_6 are $a=14.609(1) \text{ \AA}$, $c=18.36(5) \text{ \AA}$, with R factors: $R_{\text{wp}}=12.19\%$ and $R_{\text{B}}=9.32\%$.

Figure 3: Rietveld refinement of C4PI6 sample.

Table 1: Results of Rietveld refinement on CPI3 samples at room temperature.

Time	Phases		R_{wp}	R_B
	δ -CsPbI ₃	Cs ₄ PbI ₆		
10 min	100 %		10,5 %	8 %
1 hour	90,6 %	9,4 %	12,1 %	9,6 %
5 hours	54,9 %	45,1 %	12,6 %	9,8 %
10 hours	42,1 %	57,9 %	13,6 %	10,6 %
17 hours	33,2 %	66,8 %	12,8 %	8,9 %
24 hours	21,5 %	78,5 %	17,6 %	12,6 %

3.2 Luminescence and Raman maps

To better understand the relation between the time of the synthesis and the presence of the secondary phase (Cs₄PbI₆), the luminescence properties and Raman features were analysed.

The sample obtained after 10 minutes shows the typical PL of δ phase, a broad and weak emission around 550 nm. Increasing the synthesis time, the luminescence starts to be not uniform and a strong emission around 715 nm, typical of the black phases α and γ [23][31][32], appears (Figure 4).

Figure 4: Absorption and steady-state luminescence spectra of CPI3-10m a) and steady-state luminescence spectrum of CPI3-1h b). In the inset, a zoom of the range 400-670 nm.

The local properties were therefore analysed by optical microscope imaging coupled with a Raman and luminescence system. The samples appear constituted by black spots, surrounded by a white phase, mixed to a yellow phase.

The Raman spectrum, collected on the black spots, shows the presence of Cs_4PbI_6 (65 and 90 cm^{-1}) and $\delta\text{-CsPbI}_3$ (55, 107 cm^{-1}). The yellow part of the sample appears to be $\delta\text{-CsPbI}_3$ (Figure 5) [29].

Figure 5: Raman spectra of CPI3-10h sample, $\lambda_{\text{exc}} = 785 \text{ nm}$. a) Spectrum collected on a black spot, pointed out in the inset, with peaks of Cs_4PbI_6 (*) and $\text{CsPbI}_3\delta$ phase. b) Spectrum gathered on the yellow part of the sample, pointed out in the inset. The images were obtained with optical microscope imaging.

Focusing our attention on the PL at 715 nm, we performed a luminescence map. Figure 6 shows the intensity of the emission as function of the position, compared to the image collected by optical microscope. It's possible to notice as the emission is more intense in correspondence of the black spots.

Figure 6: Luminescence map of the emission at 715 nm of the sample CPI3-10h: in a) a 2D map and in the inset the image by optical microscope. In b) a 3D map and in the inset the PL emission spectrum.

To better and deeper correlate the luminescence to a specific phase, we performed a series of measurements, on 7 points (inset in Figure 7) close to an optically black point, by collecting simultaneously Raman and luminescence spectra in each point. The black spot in point 1 shows an intense luminescence at 715 nm, with a Raman spectrum typical of the γ -CsPbI₃, with the peaks at 60 and 240 cm⁻¹ [28][33]. Moving from the black spot to the yellow region, the luminescence at 715 nm decreases in intensity and simultaneously (Figure 7B and C), in the Raman spectra (Figure 7A), it's possible to observe the appearance of the secondary phase, Cs₄PbI₆ (65 and 90 cm⁻¹), and finally the δ -CsPbI₃ (58, 107 and 115 cm⁻¹) with its related broad luminescence band at 550 nm.

Figure 7: Raman and luminescence measurements on seven points in the CPI3-10h sample. a) Raman spectra, b) luminescence spectra (b) and 715 nm PL intensity (c). The spectra were collected on spatial point indicated in the inset of panel (c).

The quantum efficiency of the samples calculated at 715 nm, obtained with an integration sphere with a de-focalized beam, gives a general overview on the emission properties of the different samples (Table 2). In addition, considering that this red emission is related to a γ -phase and it is well known that the quantum efficiency of this phase is close to the unity [34], it is possible to obtain an indirect rough estimation on the amount of γ -phase in the synthesized samples.

Table 2: Quantum yield vs synthesis time.

Sample	CPI3-1h	CPI3-5h	CPI3-10h	CPI3-17h	CPI3-24h
Synthesis time	1 hour	5 hours	10 hours	17 hours	24 hours
Quantum yield	0,6 %	0,7 %	1,86 %	0,5 %	0 %

The values in Table 2 confirm the low amount of γ -CsPbI₃ deduced by X-Ray diffraction measurements, below the 1% detection limit [34][35].

In Figure 8, the photoluminescence excitation/emission maps of the samples treated at different synthesis time are reported. In a), b) and c) three CPI3 samples are reported, whilst d) shows, for

comparison, the fluorescence map of C4PI6 sample. Two different regions in the CPI3 samples can be clearly identified, in the UV (300-400 nm excitation, broad band 400-450 nm emission) and in the visible range (450-650 nm excitation, 715 nm emission). Whilst the visible region is easily assignable to the γ -phase, the UV region can be assigned to the presence of the Cs_4PbI_6 phase by comparing with the map of the C4PI6 sample. The optical features of the δ -phase are not easily detectable being overlapped by the broad emission of the Cs_4PbI_6 phase.

Figure 8: 3D-Photoluminescence excitation spectra of different samples: a) CPI3-1h, b) CPI3-5h, c) CPI3-10h, d) C4PI6.

Time-resolved photo-luminescence measurements performed on the emission at 715 nm give more insight on the properties of the recombination channel and, as a consequence, on the intrinsic properties of the luminescent phase.

Figure 9 shows the results of the measurement on two different points, on the sample synthesised in 10 hours. The sample is not uniform and different lifetimes for the same emission at 715 nm have been observed. The curves have been fitted with a multi-exponential decay function:

$$I(t) = I_0 + \sum_{i=1}^n A_i e^{-(t-t_0)/\tau_i}$$

With $I(t)$ time-dependent PL intensity, I_0 initial PL intensity, A_i amplitude, t time, t_0 initial time, τ_i the characteristic lifetime, $n=2$ and $n=3$ for point 1 and 2, respectively. Retrieved parameters are reported in Table 3. The average lifetime has been calculated using the following relation [36]:

$$\bar{\tau} = \frac{\sum_i A_i \cdot \tau_i^2}{\sum_i A_i \cdot \tau_i}$$

Figure 9: Time resolved luminescence measurement on two different points of CPI3-10h sample; $\lambda_{exc}=500$ nm.

Table 3: Fit parameters of TR-photoluminescence measurements.

	$\bar{\tau}$ (μ s)	A_1	τ_1 (μ s)	A_2	τ_2 (μ s)	A_3	τ_3 (μ s)
Point 1	0,144	1823,671	0,060	131,900	0,346	-	-
Point 2	0,908	448,511	0,093	497,428	0,399	136,149	1,548

Faster decay times from the same emitting centres are related to the presence of non-radiative path:

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}} = \gamma_R + \gamma_{NR}$$

where τ_{obs} is the decay time experimentally measured by time resolved luminescence, τ_R and γ_R (τ_{NR} and γ_{NR}) are the decay time and transition rate for a radiative (non-radiative) process. The faster the observed decay, the higher the presence of non-radiative path often related to structural defects.

In this case it is possible to argue that defective matrix non-homogeneously generates non radiative path for the emission from the γ -phase of CsPbI_3 , as can be evinced from the punctual Raman/luminescence analysis and from HRTEM images.

3.3 HRTEM and epitaxy studies

High Resolution TEM (HRTEM) structural analysis provided a direct confirmation of the features of the CPI3-10h sample, namely the presence of nanoparticles with multiple well-defined crystalline domains of different crystalline phases, usually surrounded by a thin amorphous/out-of-axis shell. 2D-FFT diffractograms were calculated for different Regions Of Interest (ROI) and the corresponding planar and angular relationships between diffraction spots were analysed against diffraction cards of the phases previously identified by XRD analysis to understand the orientation of each domain. The final results are compatible with the formation of crystalline domains of γ -CsPbI₃, δ -CsPbI₃, and Cs₄PbI₆, as reported in Figure 10, with lattice planes of each phase being indicated by different false colours.

Figure 10: Representative HRTEM images of the CPI3-10h sample. Lattice planes of γ -CsPbI₃, δ -CsPbI₃, and Cs₄PbI₆ are indicated in red, green and white, respectively. The 2D-FFT diffractograms used to calculate the orientations of each domain are reported in the central column.

Moreover, the well-defined, straight interface between the γ - and δ -phases of CsPbI₃ reported in Figure 10 was analysed to verify the possibility of epitaxial symmetry relationships between the two phases. An interface alignment and a vector alignment were identified as follows:

$$\delta\text{-phase } (0\ 2\ 2) // \gamma\text{-phase } (-1\ 3\ 1)$$

$$\delta\text{-phase } [-1\ -1\ 1] // \gamma\text{-phase } [310]$$

These symmetry relationships were used to calculate the actual lattice mismatch (m) occurring between average lattice spacings of the two phases along a given direction (table 4). In general terms,

the mismatch parameter m between the average lattice spacings of two different phases (indicated as d_1 and d_2 , respectively) can be defined as:

$$m = 2 \times |d_1 - d_2| / (d_1 + d_2).$$

The Fourier analysis of the HRTEM images at the interface between two well-defined crystal domains of γ - and δ -phases was performed by 2D-Fast Fourier Transform (FFT) of equally-sized ROIs and proved their alignment as epitaxial-related domains: six unit cells of δ -CsPbI₃ along the [0 2 2] direction correspond to eight cells of γ -CsPbI₃ along the [-1 3 1] direction, one unit cell of δ -CsPbI₃ along the [2 -1 1] direction correspond to one cell of γ -CsPbI₃ along the [1 -3 1] direction and three unit cells of δ -CsPbI₃ along the [-1-1 1] direction correspond to 4 cells of γ -CsPbI₃ along the [3 1 0] direction. The relevant epitaxially-related lattice planes are presented in Figure 11, along with the corresponding diffraction spots in the 2D-FFTs.

Table 4: Lattice mismatches among phases.

Commensurate lattice mismatches m	
δ -phase // γ -phase	m
$6*[0\ 2\ 2]//8*[-1\ 3\ 1]$	4.0%
$[2\ -1\ 1]//[1\ -3\ 1]$	1.0 %
$3*[-1\ -1\ 1]//4*[3\ 1\ 0]$	2.0%

A slight angular distortion can be observed between the 2 -1 1 spots of δ -CsPbI₃ and the 1-3-1 spots of γ -CsPbI₃ in comparison to their theoretical value, which could be attributed to local deformations in the crystalline frameworks in proximity to the interface.

Figure 11: Epitaxy study on the interface between γ -CsPbI₃ and δ -CsPbI₃, previously reported in Figure 10. γ -CsPbI₃ and δ -CsPbI₃ crystal domains in the HRTEM image (left) are depicted in red and green, respectively. The diffraction spots in the 2D-FFT diffractograms corresponding to the lattice planes used for the mismatch calculations are indicated according to the same color-coding.

A general model on the phase formation in the solid-state synthesis is proposed in Figure 12. In the first step, δ -CsPbI₃ is obtained from the precursors, CsI and PbI₂ for temperature below 300 °C. Then, as the temperature increases, the transition between the δ and α phase occurs in a relatively fast period (observed in 10 minutes). The α -phase is a cubic CsPbI₃ perovskite structure, consisting in I⁻ions corner-shared by two [PbI₆]⁴⁻ octahedra, with the Cs cation occupying the 12-fold coordination site formed in the middle of the cube of eight octahedra. The α -phase requires the correct stoichiometry in the perovskite structure and high temperature (above 320 °C) to remain stable.

As time goes on, at 400 °C, the CsPbI₃ phase partially undergoes a dynamic equilibrium consisting in its reverse dissociation into the starting precursors, CsI and PbI₂.

PbI₂ partially evaporates, leaving behind most/all the CsI and creating an amorphous layer around α -CsPbI₃. As already reported in literature, an excess of CsI in CsPbI₃ helps the formation and the stabilization of the distorted perovskite γ phase [37]. The γ phase is orthorhombic, belonging to the

Pbnm space group, and it remains stable at RT in a non-stoichiometric relationship CsI/PbI₂>1. On the other hand, the α phase converts to the δ phase at RT [14,15].

So, upon returning to RT after a variable amount of time spent at 400 °C, local variations in the CsI/PbI₂ ratio caused by the evaporation rates of PbI₂, determine which stable phases will form in the samples. α phase crystals will form in regions with an optimal CsI/PbI₂ ratio (*i.e.*=1) at high temperature, and they will transform to δ phase at RT. Whenever the ratio is higher than 1, the creation of γ -CsPbI₃ is favoured over the α . Finally, when the CsI/PbI₂ ratio $\gg$ 1, the formation of crystalline domains of secondary phase Cs₄PbI₆ is most likely, since the temporal increase of the thermal treatment generates a stronger excess of CsI, which prevents the formation of the perovskite phase and facilitates the formation of Cs₄PbI₆ (CsI/PbI₂ about 4:1).

In this sense, structural analysis performed by HRTEM shows that domains of the different phases can be observed in close proximity, which confirms the heterogeneity in sample composition that was previously indicated by optical microscopy, luminescence and Raman maps. Also, the presence of epitaxial relationships at the interface between γ and δ phase domains suggest that the structural $\alpha \rightarrow \delta$ rearranging caused by local variations in the PbI₂ ratio does not imply a drastic rearrangement of the atomic positions, so that a smooth structural transition between γ and δ phases can be maintained even with a sharp interface.

Figure 12: Model of the phase transition during the synthesis process and image of the sample after the synthesis.

4. Conclusions

The paper is focalized on the solid-state synthesis of pure inorganic Lead Halide perovskites of the class CsPbI₃.

We have shown that a pure α phase can be obtained with a brief treatment (in the order of minutes) at 400 °C without any solvent, and that it quickly passes to a stable δ phase at room temperature.

XRD analysis evidences that the increase of treatment time at steady temperature generates the formation of the secondary phase Cs₄PbI₆, while micro-Raman and micro-luminescence measurements underline the presence of the luminescent γ -phase.

The analysis of the collected data, time resolved measurements and HRTEM imaging permitted to understand the phase behaviour during the synthesis as a function of the temporal duration. After few minutes at high temperature, the CsPbI₃ phase partially undergoes a dynamic equilibrium process consisting in the reverse dissociation to its starting precursors, CsI and PbI₂. Lead iodide quickly evaporates at 400 °C, creating an excess of CsI and the consequent formation of stable perovskite γ -phase at room temperature and, in a longer temporal step, the secondary phase Cs₄PbI₆.

The samples are not uniform and present amorphous phases and defectivity in the crystals structure but remain stable at room temperature.

Beyond the importance of base studies on this important class of materials, in this work, we have shown the possibility to easily obtain bulk CsPbI₃ and we indicate the mechanism for future development and control of the phase formation of Lead halide perovskites.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request

5. Acknowledgements

Funding: This work was supported by the “Fondazione di Sardegna” within the project L.R 7. CUP F74I19000930007 “NG-Light: a new generation of phosphors”.

The authors acknowledge the CeSAR (Centro Servizi d'Ateneo per la Ricerca) of the University of Cagliari, Italy for the Time Resolved Photoluminescence experiments.

References

- [1] Mitzi DB. Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials. *Prog. Inorg. Chem.*, 2007, p. 1–121. <https://doi.org/10.1002/9780470166499.ch1>.
- [2] Stranks SD, Eperon GE, Grancini G, Menelaou C, Alcocer MJP, Leijtens T, et al. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* (80-) 2013;342:341–4. <https://doi.org/10.1126/science.1243982>.
- [3] Green MA, Jiang Y, Soufiani AM, Ho-Baillie A. Optical Properties of Photovoltaic Organic–Inorganic Lead Halide Perovskites. *J Phys Chem Lett* 2015;6:4774–85. <https://doi.org/10.1021/acs.jpcllett.5b01865>.
- [4] Xing G, Mathews N, Sun S, Lim SS, Lam YM, Gratzel M, et al. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃. *Science* (80-) 2013;342:344–7. <https://doi.org/10.1126/science.1243167>.
- [5] Walsh A. Principles of Chemical Bonding and Band Gap Engineering in Hybrid Organic–Inorganic Halide Perovskites. *J Phys Chem C* 2015;119:5755–60. <https://doi.org/10.1021/jp512420b>.
- [6] Kim H-S, Lee C-R, Im J-H, Lee K-B, Moehl T, Marchioro A, et al. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci Rep* 2012;2:591. <https://doi.org/10.1038/srep00591>.
- [7] Cho H, Kim Y-H, Wolf C, Lee H-D, Lee T-W. Improving the Stability of Metal Halide Perovskite Materials and Light-Emitting Diodes. *Adv Mater* 2018;30:1704587. <https://doi.org/10.1002/adma.201704587>.
- [8] Yang Z, Deng Y, Zhang X, Wang S, Chen H, Yang S, et al. High-Performance Single-Crystalline Perovskite Thin-Film Photodetector. *Adv Mater* 2018;30:1704333. <https://doi.org/10.1002/adma.201704333>.
- [9] Dong Q, Fang Y, Shao Y, Mulligan P, Qiu J, Cao L, et al. Electron-hole diffusion lengths > 175 μm in solution-grown CH₃NH₃PbI₃ single crystals. *Science* (80-) 2015;347:967–70. <https://doi.org/10.1126/science.aaa5760>.
- [10] Huang H, Polavarapu L, Sichert JA, Susha AS, Urban AS, Rogach AL. Colloidal lead halide

perovskite nanocrystals: synthesis, optical properties and applications. NPG Asia Mater 2016;8:e328–e328. <https://doi.org/10.1038/am.2016.167>.

- [11] Akbulatov AF, Luchkin SY, Frolova LA, Dremova NN, Gerasimov KL, Zhidkov IS, et al. Probing the Intrinsic Thermal and Photochemical Stability of Hybrid and Inorganic Lead Halide Perovskites. J Phys Chem Lett 2017;8:1211–8. <https://doi.org/10.1021/acs.jpcllett.6b03026>.
- [12] Iagher L, Etgar L. Effect of Cs on the Stability and Photovoltaic Performance of 2D/3D Perovskite-Based Solar Cells. ACS Energy Lett 2018;3:366–72. <https://doi.org/10.1021/acsenergylett.7b01196>.
- [13] Zhou Y, Zhao Y. Chemical stability and instability of inorganic halide perovskites. Energy Environ Sci 2019;12:1495–511. <https://doi.org/10.1039/C8EE03559H>.
- [14] Stoumpos CC, Malliakas CD, Kanatzidis MG. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. Inorg Chem 2013;52:9019–38. <https://doi.org/10.1021/ic401215x>.
- [15] Maronnier A, Roma G, Boyer-Richard S, Pedesseau L, Jancu J-M, Bonnassieux Y, et al. Anharmonicity and Disorder in the Black Phases of Cesium Lead Iodide Used for Stable Inorganic Perovskite Solar Cells. ACS Nano 2018;12:3477–86. <https://doi.org/10.1021/acsnano.8b00267>.
- [16] Mehdi H, Mhamdi A, Hannachi R, Bouazizi A. MAPbBr₃ perovskite solar cells *via* a two-step deposition process. RSC Adv 2019;9:12906–12. <https://doi.org/10.1039/C9RA02036E>.
- [17] Huang D, Xie P, Pan Z, Rao H, Zhong X. One-step solution deposition of CsPbBr₃ based on precursor engineering for efficient all-inorganic perovskite solar cells. J Mater Chem A 2019;7:22420–8. <https://doi.org/10.1039/C9TA08465G>.
- [18] Konstantakou M, Perganti D, Falaras P, Stergiopoulos T. Anti-Solvent Crystallization Strategies for Highly Efficient Perovskite Solar Cells. Crystals 2017;7:291. <https://doi.org/10.3390/cryst7100291>.
- [19] Wang P, Zhang X, Zhou Y, Jiang Q, Ye Q, Chu Z, et al. Solvent-controlled growth of inorganic perovskite films in dry environment for efficient and stable solar cells. Nat Commun 2018;9:2225. <https://doi.org/10.1038/s41467-018-04636-4>.

- [20] Li B, Zhang Y, Fu L, Yu T, Zhou S, Zhang L, et al. Surface passivation engineering strategy to fully-inorganic cubic CsPbI₃ perovskites for high-performance solar cells. *Nat Commun* 2018;9:1076. <https://doi.org/10.1038/s41467-018-03169-0>.
- [21] Luo P, Xia W, Zhou S, Sun L, Cheng J, Xu C, et al. Solvent Engineering for Ambient-Air-Processed, Phase-Stable CsPbI₃ in Perovskite Solar Cells. *J Phys Chem Lett* 2016;7:3603–8. <https://doi.org/10.1021/acs.jpcllett.6b01576>.
- [22] Xiang S, Fu Z, Li W, Wei Y, Liu J, Liu H, et al. Highly Air-Stable Carbon-Based α -CsPbI₃ Perovskite Solar Cells with a Broadened Optical Spectrum. *ACS Energy Lett* 2018;3:1824–31. <https://doi.org/10.1021/acseenergylett.8b00820>.
- [23] Protesescu L, Yakunin S, Bodnarchuk MI, Krieg F, Caputo R, Hendon CH, et al. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett* 2015;15:3692–6. <https://doi.org/10.1021/nl5048779>.
- [24] Ke W, Spanopoulos I, Stoumpos CC, Kanatzidis MG. Myths and reality of HPbI₃ in halide perovskite solar cells. *Nat Commun* 2018;9:4785. <https://doi.org/10.1038/s41467-018-07204-y>.
- [25] El Ajjouri Y, Palazon F, Sessolo M, Bolink HJ. Single-Source Vacuum Deposition of Mechanosynthesized Inorganic Halide Perovskites. *Chem Mater* 2018;30:7423–7. <https://doi.org/10.1021/acs.chemmater.8b03352>.
- [26] Karmakar A, Dodd MS, Zhang X, Oakley MS, Klobukowski M, Michaelis VK. Mechanochemical synthesis of 0D and 3D cesium lead mixed halide perovskites. *Chem Commun* 2019;55:5079–82. <https://doi.org/10.1039/C8CC09622H>.
- [27] Hong Z, Tan D, John RA, Tay YKE, Ho YKT, Zhao X, et al. Completely Solvent-free Protocols to Access Phase-Pure, Metastable Metal Halide Perovskites and Functional Photodetectors from the Precursor Salts. *IScience* 2019;16:312–25. <https://doi.org/10.1016/j.isci.2019.05.042>.
- [28] Straus DB, Guo S, Cava RJ. Kinetically Stable Single Crystals of Perovskite-Phase CsPbI₃. *J Am Chem Soc* 2019;141:11435–9. <https://doi.org/10.1021/jacs.9b06055>.
- [29] Satta J, Melis C, Carbonaro CM, Pinna A, Salado M, Salazar D, et al. Raman spectra and vibrational analysis of CsPbI₃: A fast and reliable technique to identify lead halide perovskite polymorphs. *J Mater* 2021;7:127–35. <https://doi.org/10.1016/j.jmat.2020.08.004>.

- [30] Lutterotti L. Total pattern fitting for the combined size–strain–stress–texture determination in thin film diffraction. *Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms* 2010;268:334–40. <https://doi.org/10.1016/j.nimb.2009.09.053>.
- [31] Zhang Q, Zhou Y, Wei Y, Tai M, Nan H, Gu Y, et al. Improved phase stability of γ -CsPbI₃ perovskite nanocrystals using the interface effect using iodine modified graphene oxide. *J Mater Chem C* 2020;8:2569–78. <https://doi.org/10.1039/C9TC06465F>.
- [32] Sutton RJ, Filip MR, Haghighirad AA, Sakai N, Wenger B, Giustino F, et al. Cubic or Orthorhombic? Revealing the Crystal Structure of Metastable Black-Phase CsPbI₃ by Theory and Experiment. *ACS Energy Lett* 2018;3:1787–94. <https://doi.org/10.1021/acseenergylett.8b00672>.
- [33] Yang Y, Robbins JP, Ezeonu L, Ma Y, Sparta N, Kong X, et al. Probing lattice vibrations of stabilized CsPbI₃ polymorphs *via* low-frequency Raman spectroscopy. *J Mater Chem C* 2020;8:8896–903. <https://doi.org/10.1039/D0TC02123G>.
- [34] Liu F, Zhang Y, Ding C, Kobayashi S, Izuishi T, Nakazawa N, et al. Highly Luminescent Phase-Stable CsPbI₃ Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield. *ACS Nano* 2017;11:10373–83. <https://doi.org/10.1021/acsnano.7b05442>.
- [35] Zhao B, Jin S-F, Huang S, Liu N, Ma J-Y, Xue D-J, et al. Thermodynamically Stable Orthorhombic γ -CsPbI₃ Thin Films for High-Performance Photovoltaics. *J Am Chem Soc* 2018;140:11716–25. <https://doi.org/10.1021/jacs.8b06050>.
- [36] Lakowicz JR. *Principles of Fluorescence Spectroscopy*. Boston, MA: Springer US; 2006. <https://doi.org/10.1007/978-0-387-46312-4>.
- [37] Becker P, Márquez JA, Just J, Al-Ashouri A, Hages C, Hempel H, et al. Low Temperature Synthesis of Stable γ -CsPbI₃ Perovskite Layers for Solar Cells Obtained by High Throughput Experimentation. *Adv Energy Mater* 2019;9:1900555. <https://doi.org/10.1002/aenm.201900555>.

Figures

Figure 1

Rietveld refinement of the sample CPI3-10m at 400 °C a) and at room temperature b).

Figure 2

Rietveld refinement of CPI3 samples at different times: a) 1h, b) 5h, c) 10h, d) 17h, e) 24h.

Figure 3

Rietveld refinement of C4PI6 sample.

Figure 4

Absorption and steady-state luminescence spectra of CPI3-10m a) and steady-state luminescence spectrum of CPI3-1h b). In the inset, a zoom of the range 400-670 nm.

Figure 5

Raman spectra of CPI3-10h sample, $\lambda_{exc} = 785$ nm. a) Spectrum collected on a black spot, pointed out in the inset, with peaks of Cs_4PbI_6 (*) and $\text{CsPbI}_3\delta$ phase. b) Spectrum gathered on the yellow part of the sample, pointed out in the inset. The images were obtained with optical microscope imaging.

Figure 6

Luminescence map of the emission at 715 nm of the sample CPI3-10h: in a) a 2D map and in the inset the image by optical microscope. In b) a 3D map and in the inset the PL emission spectrum.

Figure 7

Raman and luminescence measurements on seven points in the CPI3-10h sample. a) Raman spectra, b) luminescence spectra (b) and 715 nm PL intensity (c). The spectra were collected on spatial point indicated in the inset of panel (c).

Figure 8

3D-Photoluminescence excitation spectra of different samples: a) CPI3-1h, b) CPI3-5h, c) CPI3-10h, d) C4PI6.

Figure 9

Time resolved luminescence measurement on two different points of CPI3-10h sample; $\lambda_{exc}=500$ nm.

Figure 10

Representative HRTEM images of the CPI3-10h sample. Lattice planes of γ -CsPbI₃, δ -CsPbI₃, and Cs₄PbI₆ are indicated in red, green and white, respectively. The 2D-FFT diffractograms used to calculate the orientations of each domain are reported in the central column.

Figure 11

Epitaxy study on the interface between γ -CsPbI₃ and δ -CsPbI₃, previously reported in Figure 10. γ -CsPbI₃ and δ -CsPbI₃ crystal domains in the HRTEM image (left) are depicted in red and green, respectively. The diffraction spots in the 2D-FFT diffractograms corresponding to the lattice planes used for the mismatch calculations are indicated according to the same color-coding.

Figure 12

Model of the phase transition during the synthesis process and image of the sample after the synthesis.