Pressure-Induced Perovskite-to-non-Perovskite Phase Transition in CsPbBr$_3$

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Dedicated to Prof. Antonio Togni

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The expanding range of optoelectronic applications of lead-halide perovskites requires their production in diverse forms (single crystals, thin- and thick-films or even nanocrystals), motivating the development of diverse materials processing and deposition routes that are specifically suited for these structurally soft, low-melting semiconductors. Pressure-assisted deposition of compact pellets or thick-films are gaining popularity, necessitating studies on the pressure effects on the atomic structure and properties of the resulting material. Herein we report the phase transformation in bulk polycrystalline cesium lead bromide from its three-dimensional perovskite phase ($\gamma$-CsPbBr$_3$) into the one-dimensional polymorph ($\delta$-CsPbBr$_3$) upon application of hydrostatic pressure (0.35 GPa). $\delta$-CsPbBr$_3$ is characterized by a wide bandgap of 2.9 eV and broadband yellow luminescence at 585 nm (2.1 eV) originating from self-trapped excitons. The formation of $\delta$-CsPbBr$_3$ was confirmed and characterized by Raman spectroscopy, $^{207}$Pb and $^{133}$Cs solid-state nuclear magnetic resonance, X-ray diffraction, absorption spectroscopy, and temperature-dependent and time-resolved photoluminescence spectroscopy. No such phase transition was observed in colloidal CsPbBr$_3$ nanocrystals.

Keywords: luminescence, perovskite, NMR spectroscopy, phase transitions, lead halides.

Introduction

Three-dimensional (3D) lead halide perovskites (LHPs) with a general formula of APbX$_3$ (where A=CH$_3$NH$_3^+$ (MA), CH(NH$_2$)$_2^+$ (FA), or Cs$^+$; X=Cl, Br, or I) exhibit a set of compelling optical and electronic characteristics, such as strong optical absorption, low exciton binding energy, large charge-carrier diffusion lengths, fast radiative rates and an overall defect-tolerant behavior in their optoelectronic performance.$^{[1–5]}$ At present, LHPs are intensely researched for applications including photovoltaics and photodetectors,$^{[6–10]}$ electro-

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layers of suited thickness (cutting, polishing) and attachment to the electrical contacts has proven difficult because of the material’s softness, fragility and poor adhesion. Solution-based deposition (printing, spraying, etc.) is unsuitable for thicknesses beyond several microns. A prevailing strategy is thus growth of thick LHP layers from solutions directly on the substrate, which generally suffers from the limited control over the adhesion and specificity of growth, as well as the morphology of the resulting crystallites. In the case of CsPbBr$_3$, direct melt-casting onto the substrate is an attractive option owing to the low melting point of this semiconductor (840 K); however, these temperatures are still incompatible with common read-out electronic circuits.

Mechanical pressing may help alleviate some of these limitations and has been used to produce perovskite wafers and on-substrate thick films of MAPbI$_3$. The question arises as to the effect of mechanical pressure on the atomic structure and properties of LHPs, as well as how these effects differ for various forms and compositions of LHPs. In this study, we focus on CsPbBr$_3$ for its promise as a radiation detector material (in the bulk form) or as a narrowband, bright light emitter for LCD displays and as a quantum light source (in the form of nanocrystals, NCs).

For bulk CsPbBr$_3$, we find that isostatic pressing at 0.35 GPa induces a phase transition from the perovskite phase ($\gamma$-CsPbBr$_3$, orange-colored, 3-D corner-connected PbBr$_6^{4-}$ octahedra, Figure 1,a) into the metastable non-perovskite 1D-polymorph ($\delta$-CsPbBr$_3$, white-colored, 1D edge-sharing octahedral connectivity, Figure 1,b), which persists after the release of pressure. The resulting material exhibits broadband photoluminescence (PL) with a quantum yield (PLQY) of ca. 20% at room temperature (88% at 77 K), which we attribute to the radiative recombination of self-trapped excitons (STEs). CsPbBr$_3$ NCs did not undergo a phase transition under identical conditions (0.35 GPa, 24 h).

**Results and Discussion**

To date, the one-dimensional polymorph of CsPbBr$_3$ has received only little attention in the literature. Inclusions of 1D $\delta$-CsPbBr$_3$, next to the thermodynamically stable $\gamma$-CsPbBr$_3$, were reported from the cooling of highly concentrated solution of CsBr and PbBr$_2$ in HBr. We have recently reported largely phase-pure $\delta$-CsPbBr$_3$ (by X-ray diffraction, XRD) by the anion-exchange approach, whereby the powder of iso-

**Figure 1.** a) Crystal structure of $\gamma$-CsPbBr$_3$. b) Crystal structure of $\delta$-CsPbBr$_3$. c) The scheme of the cold isostatic pressing with an example of sample before and after 6 h pressing. d) XRD patterns of sample before and after pressing, with A being white part of the pellet (rich in $\delta$-CsPbBr$_3$) and B being orange part. Asterisk indicates the position of the diffraction peaks of the CsPb$_2$Br$_5$ impurity. Both the $\delta$-CsPbBr$_3$ and $\gamma$-CsPbBr$_3$ phase are orthorhombic and belong to space group no. 62 ($Pmnb$). The unit cell parameters of the white and orange phases are $a = 4.60$ Å, $b = 9.72$ Å, $c =$ 16.81 Å and $a = 8.21$ Å, $b = 8.25$ Å and $c =$ 11.760 Å, respectively. The $\delta$-CsPbBr$_3$ phase consists of distorted edge-sharing PbBr$_6$ octahedra, forming chains that run parallel to the $a$-axis, while the $\gamma$-CsPbBr$_3$ phase develops from the ideal orthogonal cubic structure by tilting of the PbBr$_6$ octahedra.
structural $\delta$-CsPbI$_3^{[35]}$ was treated with excess HBr/EtOH.

Owing to the smaller molar volume and hence larger density of $\delta$-CsPbBr$_3$ compared to $\gamma$-CsPbBr$_3$ (5.12 vs. 4.80 g cm$^{-3}$)$^{[32]}$ and the structural softness of these compounds, one anticipates that metastable $\delta$-CsPbBr$_3$ can also be obtained by a pressure-induced phase transition. $\gamma$-CsPbBr$_3$ powder was prepared by a precipitation method (see Supporting Information) and was pre-pressed into a pellet by a uniaxial hydraulic press. Subsequently, the pellet was loaded in the cold isostatic press (CIP) and pressurized at 0.35 GPa for different periods of time (Figure 1,c). Already after one hour of pressing small domains of white inclusions can be clearly seen, with emergence of yellow luminescence under UV illumination (Figure S1) and with the signature of $\delta$-CsPbBr$_3$ in the powder XRD patterns (Figure S2). 1D $\delta$-CsPbBr$_3$ becomes the dominant phase after pressing for more than 6 hours (Figures 1,d, S1 and S2). From XRD, the samples pressed for 24–48 hours are phase-pure $\delta$-CsPbBr$_3$ (Figure S2); however, there remains residual $\gamma$-CsPbBr$_3$ that can be detected in the optical absorption (Figure 2,a). Application of hydrostatic pressure appears essential to drive the phase transition, as the same material pressed on a uniaxial hydraulic press at similar pressure (0.88 GPa) shows no signs of phase transformation (Figure S3). Only broadening of the XRD peaks is visible, a sign of an inhomogeneously strained crystallites. This is consistent with general observations that isostatic pressing leads to higher material density than uniaxial pressing at the same pressure.$^{[36]}$ Besides microcrystal-
line pellets, polycrystalline bulk with large grain sizes (prepared as described earlier\(^{[37]}\)) and thick films of organic ligand-capped NCs\(^{[38]}\) were also subjected to isostatic pressing. NCs did not undergo any apparent phase transition after 24 hours of pressing (Figure S4,a–4,c), whereas bulk samples largely converted into a 1D-polymer (Figure S4,d–4,e).

The metastable character of $\delta$-CsPbBr\(_3\)^{[32,34]} is indicated by the gradual emergence of orange grains of $\gamma$-CsPbBr\(_3\) on white pellets after a few days of storage in ambient conditions (Figure S5,a). This process was characterized by us previously with differential scanning calorimetry, which showed that the transition from $\delta$-CsPbBr\(_3\) to $\gamma$-CsPbBr\(_3\) occurs at 151 °C with an enthalpy of 4.8 kJ mol\(^{-1}\).\(^{[32]}\) This transformation can be accelerated by grinding or heating (Figures S5,b and S6). We prepared a short experiment to visually show this transition by heating $\delta$-CsPbBr\(_3\) powder on a hot plate at 155 °C; the phase transformation into $\gamma$-CsPbBr\(_3\) is complete after just 10 minutes of heating (Figure S6). Even less stable are samples where some Br is substituted with Cl ($<8\%$, Figure S7). We note that the analogous $\delta$-phase is unknown for CsPbCl\(_3\). The white 1D $\delta$-CsPbBr\(_3\) material has a bandgap of 2.9 eV with an absorption edge peaking at 360 nm as reported previously (Figure 2,a), though it is not as clearly defined here as reported in our prior work.\(^{[32]}\)

Additionally, we observe an above-gap excitonic absorption peak at 323 nm and a band-edge shoulder near 400 nm which also likely corresponds to excitonic absorption; similar features have also been observed in isostructural 1D RbPbI\(_3\) and CsPbI\(_3\).\(^{[39,40]}\) Although the presence of $\gamma$-CsPbBr\(_3\) is not visible in XRD, small traces of the 3D phase are inferred from the absorption edge at 525 nm (2.3 eV).\(^{[41,42]}\) The PL excitation (PLE) spectra appear as molecular-like peaks with a maximum at $\sim$360 nm (3.4 eV), consistent with the absorption measurement (Figure 2,b). Under UV light, $\delta$-CsPbBr\(_3\) shows broad PL centered at 585 nm (2.1 eV) with a full width at half-maximum (FWHM) of about 550 meV (Figure 2,c). This broad-band emission is characteristic of radiative recombination of STEs, which has been intensely investigated in 0D and 1D metal-halides over the past several years.\(^{[43]}\) STEs are a type of highly localized Frenkel excitons that distort their surrounding lattice, resulting in broad and highly Stokes-shifted emission with temperature dependent PLQY and PL lifetime.\(^{[44]}\) To assess the presence of STE-based emission, temperature dependent PL, PLE, and time-resolved PL (TR-PL) were conducted (Figures 2,b, 2,c and S8). Upon decreasing the temperature from 295 K to 15 K, both PL and PLE spectra become more intense (suggesting an increasing PLQY) and narrow. Additionally, the PLE peak shifts towards shorter wavelength, while the PL peak position remains roughly constant; as a result, the Stokes shift increases by $\sim$280 meV upon cooling (Figure 2,d). We suggest that the shifted PLE peak and increased Stokes shift at low temperature originates from lattice contraction and the altered overlap of atomic orbitals in the excited state.

The temperature-dependent PL broadening was fit using the Toyozawa model to determine the exciton-phonon coupling strength and the effective phonon energy responsible for thermal broadening in this phase (Figure S9).\(^{[45]}\) For the excitation at the PLE maximum an effective phonon energy of 10.2 meV (82 cm\(^{-1}\)) was determined, which falls well within the broad range of vibrational modes observed in the Raman spectrum for this phase (Figure 3,a).

As reported for other STE-emitting metal halides, weak PL at room temperature is the result of efficient non-radiative relaxation.\(^{[46]}\) As the temperature decreases, various phonon modes are frozen out and the slow radiative recombination prevails over fast phonon-assisted non-radiative recombination. Hence, upon cooling from room temperature to 77 K, the PLQY increases from 20% to 85% (Figure 2,e) while the average PL lifetime from 0.3 to about 3 μs at 77 K, further increasing to 7 μs at 15 K (Figure 2,f). We note that the presented room-temperature PLQY is much higher than in a previous study (2%),\(^{[32]}\) where such a small value could be related to the CsPbI\(_3\) impurity or a more defected lattice.\(^{207}\)Pb solid-state NMR (ssNMR) allows for an easy distinction of all known Cs–Pb–X species due to its high sensitivity to changes in the local structure.\(^{[47,48]}\) In the $^{207}$Pb ssNMR spectrum, a single species is observed at 104 ppm with a FWHM of 10.3 kHz (Figure 3,b). The tensor of the 1D phase has a span of $\Omega = 650$ ppm and a symmetry parameter skew of $\kappa = 0.7$. The same skew was observed for the 1D CsPbI\(_3\) phase, highlighting the structural similarity between the two 1D phases.\(^{[47]}\)

The presence of spinning side bands shows the asymmetry of the lead environment; higher symmetry would result in a single line, characteristic for all 3D LHPs.\(^{[48]}\) Similar results were shown by Aebli et al.\(^{[32]}\) However, material obtained by isostatic pressing of $\gamma$-CsPbBr\(_3\) has a higher phase purity compared to material obtained by anion exchange, as deduced from the lower FWHM of the bands.

The $^{133}$Cs ssNMR spectrum shows species at 258 ppm with a FWHM of 380 Hz (Figure 3,c). The signal is shifted 150 ppm towards higher frequencies.
To rationalize the impact of isostatic pressing on the optical properties of CsPbBr$_3$, we perform confocal Raman spectroscopy and assess the vibrational modes of the metal halide sublattice before and after compression (Figures 3.a). 1D $\delta$-CsPbBr$_3$ (as obtained after pressing) exhibits a series of low-energy vibrational modes, with most intense peaks at 144 cm$^{-1}$ (17.8 meV) and 63 cm$^{-1}$ (7.8 meV), attributed to asymmetric Br–Pb–Br stretching and coupled Br–Pb–Br bending/stretching, respectively.$^{[32,40]}$ In contrast, the 3D $\gamma$-CsPbBr$_3$ phase (present before pressing) features a broad central Raman peak, a strong peak around 72 cm$^{-1}$, along with a very weak peak at 127 cm$^{-1}$, assigned to local polar fluctuations and octahedral distortion and stretching, respectively.$^{[50–52]}$ Overall, the different octahedral connectivity of 1D $\delta$-CsPbBr$_3$ and 3D $\gamma$-CsPbBr$_3$ is clearly reflected in their dissimilar Raman spectra. Following our previous study,$^{[32]}$ we suggest that the dominant asymmetric Br–Pb–Br stretching mode around 144 cm$^{-1}$ is a clear distinguishing feature in the identification of 1D $\delta$-CsPbBr$_3$ phases in a CsPbBr$_3$ sample.

Effect of pressure (up to 20 GPa, using diamond anvil cell, DAC) on optoelectronic properties and atomic structure was recently reported for CsPbBr$_3$ in the bulk$^{[53,54]}$ and nanocrystalline forms.$^{[55–58]}$ With increasing pressure, the optical (bandgap and PL peak position, PL lifetime) and electrical (electronic and ionic resistances, photocurrent) parameters of CsPbBr$_3$ have two discontinuous changes (around 1.2 GPa and 2.9 GPa), the first of which is associated with a pressure-induced isostructural phase transition where the Pb–Br bond lengths and octahedral distortions of the orthorhombic perovskite phase ($\gamma$-phase I) saturate and further compression occurs through octahedral rotation without altering the space group or atomic positions ($\gamma$-phase II, not to be confused with the non-perovskite orthorhombic structure); the second discontinuity is a transition to the amorphous phase.$^{[53–56]}$ The initial compression of the octahedra destabilizes the valence band maximum (VBM) while leaving the conduction band minimum (CBM) largely unaffected. This causes a decrease of the band gap energy that manifests itself as a redshift of the PL peak. A further increase in pressure (to 1.2–2.9 GPa) induces octahedral distortions and altered octahedral tilt angles, while preserving the overall orthorhombic crystal symmetry in CsPbBr$_3$. Both octahedral tilting and distortion reduce the Pb character of the CBM and thus the stabilization of the CBM via spin orbit coupling. Overall, the increased energy of the CBM, in conjunction with a rather unaffected VBM, results in a

Figure 3. a) Confocal Raman spectra of $\delta$-CsPbBr$_3$ and $\gamma$-CsPbBr$_3$. b) $^{207}$Pb and c) $^{133}$Cs ssNMR of $\delta$-CsPbBr$_3$, showing a single species at 104 ppm and 254 ppm, respectively. Spinning side bands are marked by asterisks.

as compared to the 3D polymorph.$^{[48]}$ Overall, no impurities were detected by ssNMR.
blue-shift of the PL spectrum.\textsuperscript{[58]} The amorphous phase obtained at higher pressures readily converts into the \(\gamma\)-phase after the release of pressure.\textsuperscript{[53,55,56]} Also \(\text{Cs}_4\text{PbBr}_6\) and \(\text{CsPb}_2\text{Br}_5\) with inclusions of \(\gamma\)-\text{CsPbBr}_3 were pressed using DAC.\textsuperscript{[59,60]} Interestingly, \text{Nguyen et al.}\textsuperscript{[59,61]} observed disappearance of the green emission from \(\text{Cs}_4\text{PbBr}_6\) with \text{CsPbBr}_3 inclusions at 3.3 GPa along with the raise of broad yellow luminescence (peak centered \(\sim 600\) nm) between 6.3 and 14.5 GPa. The latter emission was attributed to monoclinic \(\text{CsPbBr}_6\) The transition from \(\gamma\)-\text{CsPbBr}_3 to \(\delta\)-\text{CsPbBr}_3 was not inferred in these studies.

Both DAC and CIP use silicon oil as a pressure-transmitting medium. The smaller size of a DAC (around 100–250 \(\mu\)m) compared to a CIP (cylinder diameter equal to 6 cm) causes the volume ratio of sample and pressing medium to be much higher, which may cause the hydrostatic approximation to break down because particles are touching each other or the gasket/diamond. Additionally, in a CIP the material is separated from pressing medium that causes its densification and sintering, while in a DAC each micro/nanocrystal is surrounded by the pressing medium. In most of the reports there is also lack of information about the duration of compression steps, which also may be critical for formation of the \(\delta\)-\text{CsPbBr}_3 phase. We believe that the \(\gamma\)-\text{CsPbBr}_3 to \(\delta\)-\text{CsPbBr}_3 phase transition does not occur in nanocrystals because of the surface ligands, which separate the nanoparticles and are significantly more compressible. They potentially alleviate the compressive strain that induces the phase transformation to the denser 1D polymorph.

### Conclusions

In conclusion, 3D \(\gamma\)-\text{CsPbBr}_3 transforms into a metastable 1D \(\delta\)-\text{CsPbBr}_3 phase under hydrostatic pressure (0.35 GPa). The product material exhibits broadband yellow PL at room temperature originating from STEs and its structural, vibrational and optical properties were analyzed through XRD, \(^{133}\text{Cs}\) and \(^{207}\text{Pb}\) ssNMR, \textit{Raman} spectroscopy, and temperature-dependent and time-resolved optical spectroscopy. The \(\delta\)-\text{CsPbBr}_3 phase remains stable for at least one week in ambient conditions, while a phase transition back into the 3D \(\gamma\)-\text{CsPbBr}_3 phase is accelerated by grinding or heating to 155°C. The observation of rapid \(\gamma\rightarrow\delta\)-phase in \text{CsPbBr}_3 under rather mild hydrostatic pressures indicates that caution should be exercised when utilizing pressing as a route towards fabricating thick layers for various applications, \textit{e.g.} hard radiation detectors. To gauge (possibly adverse) pressure-induced effects, we recommend proper analysis of the product compound concerning its structural, vibrational, and optical properties.

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### Author Contribution Statement

A. N. carried out XRD, PL measurements and powder pressing, M. A. carried out the synthesis and NMR experiments. S. C. B. recorded the \textit{Raman} spectra and performed the temperature-dependent and time-resolved optical spectroscopy experiments. Y. S. performed QY measurements. A. N., K. M. M. and M. V. K. wrote the manuscript with the input of all co-authors.

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