



TDK Thesis

Perovskite Structures Inside Carbon and Boron Nitride Nanotubes

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Abstract

Lead halide perovskites are promising optoelectronic materials, extensively researched for manufacturing solar panels, LEDs, lasers, and various other applications. However, most lead-halide perovskites are vulnerable to environmental stressors such as humidity, oxygen, and light exposure. A potential strategy to enhance their stability is to encapsulate them inside a protective layer. In my experiments, I explored if nanotubes could be used for this purpose. Carbon and boron nitride nanotubes are long, hollow cylindrical structures with an inner diameter of a few nanometers and length of the order of micrometers. Due to their high structural resilience and modifiable surface, they are widely used as nano-containers. In this thesis, I attempted to encapsulate CsPbBr_3 into boron nitride nanotubes using various methods. Electron microscopy was used to verify the presence of the perovskite crystals within these nanostructures. The optical properties of the product were characterized using photoluminescence spectroscopy. This work contributes to the understanding of perovskite material formation in nanoscale architectures, and advancements in perovskite-based optoelectronics.

Kivonat

Az ólóm-halogenid perovszkitok ígéretes alapanyagok optoelektronikai alkalmazásokhoz. Napelemekben, LED-ekben, lézertechnológiában és számos további területen történő alkalmazásuk intenzíven kutatott terület. Csakhogy, a legtöbb ólom-halid perovszkit rendkívül érzékeny különböző környezeti stresszorokra, mint például az oxigén jelenlétére párára, illetve magára a fényre is. Egy lehetséges megoldás a stabilitásuk növelésére, a védőburokkal való bevonás. Kísérleteim során arra kerestem a választ, hogy fel lehet-e nanocsöveket ezen célra használni. A szén és bór-nitrid nanocsövek hosszú, üreges, henger alakú struktúrák, melyek belső átmérője pár nanométer, hosszuk pedig mikrométer nagyságrendű. A nagy szerkezeti stabilitásnak és módosítható felületének köszönhetően gyakran használják ezeket nanokonténereknek. Ebben a dolgozatban többféle módszert is kipróbáltam CsPbBr₃ bór-nitrid nanocsövekbe való töltésére. Elektronmikroszkópos felvételek segítségével igazoltam a perovszkit kristályok nanocsövekben való jelenlétét. Emellett fotolumineszcencia spektroszkópiával karakterizáltam a termék optikai tulajdonságait. Ez a munka hozzájárul a perovszkitok nanoszerkezetekben történő előállításának megértéséhez, valamint a perovszkit alapú optoelektronika fejlődéséhez.

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1 Introduction

In the early 21st century, researchers began to discover the excellent optoelectronic properties of perovskite crystals [1]. This made the field an extensively researched area, as they are highly efficient at converting light to electricity and vice versa. The application of such electronic devices, sourcing and detecting light, paves a new way to cutting-edge technologies, ranging from solar panels to lasers [2].

Perovskite crystals on the other hand are rather sensitive to various environmental stressors such as oxygen, humidity, and light exposure, posing significant challenges to their practical use. Scientists have discovered a range of methods to tackle this problem. For example, different compositions of the perovskite crystal can have various sensitivities to the mentioned environmental stressors [3]. Organic cations like methylammonium are more sensitive than its inorganic counterparts such as cesium (Cs). Another approach to protect the sensitive perovskite material is with an inert layer. Nanocontainers could be a good fit to do so. Nanocontainers are hollow structures with dimensions in the nanometer range. These structures are used to encapsulate material. These containers can interact with other materials on a molecular scale, while maintaining key structural properties. Naturally, this ability brings it to attention when it comes to protecting and sealing material to preserve its properties.

Nanotubes were already used before to encapsulate dye molecules [4]. Recent studies have demonstrated that the ends of carbon nanotubes can be sealed after filling by high temperature annealing, suggesting that a similar approach might also be feasible for boron nitride nanotubes (BNNT). Although a reliable technique to close BNNTs has yet to be developed, this possibility makes BNNTs promising candidates for encapsulation applications. This cannot be done with an organic dye, as they deteriorate at such high temperatures. Perovskite on the other hand is a good candidate. By encapsulating cesium lead bromide (CsPbBr_3) perovskite, we expect the material to gain stability, but maintain its photoelectric properties. This research aims to explore the growth of perovskite inside boron nitride and carbon nanotube (CNT) nanocontainers. I explored multiple methods of encapsulation and studied how the optoelectronic properties of the perovskites inside these 1D boron-nitride heterostructures have changed. Throughout the experimentation, I learned how to handle chemicals in a controlled environment, how to properly use laboratory equipment and measurement tools, and what steps to take when setting up experiments inspired by previously published articles. The research took place at Wigner Research Centre for Physics, Department of Solid State Physics.

2 Literature Review

In this section, I will give a short overview of the CsPbBr_3 perovskite, the nanocontainers used, and the measurement methods applied in their subsequent investigation.

2.1 CsPbBr_3 perovskites

People often think of perovskite and perovskite structure as alike. Perovskite can refer to a mineral composed of oxygen, titanium, and calcium in a CaTiO_3 configuration, and the structure itself composed of other atoms in an ABX_3 form (as shown in Figure 1). Such a three component structure can be described as a range of octahedra joining with their corners on a cubic lattice. These "corners" are formed by the X anions [5]. Inside each octahedron, there is a single B type atom. The A type atom can be found in the vertex of these octahedra. A and B are cations, X is an anion.

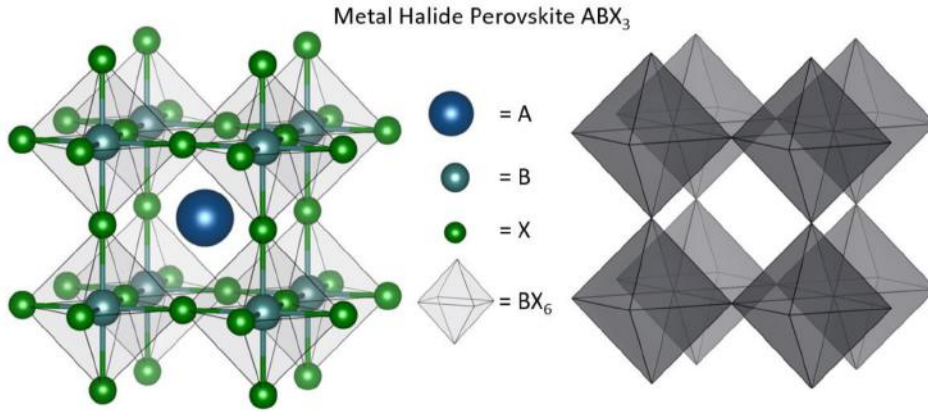


Figure 1: Perovskite ABX_3 structure [5].

Depending on the choice of atoms, the material can exhibit a wide range of properties. In this context, oxide perovskites are not of our interest, as they are not suitable for photovoltaic applications. It was discovered in 2009, that methylammonium lead iodide (MAPbI_3) exhibits remarkable photovoltaic properties for solar cell applications. MAPbI_3 has a band gap of 1.55 to 1.6 eV, which closely matches the energy distribution of sunlight [1].

Later it was discovered, that the halogens can be exchanged to boron and chlorine. Changing to MAPbBr_3 and MAPbCl_3 shifts the absorption band to shorter wavelengths, to approximately $\sim 2.21\text{--}2.30$ eV and $\sim 3.02\text{--}3.18$ eV, respectively [6]. What makes them even more unique, is that by mixing the halides, the distance between the valence and conduction band can be customized thus covering the entire visible spectrum [7]. Unfortunately, these mixed halide perovskites undergo demixing upon illumination [8],

but significant progress has been made to tackle this problem in the recent years.

In this research, I used cesium lead bromide (CsPbBr_3) perovskite. Due to the inorganic cation, this perovskite can be melted, broadening the available methods to fill them inside the nanotubes. Cesium lead bromide in its bulk crystal form typically has a relatively low photoluminescence quantum yield (PLQY), therefore CsPbBr_3 is often synthesized as nanocrystal quantum dots, typically 2–20 mg in size. These quantum dots exhibit strong quantum-size effects resulting in a significantly improved PLQY, reaching as high as 90% [9]. CsPbBr_3 filled inside boron nitride nanotubes also has an easy-to-measure photoluminescence (PL) emission at 532 nm [10].

Like I mentioned, perovskites are highly vulnerable to humidity, oxygen and light exposure. Subjecting even the more resilient perovskites to such environmental stressors results in loss of photoluminescence (shown in Figure 2). CsPbBr_3 is typically annealed at high temperatures to enhance its morphology and crystallinity. It has been observed that CsPbBr_3 shows minimal degradation below 350°C , with significant mass loss only starting beyond that temperature. Additionally, CsPbBr_3 is more stable under light illumination, as it does not decompose at temperatures below 85°C , unlike other similar materials [11].

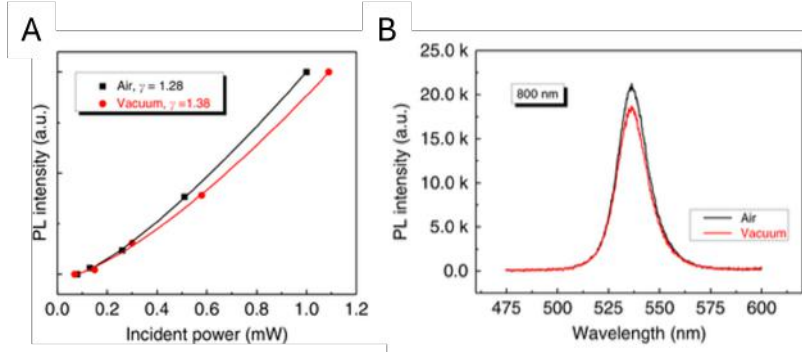


Figure 2: Optical characterization of CsPbBr_3 . (A) PL intensity as a function of excitation power, measured in air and vacuum. (B) PL spectrum of CsPbBr_3 , comparing measurements in air and vacuum [12].

CsPbBr_3 can be synthesized using various methods, like from solution of the precursor salts [3], or by solid state synthesis, in which the precursors CsBr and PbBr_2 are either processed with a ball mill, or melted at high temperatures [13]. The melting point of CsPbBr_3 is around 568°C , as found in the literature, but a recent study showed that it is in fact a two stage process [14]. Under the critical temperature the melt crystallizes at temperatures above the melting point, while when the material is heated above the critical temperature, it crystallizes by supercooling at a significantly lower temperature. This critical temperature is around 579 – 585°C depending on the heating rate. The melt becomes homogeneous at

579°C for 0.1 and 1°C/min and 582, 583, and 585°C for 3, 5, and 10°C/min, respectively. In my experiments I annealed at 570°C and 620°C.

Other researchers have already tried to coat perovskites with an inert shell, or encapsulate inside barrier matrices. For example, Zhang et al. grew perovskites by high temperature annealing inside silica molecular sieve that collapsed on the formed perovskites at temperatures $\sim 600\text{-}900^\circ\text{C}$ [13]. Silica sieve is a sponge-like material, with large surface to volume ratio, and narrow pore size distribution. This method not only ensures the isolation of CsPbBr_3 , but shows a large photoluminescence quantum yield up to 71%. Due to the complete encapsulation, the perovskite remains stable, and shows little or no degradation of the PL intensity in harsher environments.

Another attempt by the same research group uses the same mesoporous silica, however it uses a two-step synthesis [3]. The synthesized CsPbBr_3 exhibited a modest PLQY of 40-60% and a broad full width at half maximum of 20-22 nm. This broadening is likely due to the softened pore structure at high temperatures, which led to unregulated nanocrystal growth and a broad size distribution of 7-12 nm. The article suggests an alternative synthesis approach, forming perovskite directly from the precursor salts, CsBr and PbBr_2 , to achieve more controlled growth and possibly enhanced optical properties. This method showed a PLQY of 93% [3], with greatly increased stability than the previous one. In my experiments I tried both the direct melt and two step solution-based method.

2.2 Boron nitride and carbon nanotubes

Nanotubes are nanoscale cylindrical structures with a hollow core. During my experiments, I worked with boron nitride and carbon-based nanotubes. There are two different nanotube categories: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), each possessing distinct characteristics and potential applications. Conceptually SWNTs are formed by rolled-up sheets of graphene and hexagonal boron nitride [4], and MWCNTs consist of nested rolled-up sheets. Nanotubes can have diameters as small as approximately 0.5 nanometers, while some multi-walled nanotubes can have a diameter of several tens of nanometers and can extend up to millimeters in length [4]. Since their discovery in 1991, nanotubes have attracted significant research attention, showcasing promising applications in areas such as electronics, energy storage, and medicine capsules [4].

Carbon nanotubes (CNTs) are an allotrope of carbon. Graphene sheets are carbon atoms arranged in a honeycomb (hexagonal) structure. Owing to their strong covalent bonds, they exhibit an exceptional tensile strength. Depending on the structure they can either exhibit metallic, or semiconducting properties. The electronic structure of CNTs depend on the chiral vector [15]. The temperature stability of CNTs are estimated to be around

$\sim 2500^\circ\text{C}$ in vacuum, and $\sim 750^\circ\text{C}$ in air [16]. Due to the higher pyramidization angle, the end caps of the CNTs have greater reactivity than the walls. We will take advantage of this property when opening and closing nanotubes [17]. By covalent modification, various functional groups can be attached to the nanotubes, thus making them ideal for nanotechnology applications.

Boron nitride nanotubes are a polymorph of boron nitride. They are very similar to their carbon counterparts, with the carbon atoms exchanged to boron and nitrogen atoms (as shown in Figure 3). The number of walls of a BNNT usually vary from 1 to more than 10 (see Figure 12), with a distance of 0.33 nm between each wall [18]. BNNTs are insulators with a band gap of ~ 5.5 eV [19], independent of their other dimensions. The difference compared to CNTs comes from the bond structure, as the nitrogen atoms have a larger electronegativity, resulting in a more ionic-like bonding [20]. Moreover, they can withstand temperatures up to 900°C in air [19, 21]. This value is crucial for encapsulation, as in our case, the material to be encapsulated has to have a melting point below the temperature where the structure of nanotubes deteriorate. Figure 4 shows an electron microscopy image of BNNTs with open and closed ends.

For nanotubes to be efficient at encapsulating materials, a method is needed to control when such a tube is open or closed. I will demonstrate this in Section 3.

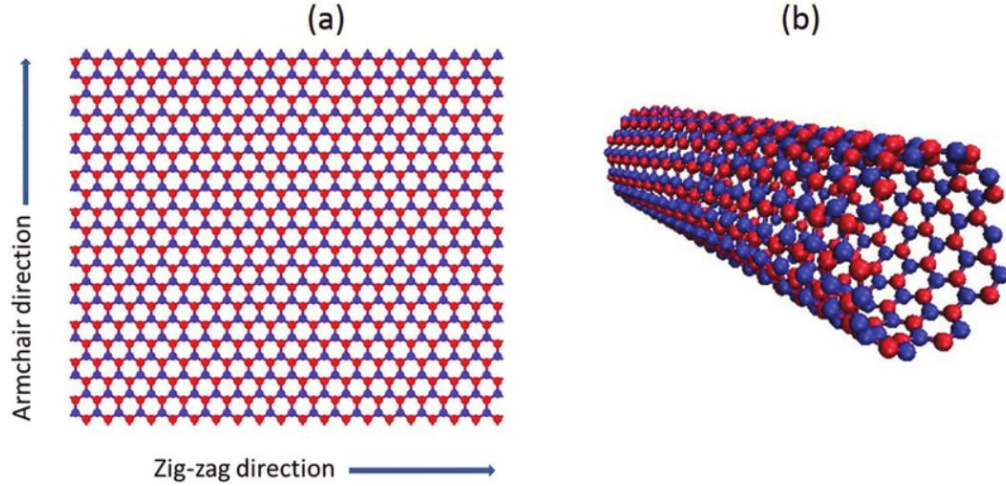


Figure 3: Atomic configuration of (a) single layer hexagonal boron nitride sheet and (b) single-walled BNNT. Red and blue dots correspond to boron and nitrogen atoms, respectively [22]. CNTs look the same with the boron and nitrogen atoms exchanged to carbon.

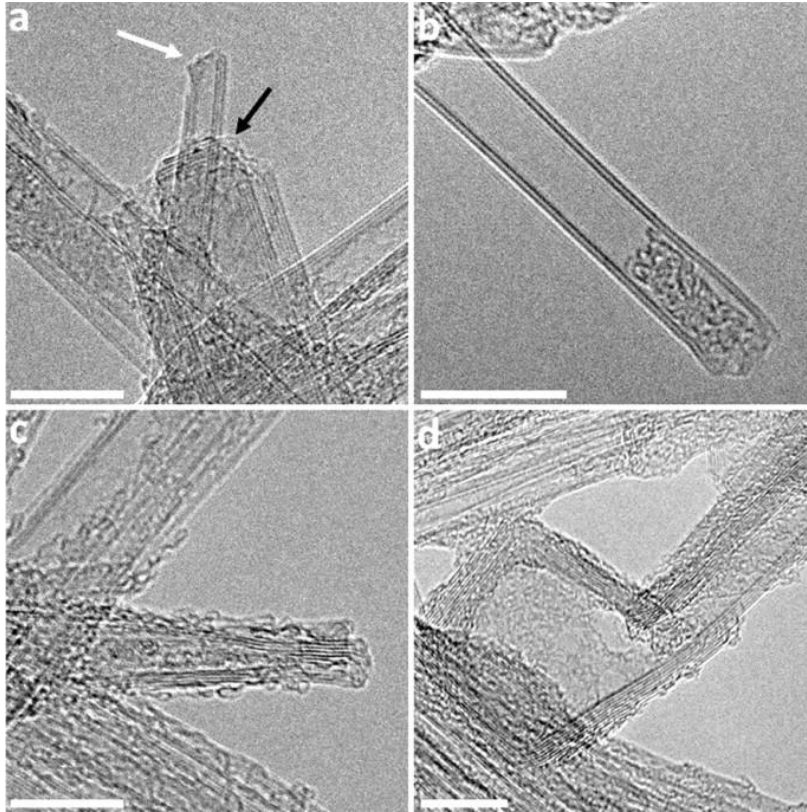


Figure 4: Types of end-caps in BNNTs: (a) a BNNT with an open angular edge end (white arrow), and a closed-end BNNT (black arrow). (b) An open end of a BNNT filled with BN clusters, and (c) a damaged narrow end of BNNT. (d) A BNNT with polygonized end; this type of end-cap is found rarely in the studied material. Scale bars correspond to 10 mg [23].

3 Experimental methods

In this section, I outlined the various techniques employed to characterize the materials used in this study. In addition, some material preparation procedures are elaborated on.

3.1 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a method based on the two-step process of absorbing light at one frequency and emitting at another. To apply the technique, first the absorbance of the material needs to be determined. When the excited electron returns to equilibrium from the higher energy state, it emits another photon [24]. A schematic illustration can be seen in Figure 5.

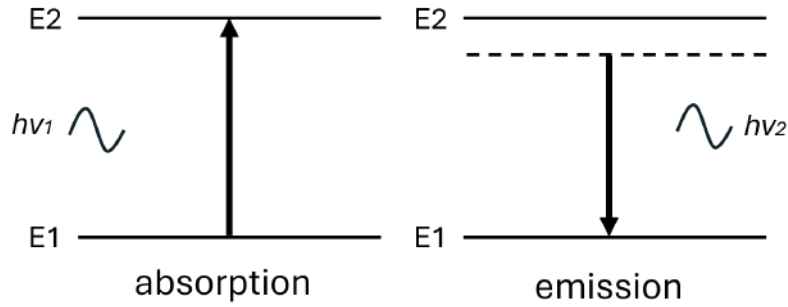


Figure 5: Schematic illustration of PL.

This phenomenon is called luminescence. The emitted photon is then detected by the spectrometer, thus constructing the luminescence spectrum providing valuable information about the electronic structure of the material. The measure of how luminescent is a material can be calculated by Einstein's equation:

$$\eta = \frac{I_{em}}{I_{abs}} \cdot \frac{f_{em}}{f_{abs}} \quad (1)$$

where η is the quantum yield or efficiency of the luminescence, I_{em} is the intensity of emitted, I_{abs} the intensity of the absorbed light, f_{em} and f_{abs} are the frequencies of the emitted and absorbed light, respectively.

Materials have emission characteristics unique to them, therefore we can identify their composition. This technique is greatly influenced by the defects, requires emissive materials and specific excitation. These make it sometimes difficult to accurately determine the energy levels of the material.

In my experiments, only very small amount of samples were available for the measurements, therefore a traditional optical microscope was modified to measure the photoluminescence. Illumination was provided by a UV led (Fig. 6). A 400 nm bandpass filter with 40 nm bandwidth was attached in front of the led to filter out the white light emission tail of the led. The PL emission of the sample was collected through a 10x magnification objective. On the emission side we used a 405 nm long pass filter, to filter out most of the excitation light and let only the PL emission of the sample (expected around 450-540 nm) to pass through. The emitted light was collected by an optical fiber placed at the objective's back image plane and analyzed with a B&W TEK Exemplar Plus spectrometer 7, which uses the Czerny-Turner configuration.

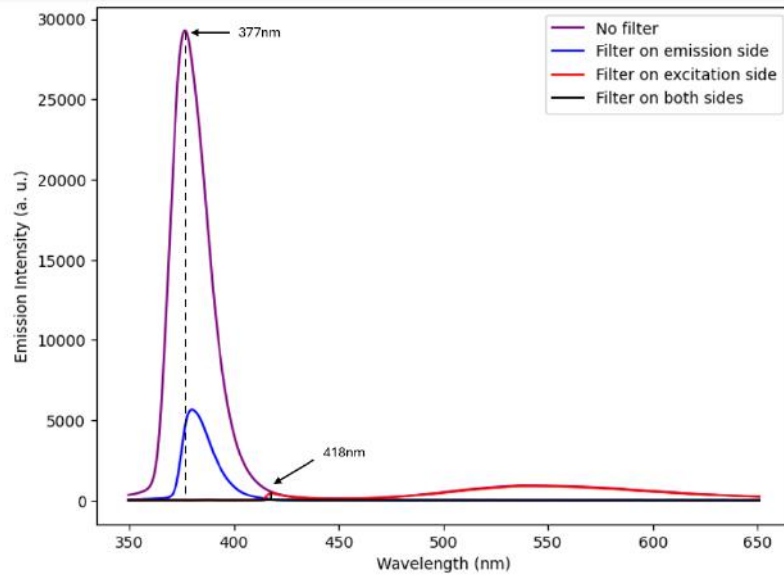


Figure 6: This figure shows the characteristics of the UV led providing excitation throughout the PL measurements. The main emission peak is found at 377 nm and broad emission shoulder centered at 548 nm. A 400 nm bandpass filter with 40 nm bandwidth was used on the excitation side, on the emission side, a 405 nm longpass filter was used.

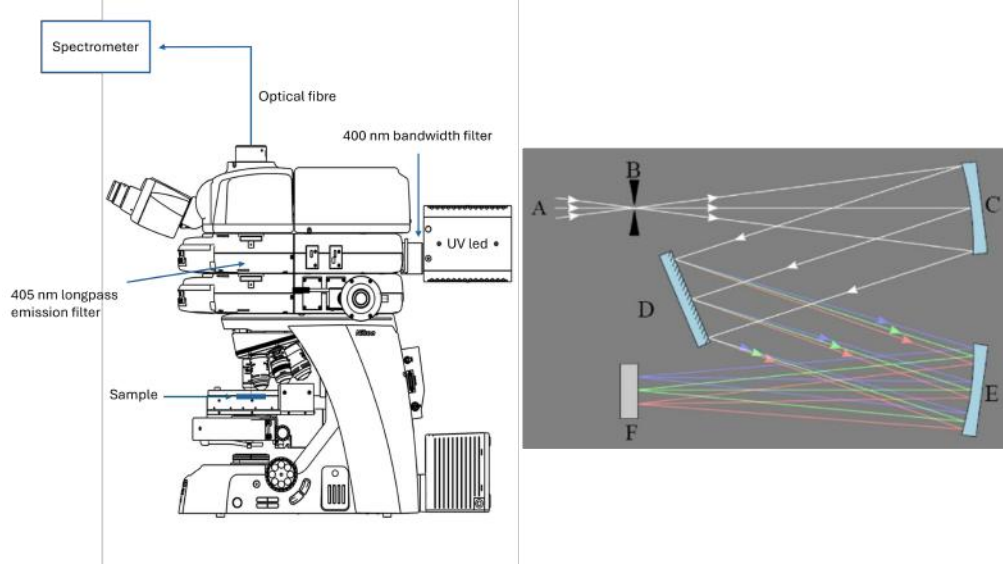


Figure 7: Left) Modified microscope. To obtain microscopic images, the optical fiber was replaced with a camera. Right) Czerny-Turner Configuration: Light from point A enters into the spectrometer at point B. The concave mirror C collimates the light, and directs it onto the grating D. The diffracted light is then focused by the concave mirror E, and reflected at the detector F.

3.2 Electron microscopy

When the dimensions of the observable sample reach the nanoscale, creating images with a standard light microscope becomes impossible no matter how many lenses are available. The physical obstacle comes from the wavelength restriction, as the wavelength of visible light is too large to make accurate measurements at the atomic scale [25]. The resolution as the function of wavelength can be calculated as follows:

$$d = \frac{0.61\lambda}{NA} \quad (2)$$

where d is the minimum resolvable distance and λ is the wavelength of the light and NA is the numerical aperture of the optical system. To get around this problem, scientists have developed the electron microscope. De Broglie showed that moving electrons can behave both as a particle and a wave. The wavelength accordingly can be calculated as follows:

$$\lambda = \frac{h}{m_e \cdot v_e} \quad (3)$$

where λ is the wavelength, m_e is the mass and v_e is the speed of an electron and h is the Planck constant. When using the equation to calculate the

wavelength of the electrons, we find that it is many orders of magnitude shorter than the wavelength of visible light. This means that electrons can be considered as a form of "invisible radiation." As a result, this property can be utilized to create images, similar to how we use visible light in imaging techniques. To make the measurement possible, both generation and manipulation of electron beams take place in vacuum. The focusing of the electron beam is done by magnetic lenses. When an electron goes through a magnetic field, it experiences a force changing its direction, except when the magnetic lines are parallel with the electron's velocity [25]. This enables the focusing. The magnification is directly proportional to the accelerating voltage, but while high accelerating voltages result in a better resolution, the higher energy electrons can cause damage to the sample. The electron beam may heat up the material creating a blurry image.

TEM imaging requires very thin samples to allow the electron beam to pass through the layer. The transmitted electrons are captured on a fluorescent screen or a digital detector. TEM can reach a 50,000,000x magnification (enough to see individual atoms) [26].

The high energy incoming electrons can knock out inner shell electrons from the atoms in the sample. When the created vacancies are filled with electrons from a higher energy shell X-rays are emitted.. Using energy-dispersive X-ray spectroscopy, we can determine the types of atoms present. The energies of these X-rays are unique to each element, which enables the identification. The method is particularly useful, because we can also calculate the proportions of various atoms present.

We used transmission electron microscopy to determine the presence and composition of the material inside the nanotubes. To image the nanotubes properly, we ideally need individual nanotubes. Nanotubes were sonicated in toluene, and a small amount of this solution was dropped onto the surface of distilled water. A lacey carbon TEM grid was pulled through this thin toluene layer. This way the solvent evaporated from the grid before the nanotubes reaggregated. The nanotubes suspended over the holes of the lacey carbon grid provide ideal candidates for imaging.

3.3 Opening of the nanotubes

Due to how nanotubes grow, manufacturers typically deliver them with closed ends, therefore nanotubes need to be opened before filling.

To open them, boron nitride nanotubes are first sonicated in ammonium hydroxide. The sample is then filtered and rinsed with distilled water. After drying, it is annealed at 800°C for an hour in air, with 10°C/min of heating and cooling to oxidize boron impurities and boron nitride nanoparticles. The sample is then washed in distilled water at 90°C to remove the formed B₂O₃ then filtered again. We obtain the opened BNNT (from here on referred to as o-BNNT) after drying at 130°C on air for 12 hours [18, 19, 27]. To my knowledge, end closing of BNNT nanotubes was not achieved

yet. This matters, because excess material cannot be washed simply off the nanotubes, as the already encapsulated perovskite may come out.

Opening carbon nanotubes is simpler, as annealing at 420°C for 20-30 minutes in air gives time for oxygen to react away with carbon located near the ends, thus opening them. Their ends can be closed again by annealing around 800-1300°C in vacuum [28].

4 CsPbBr₃ encapsulated inside BNNTs

This section outlines the experimental procedures for encapsulating CsPbBr₃ within BNNTs. Over the course of this study, six distinct samples were prepared, each with the objective of achieving effective perovskite encapsulation. Multiple techniques were employed, and comparisons made between the samples, using various measurement techniques.

Sample Name	Type of experiment
I. CsPbBr ₃ @o-BNNT-S	Direct filling to opened BNNT from water-based precursor solution
II. CsPbBr ₃ @o-BNNT-M 570A	Direct filling to opened BNNT by melt insertion (M) at 570°C in Argon (A)
III. CsPbBr ₃ @o-BNNT-M 570v	Encapsulation of CsPbBr ₃ into opened BNNT by melt insertion in vacuum at 570°C
IV. CsPbBr ₃ +BNNT-M 570v	Reference sample for CsPbBr ₃ @o-BNNT-M 570v, prepared using unopened BNNT
V. CsPbBr ₃ @o-BNNT-M 620v	Encapsulation of CsPbBr ₃ into opened BNNT by melt insertion in vacuum at 620°C
VI. CsPbBr ₃ +BNNT-M 620v	Reference sample for CsPbBr ₃ @o-BNNT-M 620v, prepared using unopened BNNT

Table 1: Name of samples and type of experiment.

4.1 Encapsulation from solution

4.1.1 Sample I. - CsPbBr₃@o-BNNT-S

The first sample was created based on an article [13] showcasing the filling of silica sieve template with CsPbBr₃. The precursors were dissolved in distilled water, and encapsulation into the BNNTs were performed from the solution-phase. This was followed by a high-temperature annealing-step to recrystallize the encapsulated material. The BNNTs used underwent the opening procedure described in Section 3.

I started by measuring out the base materials. Since the reaction to create CsPbBr₃ is $\text{CsBr} + \text{PbBr}_2 = \text{CsPbBr}_3$, I needed 1:1 ratio of CsBr and PbBr₂. I measured 22.8 mg of PbBr₂ and 13.37 mg of CsBr accordingly, and took 10 ml of distilled water with a pipette. I dissolved the precursors in the water while mixing with a magnetic stirrer at $\sim 80^\circ\text{C}$. The procedure took ~ 80 minutes. Meanwhile, I measured out 4.20 mg of BNNT using the same 1:3 ratio as the article [13]. For that amount of BNNT I took 0.387 ml from the solution, and mixed it together with the BNNT for 60 minutes at 80°C . I then evaporated the water at 80°C for 210 minutes. The BNNT appeared lightly orange and a significant amount of unencapsulated perovskite crystals could be observed. The product was annealed at 570°C for 30 minutes in air with heating and cooling rate of $5^\circ\text{C}/\text{min}$. I measured the final product’s photoluminescence with a spectrometer through a 10x

objective (in Figure 6), and compared it with that of CsPbBr_3 . The result can be seen in Figure 8.

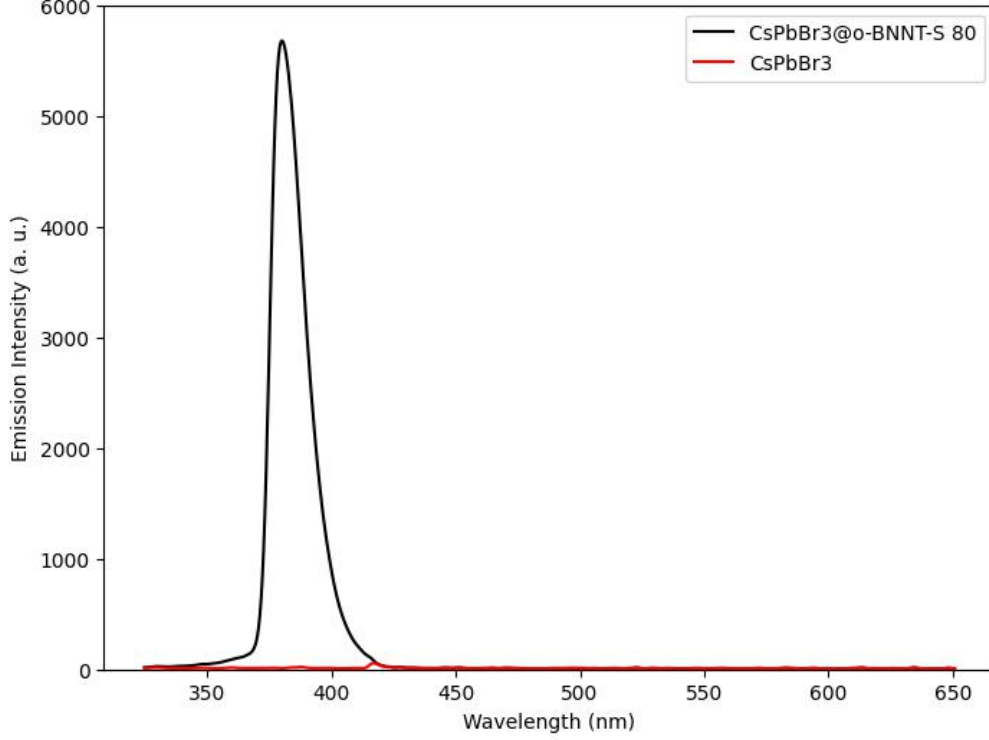


Figure 8: Photoluminescence spectrum of CsPbBr_3 @o-BNNT-S 80 prepared from water solution and CsPbBr_3 . Excitation was provided by a UV led (see Fig. 6). There is no detectable PL emission around 532 nm.

Analyzing the obtained PL spectrum of CsPbBr_3 @o-BNNT-S, we see no visible emission meaning, this experiment was unsuccessful at encapsulating perovskite. The PL measurement result was anticipated, given that the sample retained its white color after annealing.

4.2 Melt insertion

4.2.1 Sample II. - CsPbBr_3 @o-BNNT-M 570A

This sample is another attempt to grow CsPbBr_3 in BNNT, but using solid state synthesis. The boron nitride nanotubes used underwent the opening procedure described in section 3.3, and the sample was prepared in a glove box filled with Argon. This enables the synthesis of purer samples, primarily by creating an oxygen and water-free environment.

7.5 mg of CsPbBr_3 (Appx. A.1) was measured and ground together in a mortar with 15.5 mg of BNNT. The as obtained powder was then put into an open porcelain combustion boat, then loaded in to a tubular furnace with both ends plugged in. The sample was heated to 570°C at a heating rate of $2^\circ\text{C}/\text{minute}$, then held at that temperature for 1 hour. The color of the sample changed after the procedure (see Figure 9). A slight orange discoloration was observed on the furnace end cap, indicating material condensation.



Figure 9: Left: before annealing, little grains of perovskite was visible in the mixture resulting in the darker orange color. Right: after annealing, the grains disappeared and the sample became yellow.

The sample showed strong green photoluminescence under UV illumination (see Figure 11). The photoluminescence spectrum of the sample was then measured (see Figure 10). We see an intensive emission peak at 508 nm. This confirms that the nanotubes were indeed open, but to verify perovskite is actually located inside the nanotubes (and not around), the sample is measured with TEM as well.

To confirm the presence of perovskite inside the boron nitride nanotubes, the sample was measured with TEM. The measurement confirms the presence of Cs, Pb and Br inside the nanotubes, meaning that perovskite was successfully encapsulated inside BNNT (see Figure 12 and 13).

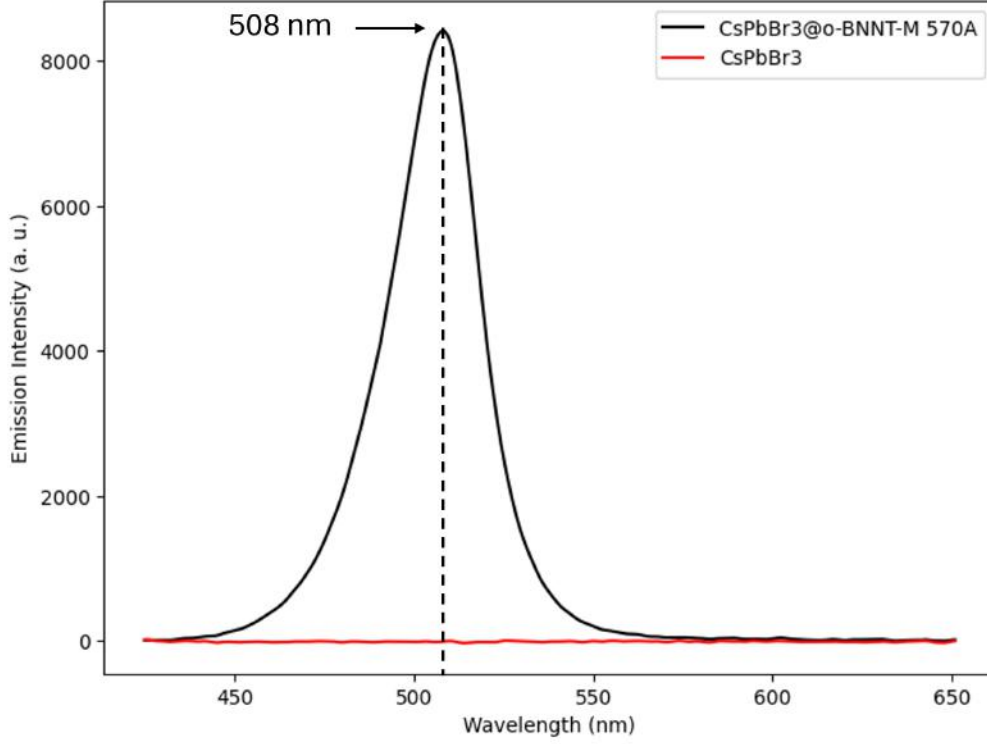


Figure 10: PL spectrum of $\text{CsPbBr}_3@o\text{-BNNT-M 570A}$ and CsPbBr_3 . An extensive emission peak is located at 508 nm, and we see no emission coming from the perovskite.

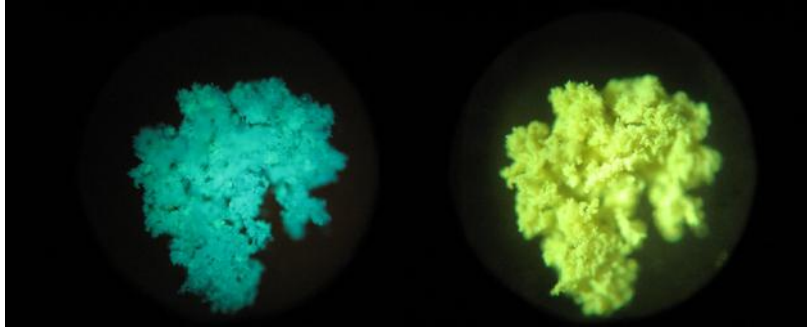


Figure 11: $\text{CsPbBr}_3@o\text{-BNNT-M 570A}$ under 10x magnification Left: UV illumination (400 nm bandpass filter with 40 nm bandwidth on the excitation side). Right: illuminated by white light with 458 nm emission filter.

4.2.2 Sample III. - $\text{CsPbBr}_3@o\text{-BNNT-M 570v}$

After the successful filling of the previous sample, I wanted to refine the experiment by enhancing the purity of the material. Due to material condensation on the furnace's end cap at $\text{CsPbBr}_3@o\text{-BNNT-M 570A}$, I annealed this sample in a closed environment. This would enable the measurement of the condensed material, or may even prevent it. To ensure that a minimal amount of perovskite remains unencapsulated, I made calculations to

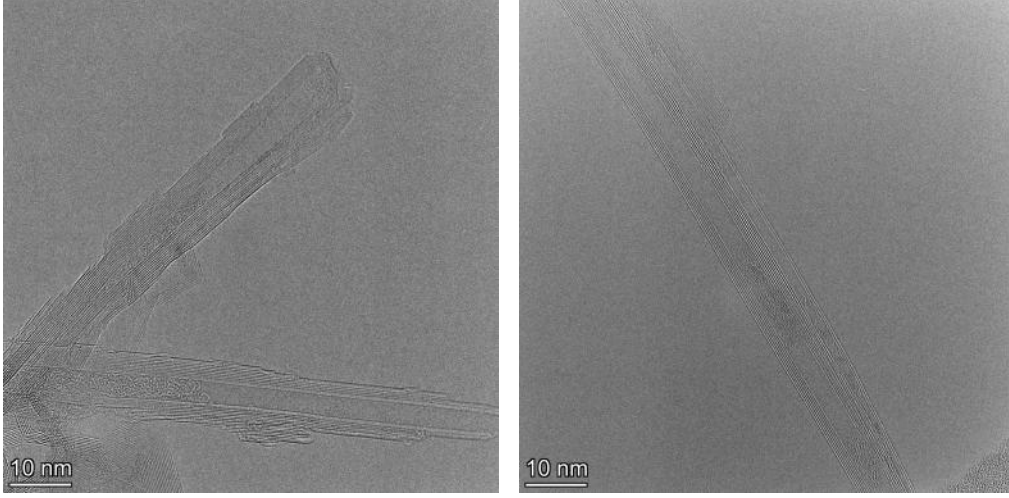


Figure 12: $\text{CsPbBr}_3@o\text{-BNNT-M 570A}$ under an electron microscope. The left picture shows a BNNT with 11 walls, while the one on the right has 6. We can also observe some material inside. The TEM images were taken by Erzsébet Dodony.

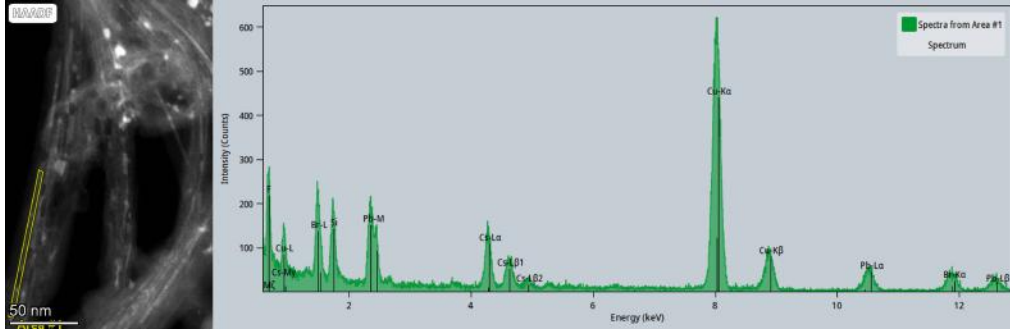


Figure 13: This figure shows the energy-dispersive X-ray spectrum (EDS) collected from a specific area of a $\text{CsPbBr}_3@o\text{-BNNT-M 570A}$. This analysis is used to determine the elemental composition of the material being studied. The yellow box in the image on the left indicates the region where the EDS spectrum was acquired. The primary elements observed are cesium (Cs), lead (Pb), and bromine (Br), which suggests that the sample is indeed containing CsPbBr_3 . Copper and silicon are likely from external contamination or from the support materials used in sample preparation. The measurement was carried out by Erzsébet Dodony on samples prepared by my advisor.

approximate the ideal CsPbBr_3 to BNNT ratio. From TEM measurements, the average number of BNNT walls was determined to be 7.6.

$$\text{Mass ratio} = \frac{4(m_B + m_N)}{d_{\text{BN}}\rho_{\text{perovskite}}} \cdot \sum_{i=1}^{n_{\text{avg}}} \frac{r_{\text{inner}} + (i-1)d_{\text{layer}}}{r_{\text{inner}}^2} \quad (4)$$

Where d_{BN} is the bond length between boron and nitrogen atoms (approximately 0.145 nm), m_B and m_N are the atomic masses of boron and nitrogen (10.81 g/mol and 14.01 g/mol respectively), $\rho_{\text{perovskite}}$ is the density of perovskite, 5.31 g/cm³ from literature [29], $d_{\text{layer}} = 0.33$ nm is the

distance between the BNNT walls [30]. Based on this calculation, the ideal mass ratio of BNNT to perovskite is 5:1. The calculation provides only a very rough estimation, as the BNNT sample contains a wide variety of nanotubes, and the BNNTs can only contain a few unit cell width of perovskites, therefore the filling of the cavity is not necessarily ideal.

I used the same opened BNNT sample as before, which I annealed for 20 minutes at 100°C in Argon to remove any water trapped inside. The CsPbBr₃ (Appx. A.2) was synthesized by Éva Kováts using a solution-based synthesis. I measured 12.6 mg of BNNT and according to the 5:1 BNNT to perovskite ratio, 2.5 mg of CsPbBr₃. These were then ground together in an agate mortar to a fine light orangish powder. The powder was loaded inside a quartz tube, ensuring the as mentioned closed environment. The quartz tube is of necessity because its melting point is way above than that of glass, approximately ~1700°C. Significant amount of the sample was lost during this procedure, because the charged BNNT powder was attracted to the outside of the quartz tube. The quartz tube was then sealed with parafilm and a vial to stop the air from getting inside, then brought outside the glove box for annealing.

Before putting into a tubular furnace, the quartz tube was sealed under vacuum (~3.3e-5 mbar) using a blowtorch (shown in Figure 15). The temperature of the sample was first brought to 520°C with a 5°C/minute ramp up temperature. To approach the melting point of CsPbBr₃ slowly, the temperature was further increased to 570°C by 1°C/minute. This is important, to ensure that the perovskite melts evenly and completely. The sample was kept at 570°C for 12 hours. The temperature was then decreased by 1°C/minute to 540°C. After waiting an hour at the crystallization temperature, it was further lowered to 500°C by 1°C/minute. It is better to cool slowly around this change of state. The content was then cooled to room temperature (~27°C) by 5°C increments per minute. After annealing, a gold-yellow rim of material condensed near the top of the tube (shown in Figure 15). This has not been measured yet, but it is most likely perovskite.

I then measured the photoluminescence of the obtained material (see Figure 16 and 14). The PL intensity peak is located at 498 nm, which is slightly lower than 532 nm, as found in literature [10].

4.2.3 Sample IV. - CsPbBr₃+BNNT-M 570v

CsPbBr₃+BNNT-M 570v is the reference sample for CsPbBr₃@o-BNNT-M 570v. Here we used as-received BNNT purified by the manufacturer, having mostly closed ends and significantly longer tubes. Therefore we expect to observe only minimal amount of encapsulated perovskite after the reaction.

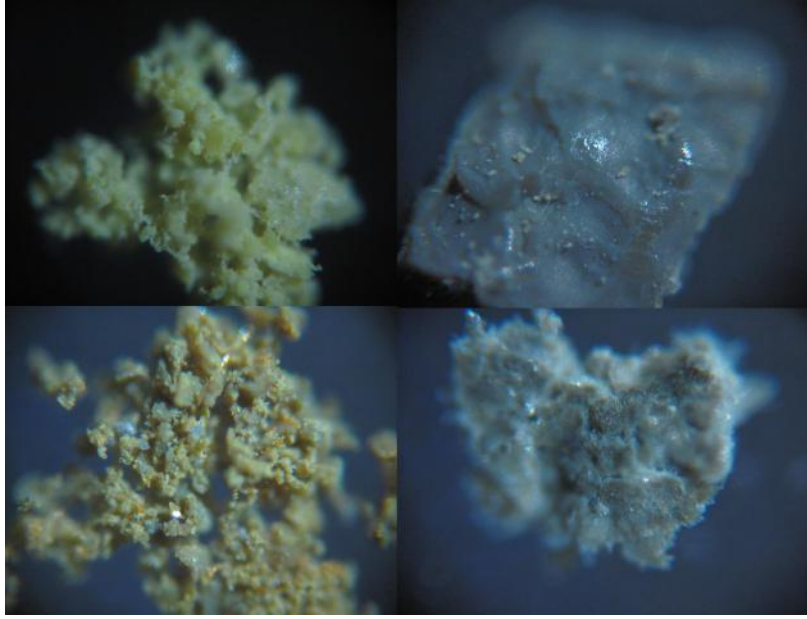


Figure 14: This image shows Top left: $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$. Top right: $\text{CsPbBr}_3\text{+BNNT-M } 570\text{v}$. Bottom left: $\text{CsPbBr}_3\text{@o-BNNT } 620\text{v}$. Bottom right: $\text{CsPbBr}_3\text{+BNNT-M } 620\text{v}$ under microscope lit with a phone torch.

The sample preparation and encapsulation procedure was identical to the one described in case of the $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$ sample, using 5.1 mg of BNNT, and 1 mg of CsPbBr_3 . I ground them together in the mortar to obtain an evenly mixed fine powder. The loaded tube was then sealed with parafilm and a vial. It was brought outside for closing under vacuum, but due to technical problems, the sample got exposed to air. A picture of the sample pre-annealing is shown in Figure 15.

The sample was then annealed together with $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$ (they underwent the same procedure). The same goldish rim was visible near the top of the tube, as (shown in Figure 15). This also means that by annealing in a closed environment did not prevent material loss.

I then measured the photoluminescence of the as-obtained material (see Figure 16 and 14). Comparing $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$ with its reference indicates, that the opening procedure made a difference, as the PL intensity of the first sample is significantly higher, while the second has no detectable PL emission. Unfortunately, due to lack of time, TEM measurement of $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$ could not be obtained, but it is highly likely, that the encapsulation was successful.

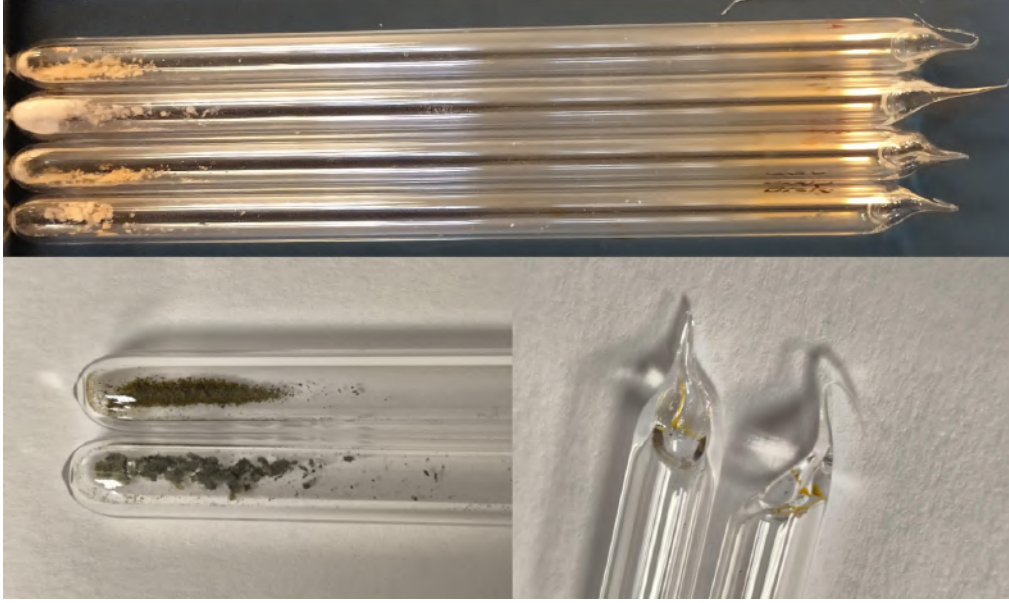


Figure 15: This figure shows samples $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$, $\text{CsPbBr}_3\text{+BNNT-M } 570\text{v}$, $\text{CsPbBr}_3\text{@o-BNNT-M } 620\text{v}$ and $\text{CsPbBr}_3\text{+BNNT-M } 620\text{v}$. Top picture: all four samples in sealed quartz tubes before annealing (from top to bottom: III, IV, V, VI). Bottom left picture: $\text{CsPbBr}_3\text{@o-BNNT-M } 620\text{v}$ (lower) and $\text{CsPbBr}_3\text{+BNNT-M } 620\text{v}$ (upper) after annealing. Bottom right picture: yellowish rim around the top of each mentioned tube. This could mean that approximating the CsPbBr_3 BNNT ratio is pointless, as the excess perovskite condenses at the top.

4.2.4 Sample V. - $\text{CsPbBr}_3\text{@o-BNNT-M } 620\text{v}$

It is observed, that even though the melting point of perovskite is $\sim 568^\circ\text{C}$, it might not melt all the way. Due to the kinetics and viscosity of molten perovskite, the filling is slow [14]. Therefore $\text{CsPbBr}_3\text{@o-BNNT-M } 620\text{v}$ was annealed at 620°C instead of 570°C . The same opened BNNT and CsPbBr_3 (Appx. A.2) was used as in $\text{CsPbBr}_3\text{@o-BNNT-M } 570\text{v}$.

6.3 mg of BNNT and 1.5 mg of CsPbBr_3 were measured. The starting materials were ground together, then loaded into a quartz tube. The quartz tube was evacuated and sealed at $\sim 1\text{e-}5$ mbar pressure.

The annealing procedure was done the same way as before, but the material was kept at 620°C for 12 hours instead of 570°C . The result is shown in Figure 15. After annealing, the same gold rim became visible as before.

PL of the sample was then measured (see Figure 16 and 14).

4.2.5 Sample VI. - $\text{CsPbBr}_3 + \text{BNNT-M 620v}$

Similarly to the samples annealed at 570°C , $\text{CsPbBr}_3 + \text{BNNT-M 620v}$ is a reference prepared for $\text{CsPbBr}_3@o\text{-BNNT-M 620v}$. The reference was made the exact same way as $\text{CsPbBr}_3@o\text{-BNNT-M 620v}$, but with potentially closed BNNTs.

6.2 mg of BNNT and 1.2 mg CsPbBr_3 was measured, then prepared like $\text{CsPbBr}_3@o\text{-BNNT-M 620v}$. The pressure inside the quartz tube was $\sim 1\text{e-}5$ mbar when closing with a blowtorch. It was annealed together with $\text{CsPbBr}_3@o\text{-BNNT-M 620v}$ (see Figure 15).

I measured the PL spectrum (see Figures 16 and 14). A comparison of the two spectra reveals that CsPbBr_3 filled into open nanotubes exhibits a significantly higher PL intensity than the reference sample. This intensity peak is located at 509 nm, which again is slightly less than 532 nm [10]. This again confirms the need for nanotube preparation in advance. The perovskite filled inside potentially closed nanotubes also has a slight intensity peak at 504 nm.

Pictures were also taken through a microscope, and the difference between the PL of CsPbBr_3 filled boron nitride nanotubes and their references is clearly visible 17. A perovskite needle was found inside $\text{CsPbBr}_3@o\text{-BNNT-M 620v}$, and it serves a great example to showcase the non-existent PL of CsPbBr_3 compared to the filled BNNTs 18.

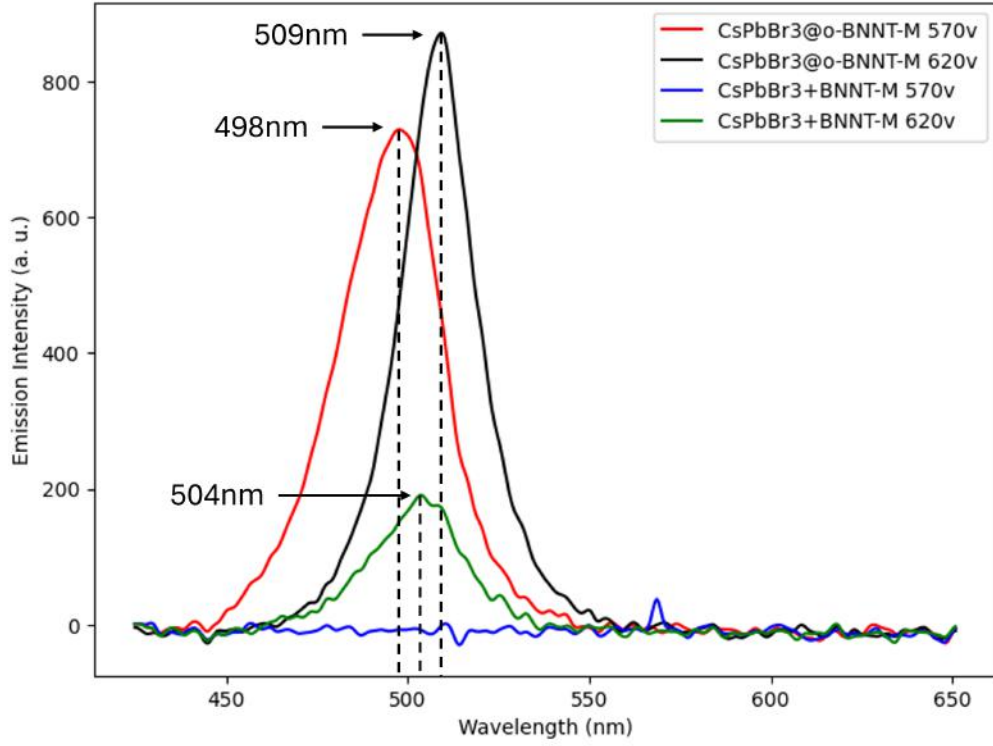


Figure 16: PL measurement of samples CsPbBr₃@o-BNNT-M 570v, CsPbBr₃+BNNT-M 570v, CsPbBr₃@o-BNNT-M 620v and CsPbBr₃+BNNT-M 620v. The PL of the CsPbBr₃ filled into opened BNNTs show greater intensity than the BNNT samples with potentially closed ends. Furthermore, annealing at 630°C instead of 570°C shifts the intensity peak from 498nm to 509nm and increases the intensity. Increasing the temperature causes CsPbBr₃+BNNT-M 620v to glow as well, although with significantly lower intensity.

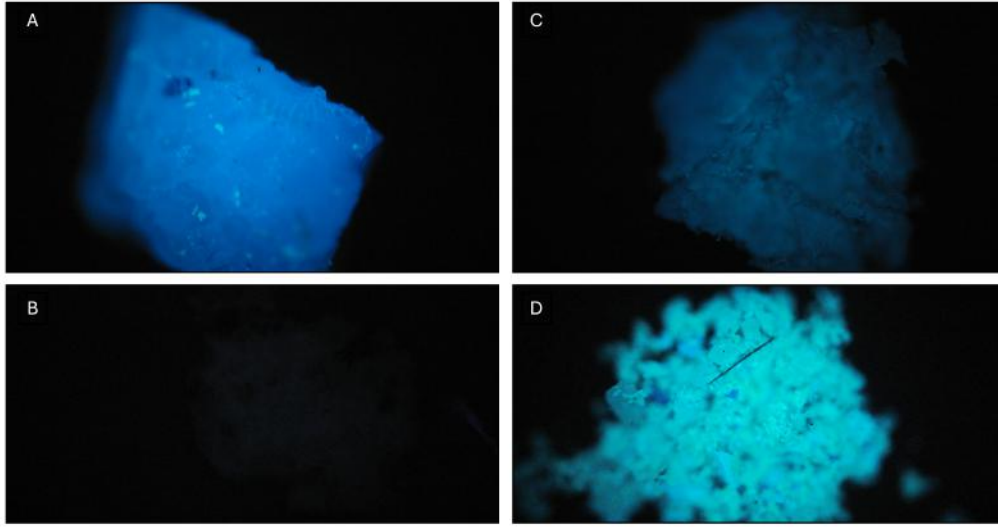


Figure 17: This image shows A) $\text{CsPbBr}_3@o\text{-BNNT-M}$ 570v. B) $\text{CsPbBr}_3+\text{BNNT-M}$ 570v. C) $\text{CsPbBr}_3+\text{BNNT-M}$ 620v. D) $\text{CsPbBr}_3@o\text{-BNNT-M}$ 620v under UV illumination. The difference between perovskite filled inside opened BNNTs and unopened BNNTs is significant as the previous glows with a bluish light.

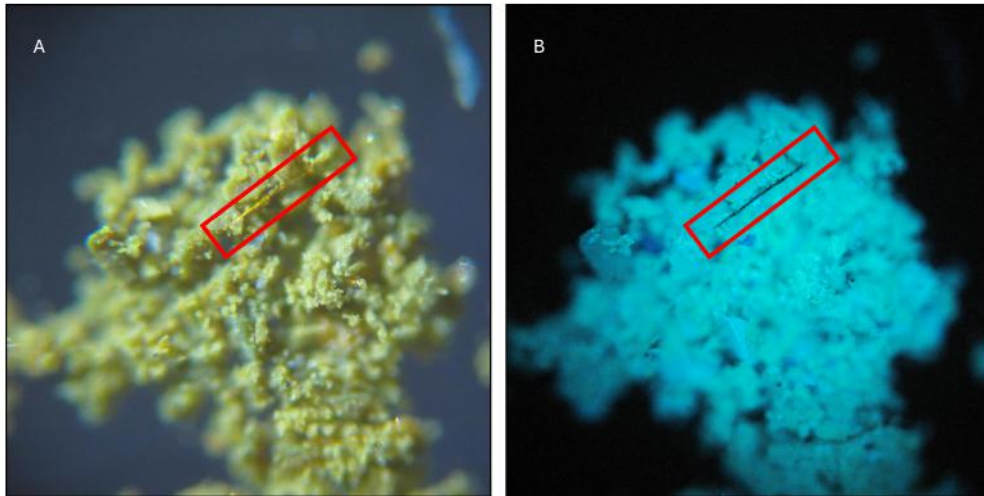


Figure 18: $\text{CsPbBr}_3@o\text{-BNNT-M}$ 620v A) illuminated by white light and B) and by UV led. A perovskite needle is highlighted by the red rectangle in both pictures. The difference between perovskite inside the BNNTs and the needle is clearly visible on B), as it shows no luminescence.

4.3 Discussion

The results of this study reveal important insights into the synthesis of CsPbBr_3 within BNNTs, regarding PL characteristics. The observed shift of the PL peak (from 532 nm) towards shorter wavelengths in our samples (see Figure 16) indicates that the particle size is reduced. This aligns with existing literature [10, 31, 32], which indicate that smaller quantum dots exhibit higher bandgap energies, leading to blueshifts in emission wavelength. A study [3] suggests that the photoluminescence characteristics of quantum dots can vary based on shape, such as rod-like or cuboid structures. In the study by Zhang et al., the authors reported a PL emission peak at 520 nm for CsPbBr_3 nanocrystals, with narrow size distribution of 4.2 to 6.8 nm, synthesized within mesoporous silica templates. In contrast, I found that CsPbBr_3 nanocrystals encapsulated within BNNTs exhibit a PL emission peak at 509 nm. This blue shift could be explained by the smaller perovskite crystals formed inside the BNNT matrices.

Another important aspect of the research was the pre-processing of the BNNTs. The delivered nanotubes came with mostly closed ends, which made the filling highly inefficient, causing low PLQY (see Figure 16, 17, 11). By subjecting the nanotubes to an opening procedure, the filling efficiency was significantly improved. I also found that approximating the proper ratio of materials is rather unnecessary, as most of the excess perovskite can be removed by tilting the tube.

5 Summary and outlook

This thesis investigates methods for filling cesium lead bromide (CsPbBr_3) perovskite into boron nitride nanotubes (BNNTs), to uncover their potential applications in optoelectronics. The research probes various techniques for encapsulation, such as solid-state synthesis and growing the perovskite from a precursor solution, while discussing the impact of different annealing temperatures.

I showed that CsPbBr_3 growth from precursor solution is ineffective when filling BNNTs, as the experiment was unsuccessful in encapsulation. On the other hand, solid-state synthesis showed promising results, and I managed to increase its efficiency by an alternative annealing procedure.

In the future, I want to verify that the PL intensity and its peak wavelength increases with the annealing temperature. To do this, I would synthesize three more samples annealed at 590°C , 610°C and 650°C , then plot all five on the same diagram. I would also like to develop a method to separate filled and unfilled nanotubes, as well as a technique to remove perovskite grown outside the walls. These are challenging problems because there is no technique yet to close the ends of BNNTs, therefore the payload could be lost during the procedure. I would also like to verify that overloading the BNNTs with perovskite results in more filled nanotubes, as excess perovskite seems to sublime away.

Unfortunately, due to lack of time to finish all the experimental work, results on the CsPbBr_3 @CNT sample had to be excluded from this thesis, but I plan to investigate the dependency of their optoelectronic properties on the annealing temperature, and to experiment with filling techniques.

References

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, “Organometal halide perovskites as visible-light sensitizers for photovoltaic cells”, *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6050–6051, 2009.
- [2] D. Zhou, T. Zhou, Y. Tian, X. Zhu, and Y. Tu, “Perovskite-based solar cells: Materials, methods, and future perspectives”, *Journal of Nanomaterials*, vol. 2018, no. 1, p. 8148072, 2018. DOI: <https://doi.org/10.1155/2018/8148072>. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1155/2018/8148072>.
- [3] Q. Zhang, W. Zheng, Q. Wan, M. Liu, X. Feng, L. Kong, and L. Li, “Confined synthesis of stable and uniform cspbbr₃ nanocrystals with high quantum yield up to 90% by high temperature solid-state reaction”, *Advanced Optical Materials*, vol. 9, no. 11, p. 2002130, 2021.
- [4] C. Allard, L. Alvarez, J.-L. Bantignies, N. Bendiab, S. Cambre, S. Campidelli, J. A. Fagan, E. Flahaut, B. Flavel, F. Fossard, E. Gaufres, S. Heeg, J.-S. Lauret, A. Loiseau, J.-B. Marceau, R. Martel, L. Marty, T. Pichler, C. Voisin, S. Reich, A. Setaro, L. Shi, and W. Wenseleers, “Advanced 1d heterostructures based on nanotube templates and molecules”, *Royal Society of Chemistry*, vol. 37, pp. 1–37, 2024. DOI: <https://doi.org/10.1039/d3cs00467h>.
- [5] J. S. Rodríguez Hernández, *Structural-property relationships in metal halide like-perovskites under extreme conditions*, 2023.
- [6] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, and L. M. Herz, “High charge carrier mobilities and lifetimes in organolead trihalide perovskites”, *Advanced Materials*, vol. 26, no. 10, p. 1584, 2014.
- [7] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok, “Chemical management for colorful, efficient, and stable inorganic–organic hybrid nanostructured solar cells”, *Nano Letters*, vol. 13, no. 4, pp. 1764–1769, 2013.
- [8] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, and M. D. McGehee, “Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics”, *Chemical Science*, vol. 6, no. 1, pp. 613–617, 2015.
- [9] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, and M. V. Kovalenko, “Nanocrystals of cesium lead halide perovskites (cspb_x₃, x= cl, br, and i): Novel optoelectronic materials showing bright emission with wide color gamut”, *Nano letters*, vol. 15, no. 6, pp. 3692–3696, 2015.
- [10] S. Ullah, J. Wang, P. Yang, L. Liu, S.-E. Yang, T. Xia, H. Guo, and Y. Chen, “All-inorganic cspbbr₃ perovskite: A promising choice for photovoltaics”, *Materials Advances*, vol. 2, no. 2, pp. 646–683, 2021.
- [11] Y.-B. L. Shan-Shan Rong M. Bilal Faheem, “Perovskite single crystals: Synthesis, properties, and applications”, *Journal of Electronic Science and Technology*, vol. 19, pp. 1/18, 2021. DOI: 10.1016/j.jnlest.2021.100081.
- [12] Y. Wang, Y. Ren, S. Zhang, J. Wu, J. Song, X. Li, J. Xu, C. H. Sow, H. Zeng, and H. Sun, “Switching excitonic recombination and carrier trapping in cesium lead halide perovskites by air”, *Communications Physics*, vol. 1, no. 1, p. 96, 2018.
- [13] Q. Zhang, B. Wang, W. Zheng, L. Kong, Q. Wan, C. Zhang, Z. Li, X. Cao, M. Liu, and L. Li, “Ceramic-like stable cspbbr₃ nanocrystals encapsulated in silica derived from molecular sieve templates”, *Nature Communications*, vol. 11, no. 1, p. 31, 2020.

- [14] A. Kanak, O. Kopach, L. Kanak, I. Levchuk, M. Isaiev, C. J. Brabec, P. Fochuk, and Y. Khalavka, “Melting and crystallization features of CsPbBr_3 perovskite”, *Crystal Growth Design*, vol. 6, pp. 4115–5121, 2022. DOI: 10.1021/acs.cgd.1c01530.
- [15] C. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zólyomi, and J. Kúrti, “Assignment of chiral vectors in carbon nanotubes”, *Physical Review B*, vol. 68, no. 23, p. 235 404, 2003.
- [16] Z. Han and A. Fina, “Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review”, *Progress in Polymer Science*, vol. 36, no. 7, pp. 914–944, 2011, Special Issue on Composites. DOI: <https://doi.org/10.1016/j.progpolymsci.2010.11.004>. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0079670010001243>.
- [17] G. Tobias, L. Shao, C. G. Salzmann, Y. Huh, and M. L. Green, “Purification and opening of carbon nanotubes using steam”, *The Journal of Physical Chemistry B*, vol. 110, no. 45, pp. 22 318–22 322, 2006.
- [18] M. Menon and D. Srivastava, “Structure of boron nitride nanotubes: Tube closing versus chirality”, *Chemical Physics Letters*, vol. 307, no. 5-6, pp. 407–412, 1999.
- [19] H. Chen, Y. Chen, J. Yu, and J. S. Williams, “Purification of boron nitride nanotubes”, *Chemical Physics Letters*, vol. 425, no. 4-6, pp. 315–319, 2006.
- [20] Q. Weng, X. Wang, X. Wang, Y. Bando, and D. Golberg, “Functionalized hexagonal boron nitride nanomaterials: Emerging properties and applications”, *Chemical Society Reviews*, vol. 45, no. 14, pp. 3989–4012, 2016.
- [21] D. Golberg, Y. Bando, C. Tang, and C. Zhi, “Boron nitride nanotubes”, *Advanced Materials*, vol. 19, no. 18, pp. 2413–2432, 2007.
- [22] K. R. Parashar Avinash, “Atomistic modeling of bn nanofillers for mechanical and thermal properties: A review”, *Nanoscale*, vol. -, pp. -, 2015. DOI: 10.1039/C5NR06917C.
- [23] A. Matatyaho Ya’akobi, C. J. Ginestra, L. R. Scammell, M. W. Smith, M. Pasquali, and Y. Talmon, “Electron microscopy study of bnnts synthesized by high temperature–pressure method and purified by high-temperature steam”, *Journal of Materials Research*, vol. 37, no. 24, pp. 4508–4521, 2022.
- [24] T. Aoki, “Photoluminescence spectroscopy”, in *Characterization of Materials*. John Wiley Sons, Ltd, 2012, pp. 1–12. DOI: <https://doi.org/10.1002/0471266965.com058.pub2>. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/0471266965.com058.pub2>.
- [25] R. F. Egerton *et al.*, *Physical principles of electron microscopy*. Springer, 2005, vol. 56.
- [26] E. Ruska, “The development of the electron microscope and of electron microscopy”, *Reviews of modern physics*, vol. 59, no. 3, p. 627, 1987.
- [27] K. E. Walker, G. A. Rance, Á. Pekker, H. M. Tóháti, M. W. Fay, R. W. Lodge, C. T. Stoppiello, K. Kamarás, and A. N. Khlobystov, “Growth of carbon nanotubes inside boron nitride nanotubes by coalescence of fullerenes: Toward the world’s smallest coaxial cable”, *Small Methods*, vol. 1, no. 9, p. 1 700 184, 2017.
- [28] M. Martincic, S. Vranic, E. Pach, S. Sandoval, B. Ballesteros, K. Kostarelos, and G. Tobias, “Non-cytotoxic carbon nanocapsules synthesized via one-pot filling and end-closing of multi-walled carbon nanotubes”, *Carbon*, vol. 141, pp. 782–793, 2019.

- [29] S. M. Qaid, B. Al-Asbahi, H. M. Ghaithan, M. AlSalhi, *et al.*, “Optical and structural properties of cspbbr3 perovskite quantum dots/pfo polymer composite thin films”, *Journal of colloid and interface science*, vol. 563, pp. 426–434, 2020.
- [30] B. Fakrach, Y. Kensi, M. Boutahir, A. Rahmani, H. Chadli, and A. Rahmani, “Infrared spectroscopy calculations of multi-walled boron nitride nanotubes: Inner diameter and wall thickness effects”, *Journal of Molecular Structure*, vol. 1254, p. 132 306, 2022.
- [31] J. Chen, K. Zidek, P. Chábera, D. Liu, P. Cheng, L. Nuuttila, M. J. Al-Marri, H. Lehtivuori, M. E. Messing, K. Han, *et al.*, “Size-and wavelength-dependent two-photon absorption cross-section of cspbbr3 perovskite quantum dots”, *The Journal of Physical Chemistry Letters*, vol. 8, no. 10, pp. 2316–2321, 2017.
- [32] Y. Tong, E.-P. Yao, A. Manzi, E. Bladt, K. Wang, M. Dublinger, S. Bals, P. Müller-Buschbaum, A. S. Urban, L. Polavarapu, *et al.*, “Spontaneous self-assembly of perovskite nanocrystals into electronically coupled supercrystals: Toward filling the green gap”, *Advanced Materials*, vol. 30, no. 29, p. 1 801 117, 2018.

A Appendix

Sample Index	Materials and Properties
I. CsPbBr ₃ @o-BNNT-S	CsBr - 99.999% trace metal basis from Sigma Aldrich, PCode: 1003681471 PbBr ₂ - 99.999% trace metals basis from Sigma Aldrich, PCode: 1003681527 BNNT - opened using ammonia treatment from BNNT, SP10RP11B Refined Powder with BN content > 99%, lot: YB03200828E from BNNT, LLC
II. CsPbBr ₃ @o-BNNT-M 570A	CsPbBr ₃ - prepared using solid-state synthesis, BNNT - opened using ammonia treatment from BNNT, SP10RP11B Refined Powder with BN content > 99%, lot: YB03200828E from BNNT, LLC
III. CsPbBr ₃ @o-BNNT-M 570v	CsPbBr ₃ - prepared from solution BNNT - opened using ammonia treatment from BNNT, SP10RP11B Refined Powder with BN content > 99%, lot: YB03200828E from BNNT, LLC
IV. CsPbBr ₃ +BNNT-M 570v	CsPbBr ₃ - prepared from solution BNNT - as-received SP10RP11B Refined Powder, with BN content > 99%, lot: YB03200828E from BNNT, LLC
V. CsPbBr ₃ @o-BNNT-M 620v	CsPbBr ₃ - prepared from solution BNNT - opened using ammonia treatment from BNNT, SP10RP11B Refined Powder with BN content > 99%, lot: YB03200828E from BNNT, LLC
VI. CsPbBr ₃ +BNNT-M 620v	CsPbBr ₃ - prepared from solution BNNT - as-received SP10RP11B Refined Powder, with BN content > 99%, lot: YB03200828E from BNNT, LLC

Table 2: Name of samples and origin of used materials.

A.1 Synthesis of CsPbBr₃ by solid state synthesis

CsPbBr₃ were prepared using solid state synthesis using the precursors CsBr and PbBr₂. The precursors were ground together to a fine powder inside an Argon filled glove box. The powder was annealed in an open combustion boat inside the glove box at 480°C for 5 hour. The precursors used were the following:

CsBr - British Drug House, 99.5% purity

PbBr₂ - 99.999% metal basis, Sigma Aldrich

A.2 Synthesis of CsPbBr₃ from solution

CsBr and PbBr₂ was dissolved in DMSO in 1:1 ratio. After 15 minutes of sonication the solution was filtered through a PTFE syringe filter of 0.2µm pore size. The crystallization was induced by exposing the solution to dichloromethane vapor. The material was prepared by Éva Kováts. The precursors used were the following:

CsBr - 99.999% trace metal basis from Sigma Aldrich
PbBr₂ - 99.999% trace metals basis from Sigma Aldrich