



# LUND UNIVERSITY

## Investigation on Stability of Cesium Lead Bromide quantum dots

BACHELOR'S THESIS

AUTHOR: LINA LE

SUPERVISORS: Dr. Kaibo Zheng  
PhD student Junsheng Chen

EXAMINER: Professor Tõnu Pullerits

## Contents

Abstract .....	2
Populärvetenskaplig sammanfattning .....	2
1. Introduction .....	3
2. Background .....	3
3. Method .....	5
3.1. Samples' preparation.....	5
3.2. Absorbance.....	5
3.3. Photoluminescence (PL) .....	5
3.4. Quantum yield (QY).....	5
3.5. Full width at half maximum .....	6
4. Result and Discussion .....	9
5. Conclusion.....	14
Acknowledgement.....	14
References .....	14

## Abstract

Monodisperse colloidal quantum dots of fully inorganic cesium lead bromide  $\text{CsPbBr}_3$  are synthesised at two distinguished temperatures (120 and 180°C) using inexpensive commercial precursors. The stability of these quantum dots is studied under three different conditions by measuring absorption as well as photoluminescence as functions of time. For both kinds of quantum dots, the light affect their stability while temperature is not an important factor. Quantum dots with low synthesis temperature does not have a clear cubic phase compared to the ones with higher synthesis temperature. Another property that we think might happen for only low temperature synthesised quantum dots is forming of bigger quantum dots through a shrinking-expanding process.

## Populärvetenskaplig sammanfattning

Kolloidal nanokristaller är små kristaller (2-20 nm) som bildar till ett ordnat nätverk. Kolloidal nanokristaller kallas också för nanokristall quantum dots (QDs). Cesium bly bromid  $\text{CsPbBr}_3$  är inorganisk quantum dots med hög stabilitet. Vårt syfte är att bekräfta om  $\text{CsPbBr}_3$  quantum dots är stabila under olika förhållande. Cesium bly bromid QDs syntetiseras vid 120° och 180°C. För varje serie preparerar vi tre prover. De tre proverna sparas i följande konditioner: utan ljus, vid låg temperatur samt utan ljus och med ljus. Vi har observerat att ljuset är den viktigaste faktor som påverkar stabilitet av QDs. Quantum dots som syntetiseras vid lägre temperaturen visar otydligt det kubiska mönstret. Ett förslag för att förklara hur de QDs med låg syntes temperatur ändrar är att några QDs krymper medan andra expanderar.

## 1. Introduction

In the last three years, the halide perovskite materials have attracted huge interest because of their amazing properties as a highly effective semiconductor not only for the solar cell but also for the LEDs and laser <sup>[1]</sup>. All inorganic perovskites have higher stability than hybrid organic-inorganic halides and have huge potential in various optoelectronics. The synthesis, crystallography, and photoconductivity of direct bandgap  $\text{CsPbX}_3$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) have been reported more than 50 years ago but they have not been studied in form of colloidal nanomaterials <sup>[2]</sup>. In this work, we report the stability of quantum dots that have synthesized at 120°C as well as 180°C. Cesium lead Bromide in form of colloidal nanocrystals are thought to have high stability. This investigation is to verify if  $\text{CsPbX}_3$  quantum dots with different synthesis temperature are stable under various conditions. Absorption and photoluminescence were measured to explore the stability of quantum dots under three conditions.

## 2. Background

Tandem solar cells offer an opportunity for increasing the efficiency of existing solar cell technologies without an enormous cost increase. A semiconductor that can be made on a large scale with a bandgap around 1.8 eV is necessary for the manufacture of low cost double-junction solar cells on crystalline Si <sup>[3]</sup>. We have big interest in double-junction solar cells because they can achieve the maximum efficiency within the Shockley-Quiesser limit and be obtained via simple, scalable, low-temperature process <sup>[4]</sup>.

Perovskites absorber materials are required to display long-term stability at 85°C, the upper end of the operational temperature range, and should ideally be stable at 150°C. Organic-inorganic hybrid perovskites such as  $(\text{FA})\text{PbI}_3/(\text{MA})\text{PbBr}_3$  ( $\text{MA}=\text{CH}_3\text{CH}_3$ ,  $\text{FA}=\text{HC}(\text{NH}_2)_2$ ) mixtures have been got huge consideration as absorber materials in single-junction cells because of its record power conversion efficiency of over 20% <sup>[3,5]</sup>. But  $(\text{MA})\text{PbX}_3$  compounds have been shown to be unstable at 85°C due to the volatility of the organic MA cation <sup>[6]</sup>. To solve this problem, the investigation of  $\text{CsPbX}_3$  materials have been started because the inorganic Cs cation is much less volatile.

Semiconducting metal halide perovskites are being studied intensively in optoelectronics, for example voltaic and light emission because of their excellent photophysical properties <sup>[7]</sup>.  $\text{CsPX}_3$  ( $\text{X}=\text{Cl}, \text{Br}$  and  $\text{I}$ ) perovskite-based colloidal nanocrystals (NCs, typically 2-20 nm large) also known as perovskite quantum dots (QDs) have constructed and investigated. Fully

inorganic CsPbX<sub>3</sub> perovskites feature a very favourable combination of quantum-size effects, enhancing their optical with respect to their bulk counterparts, versatile surface chemistry, and a free colloidal state, allowing their dispersion into a variety of solvents [2].

A facial colloidal synthesis monodisperse has been reported, 4-15 nm CsPbX<sub>3</sub> nanocrystals with cubic shape and cubic perovskites crystal structure [2]. CsPbX<sub>3</sub> reveals compositional bandgap engineering, the excitation Bohr diameter up to 12 nm [2] and size-tunability of their bandgap energies through the whole Vis region 410-700 nm. Photoluminescence (PL) of CsPbX<sub>3</sub> is characterized by narrow emission line width of 12-42 nm, high quantum yield of 50-90%, and a short radiative lifetimes of 1-29 ns. Earlier study has published that cesium lead halide nanocrystals crystallize in orthorhombic, tetragonal and cubic polymorphs of the perovskites lattice with a cubic phase being the high-temperature state for all compounds but in later research it is found that all CsPbX<sub>3</sub> nanocrystals crystallize in cubic shape which can be recognised to the combined effect of the high synthesis temperature and influence from the surface energy [2,5,6].

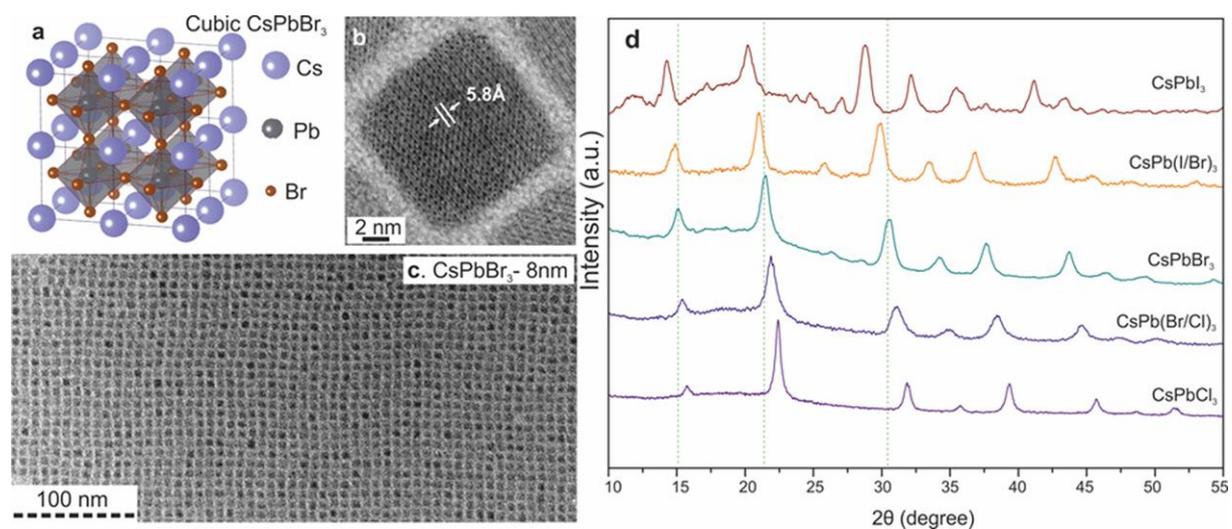


Figure 1. Monodisperse CsPbBr<sub>3</sub> nanocrystals and their structural characterization. (a) Schematic of the cubic perovskites lattice; (b,c) typical transmission electron microscopy (TEM) images of CsPbBr<sub>3</sub> nanocrystals; (d) X-ray diffraction pattern for typical ternary and mixed halides nanocrystals. [2]

## 3. Method

### 3.1. Samples' preparation

Two colloidal solutions of CsPbBr<sub>3</sub> was synthesized at two special temperatures 120°C (smaller quantum dots) respectively 180°C. These colloidal solutions were diluted so that the absorbance was around 0.2. For each set, three sample were prepared:

Sample 1: was put in a locker to avoid the light (shown as no light in graphs)

Sample 2: was put in refridgerator at 5°C (shown as low temperature).

Sample 3: was put under the light of a fumehood. From day 8, the light was switched to LED (shown as light).

### 3.2. Absorbance

UV-Vis absorption spectra for colloidal solutions of CsPbBr<sub>3</sub> were collected in transmission mode.

### 3.3. Photoluminescence (PL)

Photoluminescence was achieved with excitation light at 430 nm. For each sample, the intensity was measured three times. The photoluminescence as a function of wavelength (420 – 650 nm) is shown in Figure 2. To estimate how the photoluminescence peak was shifted, the average PL was normalized and also plotted against wavelengths (Figure 3).

### 3.4. Quantum yield (QY)

Quantum yield is the ratio of absorbed photons to emitted photons. It is difficult to determine the absolute QY so the most convenient way is to calculate the relative quantum yield by comparison to a reference with a well known QY. There are two methods for calculating relative QY: a single point and a comparative method. The single point method uses a integrated emission intensity from a single sample and a reference pair at same concentration. This method is fast and easy to perform but it is sometimes unreliable because of the inaccurated measurement of absorbance. The comparative method use reference with known QY. It takes more time but provides much higher accuracy. That is the reason we used this method to determine the QY of CsPbBr<sub>3</sub> nanocrystals.

The quantum yields of the quantum dots are determined from the following equation:

$$\phi_{f,s} = \phi_{f,st} \frac{F_x}{F_{st}} \frac{f_{st}(\lambda_{ex})}{f_s(\lambda_{ex})} \frac{n_x^2}{n_{st}^2}$$

$$f(\lambda_{ex}) = 1 - T(\lambda_{ex}) = 1 - 10^{-A(\lambda_{ex})} = 1 - 10^{-\varepsilon(\lambda_{ex})cl}$$

Where

$\phi_{f,s}$  is the quantum yield for the CsPbBr<sub>3</sub> quantum dots.

$\phi_{f,st}$  is the quantum yield for the fluorescein (0.1 M NaOH),  $\phi_{f,st} = 0.95$

$F_{st}$  is the area under the emission spectrum of the reference.

$F_x$  is the area under the emission spectrum of the CsPbBr<sub>3</sub> quantum dots.

$n_x$  is the refractive index for toluen,  $n_x = 1.4961$ .

$n_{st}$  is the refractive index for DMSO,  $n_{st} = 1.33$ .

### 3.5. Full width at half maximum

FWHM is the width of photoluminescence spectrum. It is evaluated by measuring the difference between two wavelength values (on x-axis) at the half maximum (on y-axis).

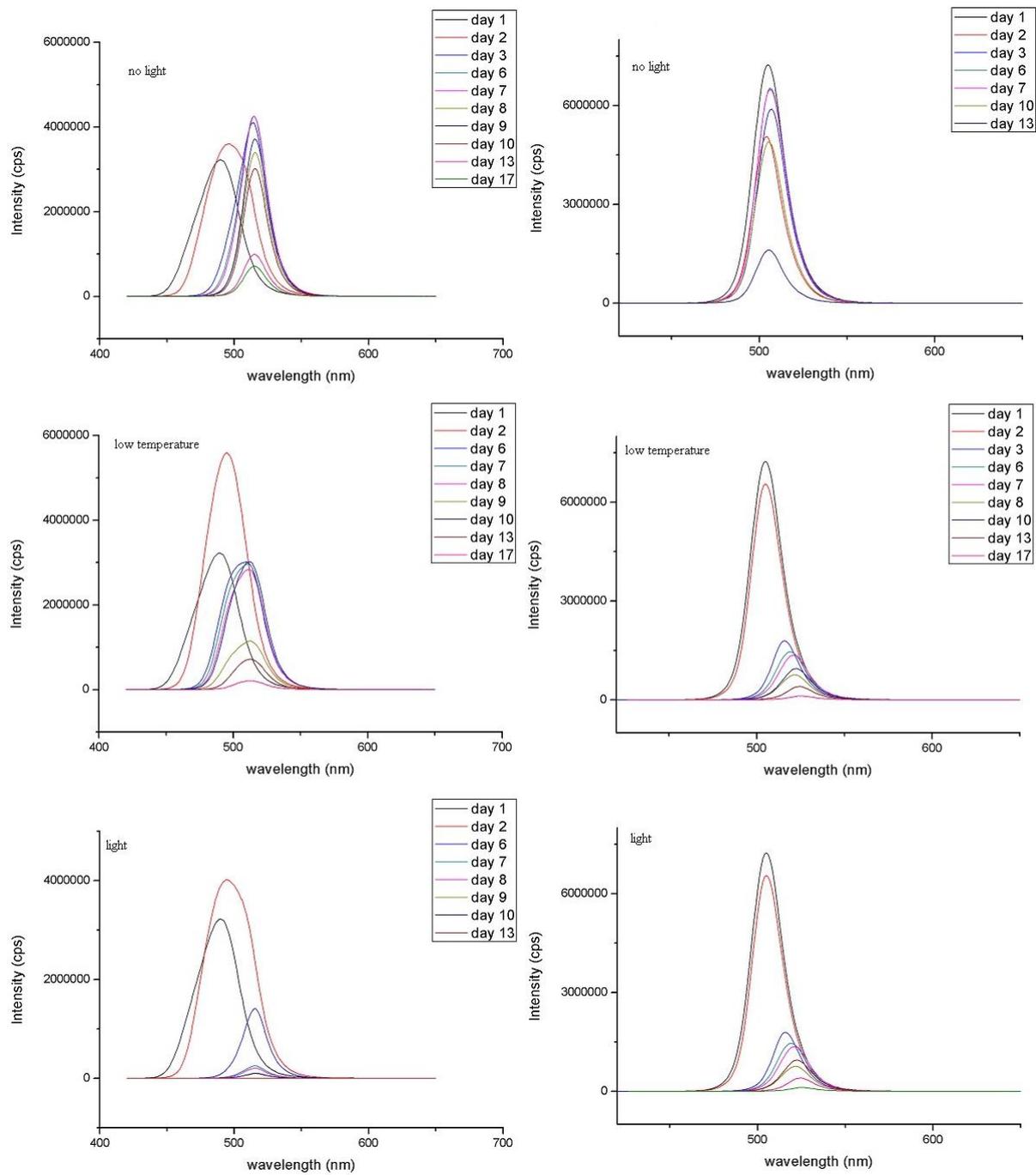


Figure 2. Photoluminescence as function of wavelength. (left) synthesised at 120°C; (right) nanocrystals were synthesised at 180°C.

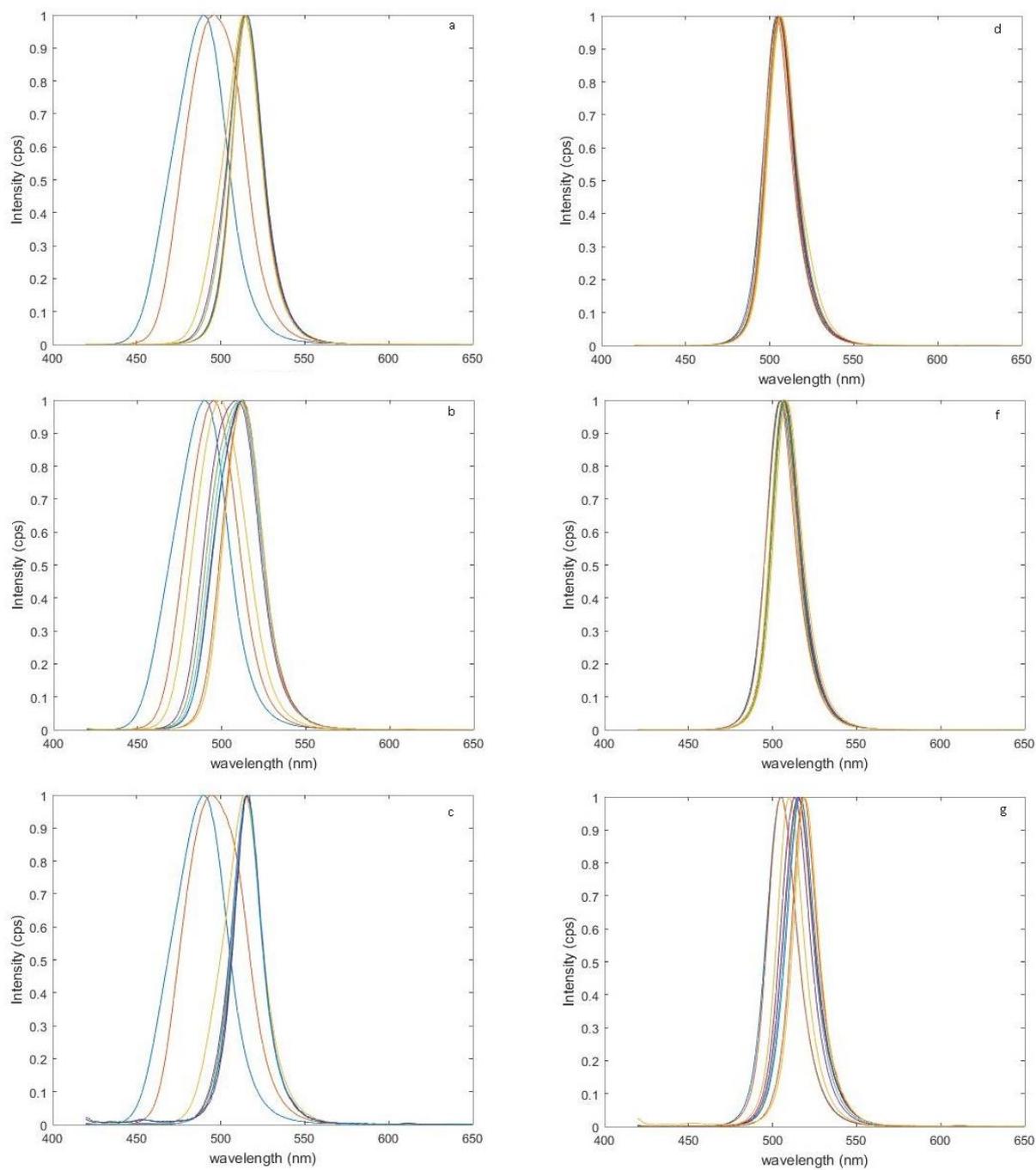


Figure 3. Normalized photoluminescence as function of wavelength. (a,b,c) synthesised at 120°C. Three different samples were stored in without light, at low temperature respectively under light condition; (d,e,f) nanocrystals were synthesised at 180°C and were investigated under the same three conditions as 120°C-samples.

## 4. Result and Discussion

**Absorption spectrum:** In figure 9, a clear red shift is observed for all three samples of 120°C-series. To discuss which possible mechanism did occurred for each sample, the variations are explained in term of aggregation as well as diminishing of QDs. For sample 1 respectively 2, the red tails is shown. This might be the result of aggregation. Sample 3 also shows a decreasing in absorption. Absorbance is an indicator of concentration. Lower absorbance implies a lower concentration. We can conclude that light can make our quantum dots collapse.

As we expected 180°C-samples were much more stable than 120°C samples, there is no obvious red shift in absorption spectrum for sample 1 and 2, only red tails are presented. For sample 3, the same change as 120°C-sample 3 is noticed which are the minimizing of concentration in addition to the red tail. So for both 120°C and 180°C- samples, the light appears to be the cause to the breakdown process of quantum dots. The aggregation occurs in parallel and regardlessly.

**Photoluminescence:** One interesting feature of 120°C-samples is the intensity was increased under the first three days (Figure 6). This gives us a suggestion to understand what really happened. In this case, the number of atoms are constant so what can be varied is the number of quantum dots which indicates the fact that some of quantum dots were shrinking while the others were expanding. After these days, the quantum dots tend to aggregate if the there was no light involved. When quantum dots were in contact with light, the falling apart process would be favoured.

According to what we see in absorption spectrum together with the decay of intensity, it is reasonable to conclude that quantum dots that were synthesized at 180°C remained the same size under whole investigation (Figure 7). For sample 3 of this series, the quantum dots fell apart as well.

Quantum yield gives the information about how the quality of QDs changes with time. QY remains almost at the initial level when the sample is no exposed to light. In the other way, light QY tends to decrease intensively. Figure 4 shows that an ensemble of colloidal CsPbBr<sub>3</sub> exhibits about 80% PL quantum yield with narrow spectral width.

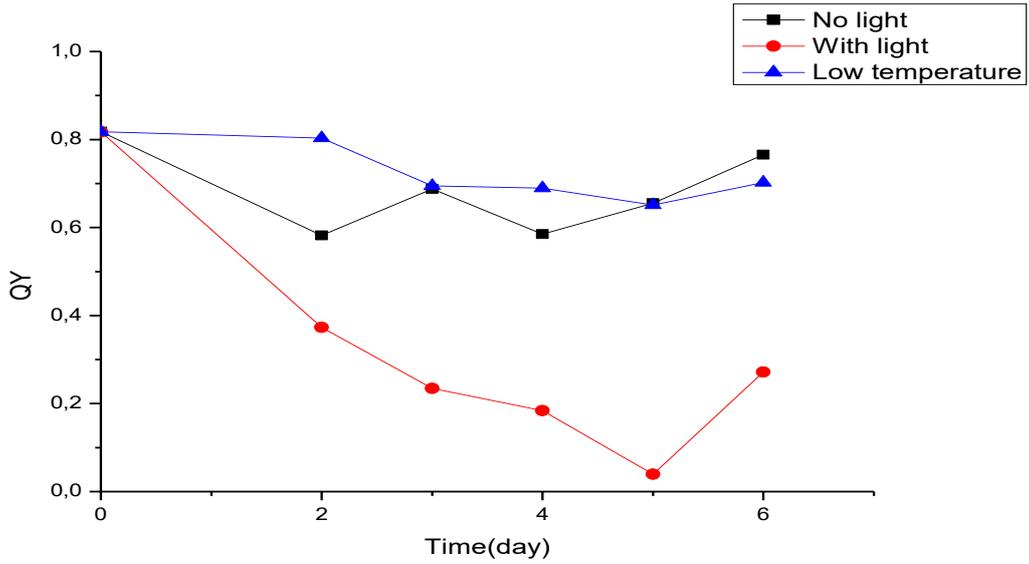


Figure 4. Quantum yields of 180°C-samples as function of time.

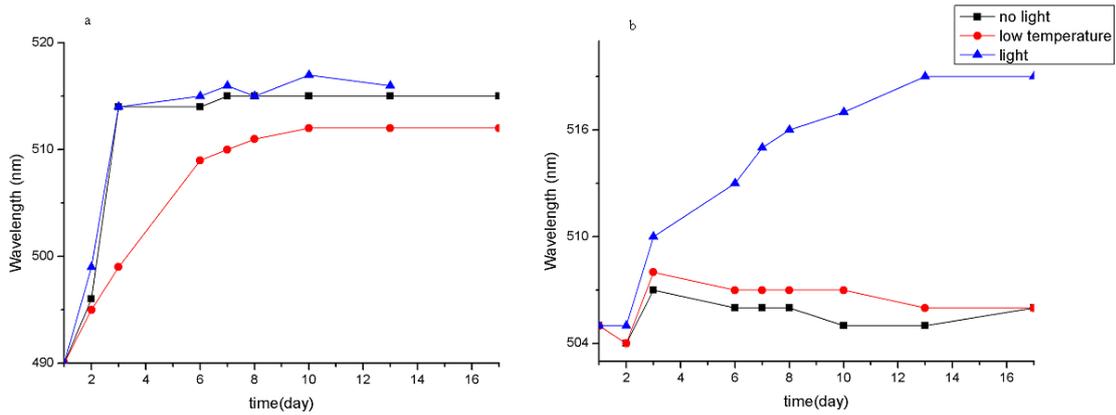


Figure 5. Photoluminescence peak position as a function of time for a) 120°C-samples and b) 180°C-samples.

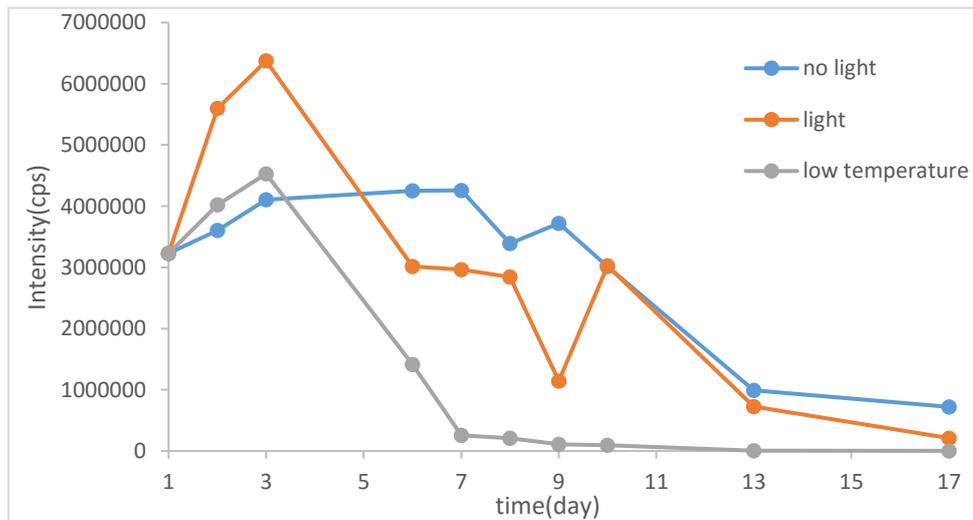


Figure 6. Photoluminescence peak is increased under day 1-3 for 120°C-samples and then decreased for all later days.

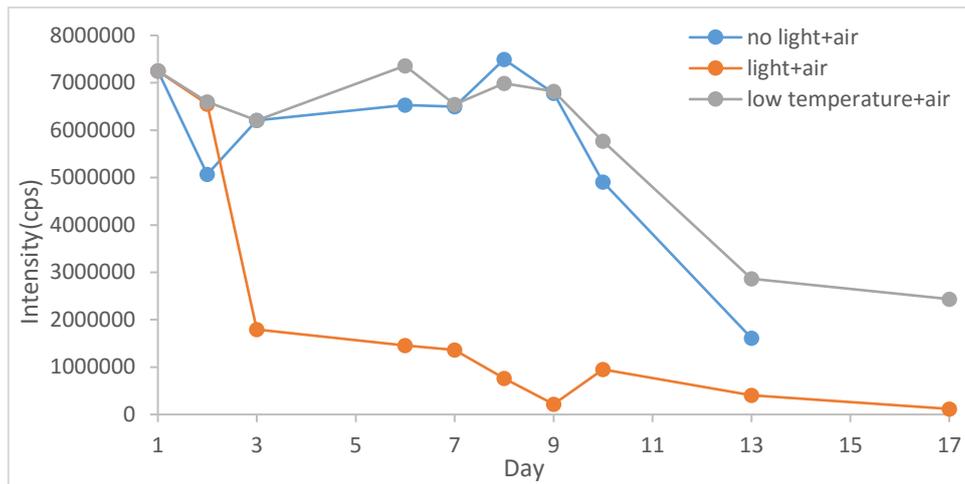


Figure 7. Photoluminescence peaks of 180°C-samples are decreased in general. The most explicit reduction occurs at day 2 for sample 3 and at day 9 for sample 1 as well as 2.

**Full width at half maximum (FWHM):** is related to the size distribution. As the intensity is increased for 120°C-samples, FWHM of sample 1 and 3 also raised under day 1-2. From day 1 to day 2, the quantum dots kept growing in size and the process reached its equilibrium at day 3 which is marked as vast drop of FWHM. After day 3, all quantum dots are thought to be attain the same size. For QDs that were synthesised at 180°C, they do not form bigger QDs but only aggregate and break down if they are in contact with light. Thus, FWHM of 180°C-samples are declined. The most intensive decrease occurs for sample that was stored under light.

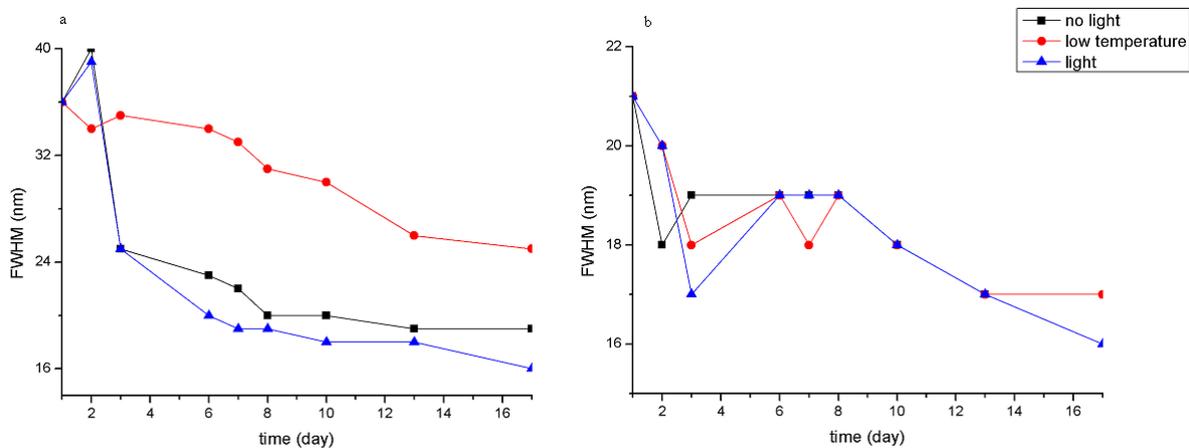


Figure 8. a) Size distribution is increased for sample 1 and 2 of 120°C-series because of difference in size in the the skrinking-expanding process

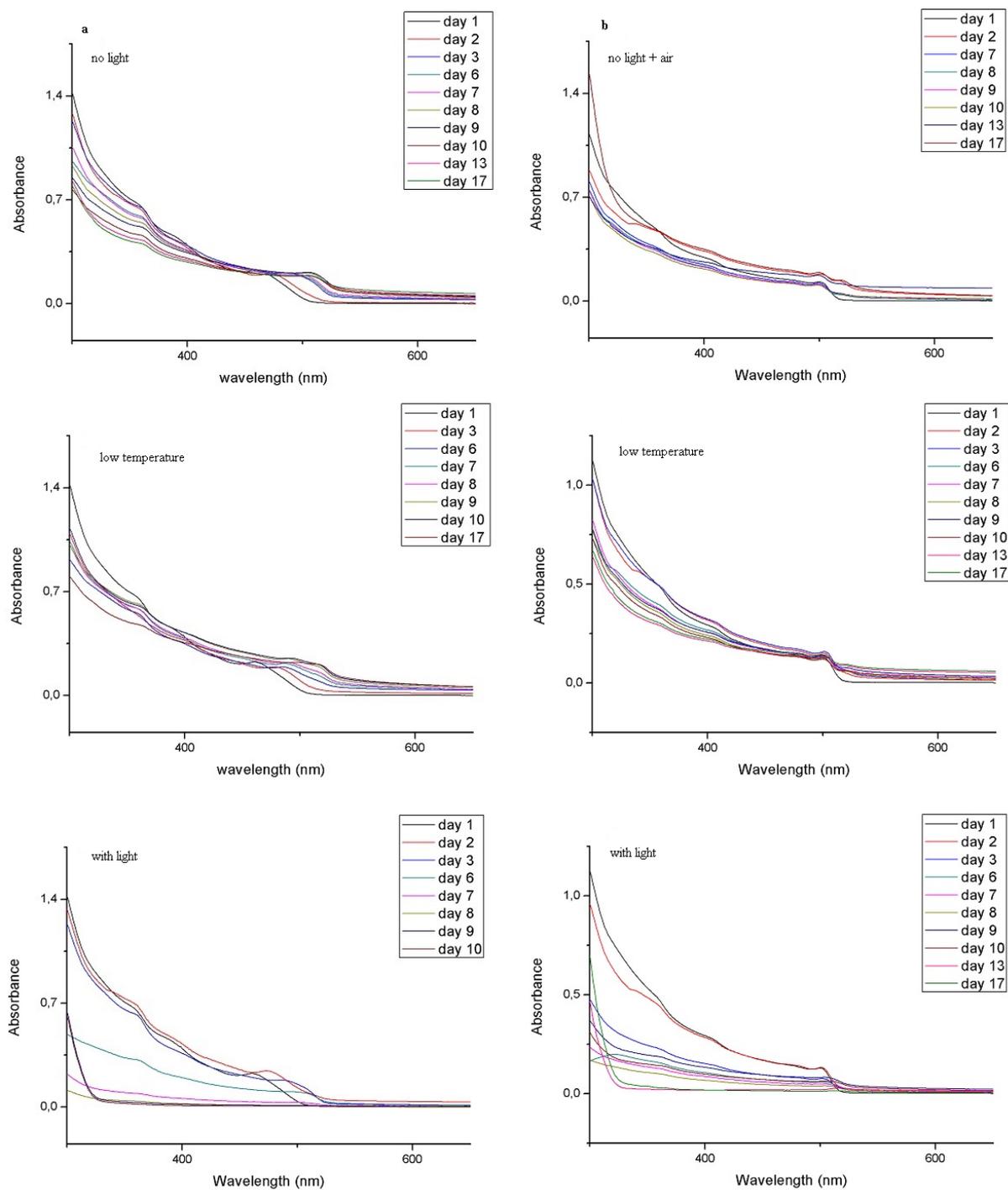


Figure 9. Absorption spectrums of different samples that were synthesized at (a) 120°C (b) 180°C. Non-zero red tail, red shift and lower absorption are presented for 120°C. No sign of red shift is shown showed for sample 1 and 2 of 180°C-series but sample 3 has all three changes.

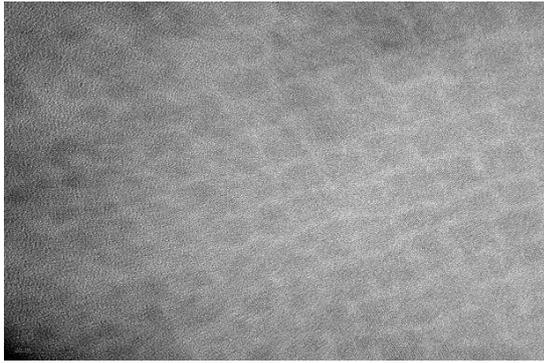


Figure 10. Transmission electron microscopy (TEM) image of CsPbBr<sub>3</sub> nanocrystals which were synthesised at 120°C

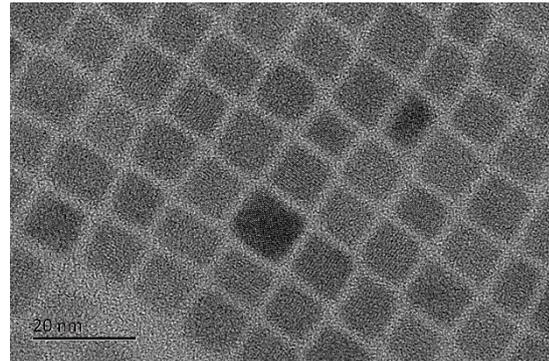
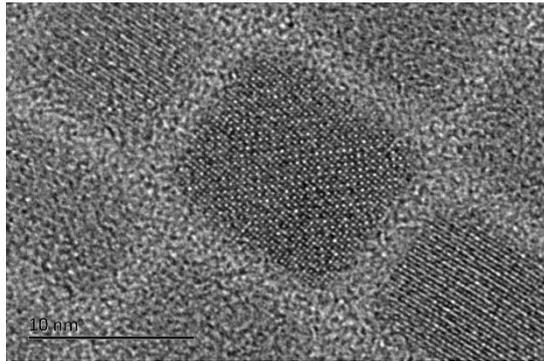


Figure 11. Transmission electron microscopy (TEM) image of CsPbBr<sub>3</sub> nanocrystals which were synthesised at 180°C.

Look at figure 10 and 11, cesium lead bromide nanocrystals is known to crystallize in cubic shape at high synthesis temperature. The TEM images of CsPbBr<sub>3</sub> nanocrystals at different synthesis temperature are in good agreement with what we expected. Nanocrystals that has lower synthesis temperature show imperfect cubic phase while cubic phase is clearly shown for the high synthesis temperature nanocrystals.

## 5. Conclusion

The light is the major factor that affect the stability of CsPbBr<sub>3</sub> quantum dots. Light speeds up the breakdown process of the quantum dots. In cases without light, quantum dots tend to aggregate. An interesting feature that is available only for quantum dots with lower synthesis temperature (120°C) is thought to form larger quantum dots. Quantum dots with this synthesis temperature does not show the perfect cubic phase which is seen clearly for the quantum dots with higher synthesis temperature (180°C).

## Acknowledgement

I would like to thank my supervisors Dr. Kaibo Zheng, Junsheng Chen as well as my examiner Professor Tõnu Pullerits for their guidance under the time I was doing my thesis. I also would like to thank Dongzhou Liu for letting me use his Matlab codes, quantum yield graphs and TEM images.

## References

- (1) Song, J.; Li, J.; Li, X.; Xu, L.; Dong, Y.; Zeng, H. *Adv. Mat* **2015**.
- (2) Protesescu, L.; Yakunin, S.; Bodnarchuk M. I.; Krieg, F.; Caputo, R.; Hendo C. H.; Yang R. X.; Walsh A.; Kovalento, M. V. *Nano Lett.* **2015**, 15, 3692-3696.
- (3) Beal, R. E.; Slotcavage, D. J.; Leijtens, T.; Bowring, A. R.; Belisle, R. A.; Nguyen, W. H.; Burkhard, G. F.; Hoke, E. T.; McGehee, M. D. *J. Phys. Chem* **2016**, 7, 746-751.
- (4) Bailie, C. D.; McGehee, M. D. *MRS Bull.* **2015**, 40, 681-686.
- (5) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. *Nature* **2015**, 517, 476-480.
- (6) Conings, B.; Drijkoningen, J.; Gauquelin, N.; BAbyigit, A.; D'Haen, J.; D'Olieslaeger, L.; Ethirajan, A.; Verbeeck, J.; Manca, J.; Mosconi, E. *Adv. Energy Mater.* **2015**, 5 (15), 1500477.
- (7) Kim, Y.; Yassitepe, E.; Vonznyy, O.; Comin, R.; Walters, G.; Gong, X.; Kanjanaboos, P.; Nogueira, A. F.; Sargent, E. H. *Appl. Mater. Interfaces* **2015**.