

# Novel Rubidium lead chloride nanocrystals: Synthesis and characterization

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## Abstract

Alkali ternary lead halides were studied intensively in the past few years, especially due to the great interest in perovskite materials. In this paper we report on novel rubidium lead chloride nanocrystals (NCs) with the formula  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$ , which adopt a tetragonal symmetry. The NCs were characterized and found to be active in the UV region, with a band-gap of  $\sim 4.05$  eV. The roles of the ligands, oleic acid and oleylamine, were investigated and found to strongly affect the morphology and composition of the NCs, through the stabilization of the facilitated crystallization of the ionic precursors. The effective masses were observed by density functional theory (DFT) calculations, using the dielectric function, and the Bohr exciton radius and exciton binding energy of the NCs were estimated. Moreover the results were supported by the DFT calculations for the electronic properties and atomic structure.

## Introduction

Recently, the knowledge about ternary lead halides was increased rapidly with the evolving research about perovskite compounds. Organic-Inorganic and fully-inorganic perovskite materials were studied intensively in the last few years, mostly in the optoelectronic and solar fields. The excellent properties of perovskites as light harvesting materials in the visible spectrum showed a great applicative potential, both in bulk and nanometric forms. Particularly, the enthusiasm around the fully-inorganic perovskite derived, at first, from stability issues. Eperon et al. reported that replacing the common organic methylammonium (MA) cation with the inorganic cesium cation highly improves the thermal stability of the perovskite, which is a decisive factor in solar cells activity.<sup>1</sup> The major studies of nanometric fully-inorganic perovskite dealt with the Cs-based perovskite. Protesescu et al. reported on fully-inorganic nanocrystals (NCs) with intriguing optical properties, bright and sharp emissions, high photoluminescence quantum yields (PLQY), and high absorption coefficients.<sup>2</sup> Few works reported on tuning the composition of the perovskite by replacing certain atoms in the perovskite formula  $AMX_3$  (A-cation, M- divalent metal, X- halide) in order to discover new features and improvements, including mix cation systems.<sup>3,4,5,6</sup> One of the possible A-cation candidates that was suggested to replace the MA cation<sup>7,3</sup> was the rubidium (Rb) cation, for its advantage as an oxidation-stable mono-valent cation. The formability of Rb-based perovskite can be calculated by the tolerance factor equation  $t = \frac{(r_A + r_X)}{[\sqrt{2}(r_M + r_X)]}$ , which determines whether a compound will form perovskite structure or not.<sup>8</sup> Based on the tolerance factor, it was claimed that  $Rb^+$ , only slightly smaller than  $Cs^+$ , is too small in order to fit in the cubohedral cage of the A-cation in the bulk perovskite structure<sup>3,9</sup>, according to the perovskite expected formability range  $0.813 < t < 1.107$ .<sup>10,11</sup> The tolerance factors of  $RbPbCl_3$ ,  $RbPbBr_3$ , and  $RbPbI_3$  are 0.785, 0.781, and 0.776, respectively. Apparently, the Rb cation does not fit in the perovskite bulk structure, but on the other hand, the synthesis of nanometric Rb-based perovskite was never been published. The surface chemistry of nanocrystals differs from bulk due to a looser structure, thus it is conceivable that perovskite formation would occur in the nanoscale in different conditions than bulk. For instance,  $CsPbI_3$  was investigated as a light harvesting bulk material in solar cells and found to be very problematic for its unstable cubic black phase and high annealing temperature.<sup>1</sup> However, the synthesis of

CsPbI<sub>3</sub> NCs is simple in which cubic CsPbI<sub>3</sub> perovskite NCs are obtained at lower temperatures.<sup>2</sup> Likewise, it is very intriguing to learn how the replacement of the A-cation will affect the properties of the perovskite crystal, optics, and activity in the nanometric sizes. Ghanbari and co-workers reported on RbPbI<sub>3</sub> nanostructures for photocatalysis, synthesized by hydrothermal method, and investigated how different molar ratios of RbI:PbI<sub>2</sub>, reaction time and temperature affect the size and shape of the product.<sup>12</sup> Moreover, RbPbI<sub>3</sub> nanowires were reported. The RbPbI<sub>3</sub> nanowires were found to absorb below 450 nm and exhibited a good photoresponsive activity, suggesting a potential in the optoelectronic field.<sup>13</sup> According to the literature, integrating Rb in the perovskite lattice result in structural distortions that can lead to a different perovskite or non-perovskite phase.<sup>14,15</sup> Beck et al. reported for the first time and investigated the synthesis and crystal structure of Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> phase.<sup>16</sup> Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> was found to crystallize in the tetragonal space group *P4/mbm* with a variety of different coordination polyhedra for the cations. Later, Monzel et al.<sup>17</sup> reported on redetermination of the phase diagram RbCl/PbCl<sub>2</sub>, which was first reported by K. Treis<sup>18</sup> at 1914. They stated that RbPbCl<sub>3</sub> is unstable at room temperature and can be stabilized only above 320 °C. The reinvestigation also revealed the existence of the Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> phase, which is stable at room temperature. Furthermore, Linaburg reported on perovskite phases of RbPbCl<sub>3</sub>, RbPbBr<sub>3</sub>, and RbPbI<sub>3</sub> adopting a cubic symmetry at elevated temperatures, while in room temperature a mixture of tetragonal Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> and monoclinic RbPb<sub>2</sub>C<sub>5</sub> phases is obtained.<sup>9</sup> This reinforces the possibility to fabricate rubidium lead halide crystals. It is important to develop more perovskite and perovskite-like compositions and structures in order to expand their variety of applications. As mentioned above, RbPbCl<sub>3</sub> has the highest tolerance factor, what encouraged us to perform a synthesis of nanometric RbPbCl<sub>3</sub> NCs.

Herein, we report on the synthesis of novel rubidium lead chloride NCs with the formula Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub>. This is the first report on NCs of this material, also using rubidium carbonate (Rb<sub>2</sub>CO<sub>3</sub>) as a new precursor for obtaining this compound, other than RbCl.<sup>9,3</sup> Physical, structural, and optical characterizations are shown and discussed. To support the experimental results, we performed theoretical calculations, using density functional theory (DFT) method<sup>19</sup>, to determine the effective masses, dielectric constant, and the Bohr radius of the NCs.

## Results and discussion

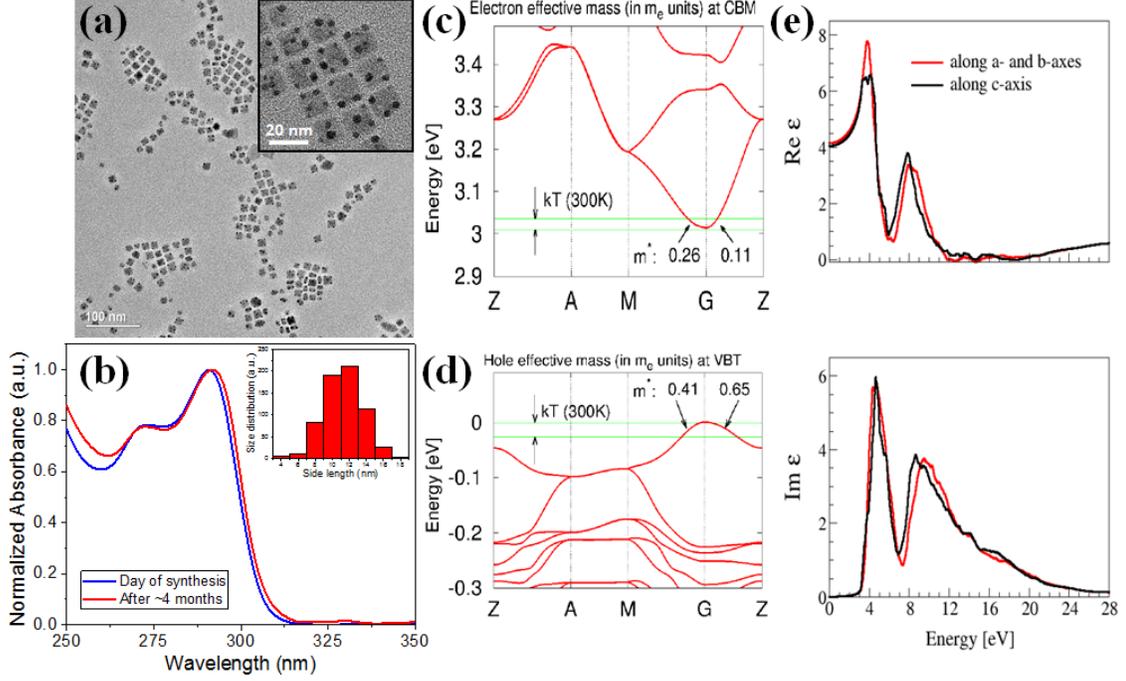
The rubidium lead halide NCs were synthesized by a hot injection method according to the published procedure of protesescue et al.<sup>20,2</sup> Briefly, two precursor solutions were prepared. The first solution contains  $\text{Rb}_2\text{CO}_3$ , oleic acid (OA), and 1-octadecene (ODE) the second solution contains lead chloride ( $\text{PbCl}_2$ ), OA, oleylamine (OLA), tri-n-octylphosphine (TOP), and ODE, while OA and OLA were in a volume ratio of 1:1. Both flasks were heated to 120 °C for 1 hour under vacuum conditions for degassing. Afterwards, the temperature was raised to 150 °C in both flasks under Argon flow. A desired volume of Rb-oleate precursor was injected into the  $\text{PbCl}_2$  precursor solution and the reaction was quenched with an ice bath after a few seconds. The product was precipitated twice with isopropanol to give a white precipitate and re-dispersed with hexane for further characterizations.

**Figure 1a** shows high resolution transmission electron microscope (HR-TEM) images of the as-synthesized NCs with a square-like shape. The inset of figure 1a presents a magnified image of the NCs, revealing some clear black spots upon the NCs (discussed below in further details).

Figure 1b presents the absorbance spectra of the NCs measured at the day of the synthesis and after ~4 months while stored in ambient conditions. The absorbance peaks remained unchanged, showing the long-term stability of these NCs. The absorbance peak is located at ~291 nm and the onset is at ~306 nm, which corresponds to a band-gap of ~4.05 eV. Therefore, the optical activity of the obtained NCs is in the UV spectral region. The band gap of the bulk crystal is 3.01 eV obtained with DFT calculations and 4.13 eV with the pseudopotential self-interaction correction (pSIC) method<sup>21</sup>. This is in a good agreement with the absorption measurement (see figure S1 in the supporting information (SI)). The inset in figure 1b shows a size distribution histogram, based on more than 600 NCs, evaluating the average side length of the NCs to be  $11.29 \pm 0.04$  nm (the size distribution histogram was calculated from data obtained using ImageJ software). In this particles analysis there was an assumption of square-shaped NCs.

The band-structure derived effective masses, averaged over the crystal directions at the valence band top (VBT) and conduction band minimum (CBM), which are 0.53 and 0.19 of the electron mass ( $m_e$ ) for holes and electrons, respectively (see figures 1c,d). These

numbers, together with the calculated dielectric function and its static value  $\epsilon(0)/\epsilon^{\text{vacc}} = 4.1$  (figure 1e), led to the exciton Bohr radius  $a_0 = 1.584$  nm and the exciton binding energy  $E_b = 0.111$  eV. There is a close resemblance between the obtained parameters for  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  and the corresponding numbers for cesium lead halide ( $\text{CsPbX}_3$ ) compounds.<sup>2</sup>



**Figure 1.** (a) A high resolution transmission electron microscopy (HR-TEM) image of rubidium lead chloride NCs. Inset: a magnified image of a few particles. (b) Absorbance spectra of the NCs at the day of the synthesis and after four months. Inset: A size distribution histogram of the NCs measured on 647 NCs. (c) The conduction band minimum (CBM) and the electron effective masses along G-M and G-Z crystal directions. (d) The same as (c) for the valence band top (VBT). (e) The dielectric function: its real part (upper panel) and imaginary part (bottom panel), calculated along the crystal directions (red and black lines).

Furthermore, the crystal structure of the NCs was investigated via structural analysis. X-ray diffraction (XRD) measurement was performed and the results are presented in **figure 2a**. The XRD pattern corresponds to a  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  tetragonal phase, which is a non-perovskite phase. This phase was discovered by Monzel et al.<sup>17</sup> during their work on redetermination of the phase diagram  $\text{RbCl}/\text{PbCl}_2$ , as mentioned earlier. An important insight of this work was that the perovskite phase  $\text{RbPbCl}_3$  cannot exist at room temperature, but as a mixture of the two previously unknown phases,  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  and

RbPb<sub>2</sub>Cl<sub>5</sub>. Only with the application of heat, a phase transition can occur to get the perovskite phase. The first phase transition occurs above 320° to a tetragonal phase of RbPbCl<sub>3</sub>. Higher temperatures resulted in the cubic phase of RbPbCl<sub>3</sub> perovskite. A repeating XRD measurement of the NCs detected 9.8% of Pb<sub>2</sub>O<sub>3</sub> phase inside the Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> NCs and 90.2% of Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> phase (see figure S2 in the SI section). The Pb<sub>2</sub>O<sub>3</sub> phase can be assigned to the black spots in the Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> NCs shown in figure 1a. Previous works on CsPbX<sub>3</sub> NCs reported on black spots that appear as a response to the electron beam during the TEM analysis.<sup>22</sup> In this case, the black spots were integrated in the NCs and were observed in “fresh” areas of the TEM grid, with minimal exposure to the beam. Nonetheless, the black spots became clearer and larger with longer exposure to the electron beam along with decomposition of the brighter parts. There is an obvious difference in the contrasts of the grey nanocrystals and the black spots on top of them (figure 1a). This can imply for high concentration of Pb, which have higher electron density than the other atoms in this compound, resulting in a higher contrast.

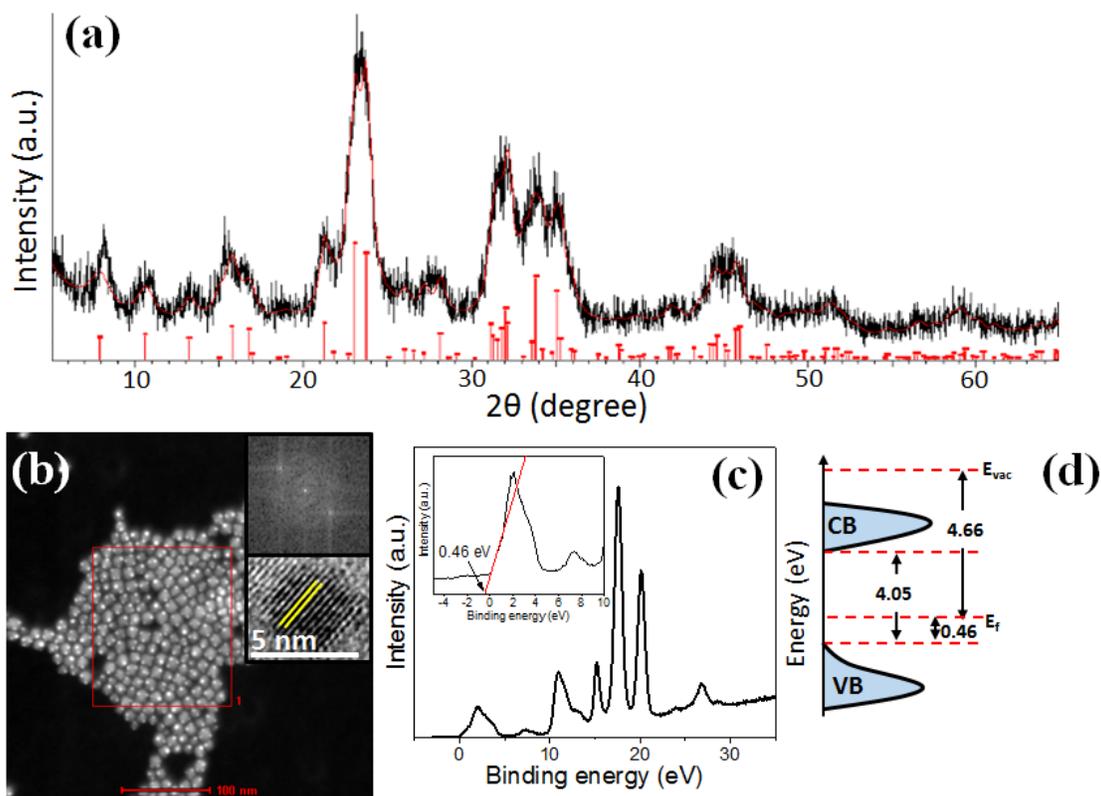
Dark scanning transmission electron microscopy (STEM) and energy-dispersive x-ray spectroscopy (EDS) were applied in order to confirm the composition of the NCs and the black spots inside the NCs, as can be seen in figure 2b and figure S3. In figure S3, the EDS spectrum detected the atoms Rb, Pb, Cl and O in the region of interest. Following quantification analysis determined the atomic percentage of the atoms to be 17.40, 28.89, 37.62, and 16.07, respectively. The reasonable assumption is that the ratio between Rb and Pb is ~1:1, according to the XRD, so that the remained Pb are possibly bound to the detected O atoms to create a lead oxide phase or alternatively, metallic lead nanoparticles, as previously reported for similar observations.<sup>23</sup>

The inset of figure 2b shows HR-TEM image of a black spot (within the NC) with the corresponding fast Fourier transform (FFT), related to plain (111) of metallic Pb. More areas were scanned and the results are presented in the SI section (figure S4). EDS analysis (figure S3) indicated a higher content of Pb, reinforcing the assumption of the black Pb-rich particles within the Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> NCs to be either lead oxide or metallic Pb nanoparticles. It is predicted that the Pb-terminated surface opens the octahedral hole with Rb<sup>+</sup> in the center, which is a sensitive adsorption site for the oxygen atom from the oleic acid; leading to a termination of its molecules with the H-C=O group, instead of COOH.

This scenario is consistent with the crystallographic data which report 9.8% of  $\text{Pb}_2\text{O}_3$  phase in the reported NCs (figure S2). The rubidium atom takes a role of a cation in the crystal, thus its properties to bind oxygen are opposite to the electron-rich elements of the VI-group (i.e. Se) – present for example in PbSe where the  $\text{Pb}_x\text{O}_y$ -type structures are not found.<sup>24</sup>

X-ray photoelectron spectroscopy (XPS) analysis (figure S5) detected the presence of Rb, Pb, and Cl atoms with a ratio of ~1:1 between Rb and Pb, as expected. The atomic percentage of Cl was lower than expected, as described in table S1 in the SI section. This may occur due to evaporation of  $\text{Cl}_2$  molecules during the measurement.

In order to study the electronic properties of these  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  NCs more deeply, valence band (VB) XPS measurement and surface photovoltage spectroscopy (SPV) were performed. The valence band XPS measurement was applied for determination of the valence band (figure 2c). This measurement gives information about the density and occupancy of electronic states in the valence band of the material, while the edge of the graph gives an evaluation of the VBT. The inset of figure 2c presents the extracted VB value, 0.46 eV below the Fermi level. The work function of the NCs was measured using the SPV method and found to be 4.63 eV. An overview of the band diagram of the NCs is presented in figure 2d.

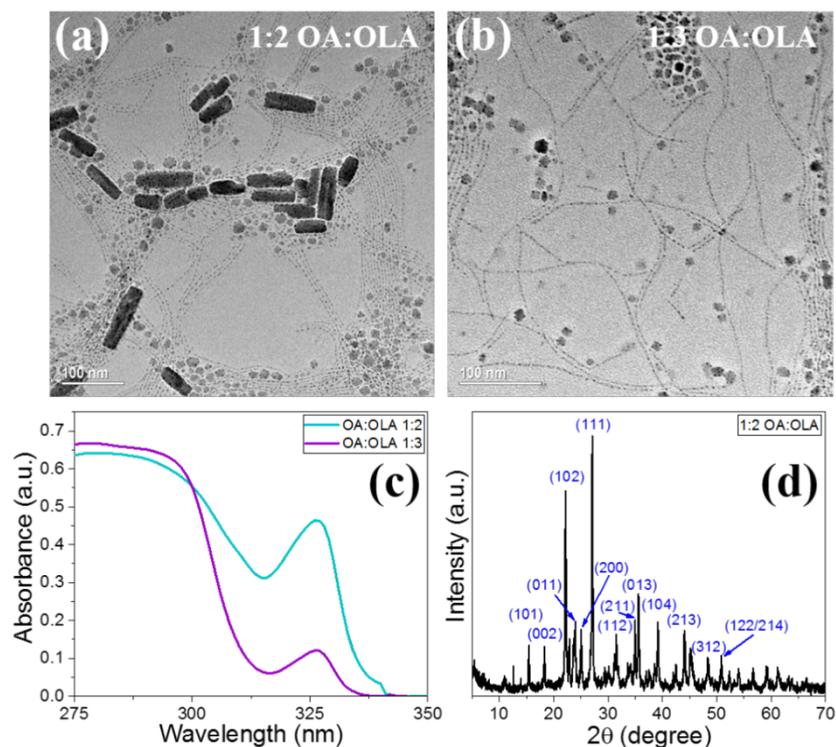


**Figure 2.** (a) Experimental (black) and simulated (red) x-ray diffraction (XRD) patterns of rubidium lead chloride NCs that show the correspondance to a tetragonal  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  phase. (b) A scanning transmission electron microscopy (STEM) image. Insets: high magnification of a Pb-rich particle inside a  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  NC with d-spacing that corresponds to plane (111) of metallic Pb and its corresponding FFT. (c) X-ray photoelectron spectroscopy (XPS) spectrum of the NCs measuring electronic states in the valence band. Inset: a magnified area of the graph near the valence band edge. (d) A schematic overview of the band diagram of the NCs.

To learn more about the influence of the ligands on the features and the crystallization process of the  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  NCs, a study of the ligands' roles was conducted. As described earlier, the ligands ratio in the  $\text{PbCl}_2$  precursor solution was 1:1. While keeping the total molar content of both ligands constant, mixtures of OA:OLA in a volume ratios of 1:2 and 1:3 were synthesized and studied. The use of oleic acid and oleylamine pair is well-known in the syntheses of perovskite NCs.<sup>25</sup> There is a dynamic equilibrium of acid/base in similar colloidal systems.<sup>26</sup> In this case, the oleic acid donates a proton to the oleylamine and turns into an oleate anion, as the oleylamine ligand is protonated and turns into an oleylamminium cation.<sup>27</sup> **Figure 3a** depicts an HR-TEM image of 1:2 OA:OLA NCs in

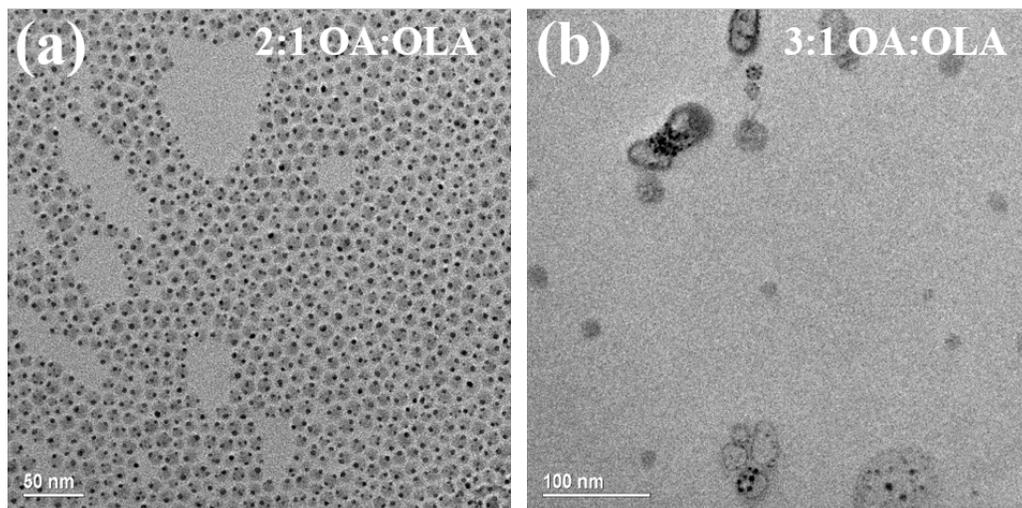
which few morphologies are observed, including relatively large rectangles, long thin nanowires (NWs) consist of small black dots, and distorted square-like phase, similar to the NCs with 1:1 ratio (figure 1a). Upon increasing the OLA concentration to 1:3 OA:OLA, as shown in the HR-TEM image in figure 3b, there are similar observations as the 1:2 OA:OLA NCs. In this case, the large rectangles do not appear. A synthesis with OLA alone (without OA) was carried out as well for a complete investigation, however, a minimal volume of OA is necessary in order to completely dissolve the  $\text{PbCl}_2$ . Therefore, the OA has an important role in solubilizing the  $\text{PbCl}_2$ .<sup>2</sup> Based on the HR-TEM images, it seems that an increase of OLA excess in this synthesis affects the NCs' shape. It was previously claimed that acid-base pair has a definite impact on the morphology and optical properties of a similar system of perovskite NCs.<sup>26</sup> The new morphologies can be an indication that the binding of OLA to the surface is chemical and not physical, so variable amounts of OLA ligands can change the growth directions of the NCs by blocking certain crystallographic facets. However, if the concentration of OLA is increased at the expense of the OA, it may reduce the protonation process, resulting in less protonated OLA species, i.e., less oleylammonium cations. These conditions may increase the coordinative bonding of the unprotonated OLA species with the  $\text{Pb}^{2+}$  cations on the surface, rather than the electrostatic interaction of the oleylammonium cations with the  $\text{Cl}^-$  anions in the lattice. This can explain the elongated structures that appear in figures 3a,b. The absorbance measurement is shown in figure 3c presenting an optical red shift, relative to the OA:OLA 1:1 case, with peak position at  $\sim 326$  nm and onset at  $\sim 336$  nm. The unexpected optical shift can indicate a possible change in the chemical composition. To decipher these results, XRD measurement was applied for the 1:2 product. Surprisingly, the XRD spectrum detected a main orthorhombic  $\text{Pb(OH)Cl}$  phase (figure 3d). The XRD peaks perfectly matched the standard XRD pattern of orthorhombic  $\text{Pb(OH)Cl}$ . Previously, few works reported on the mineral  $\text{Pb(OH)Cl}$ .<sup>28,29,30,31</sup> Chen et al. reported on  $\text{Pb(OH)Cl}$  nanotubes that absorb in the UV region, at 258 nm and 292 nm<sup>28</sup>, which is similar to the absorbance of the obtain nanostructures. A possible explanation to the phase transfer into  $\text{Pb(OH)Cl}$ , based on both TEM and XRD analyses, is that higher content of unprotonated OLA ligands may interact with larger areas on the surface of the NCs and avoid Rb-oleate species from participating in the crystallization of the NCs, yielding in another Rb-free crystal phase of  $\text{Pb(OH)Cl}$ . In

addition to the Pb(OH)Cl phase, the XRD of the 1:2 product also detected minor content of Pb<sub>2</sub>O<sub>3</sub> and Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> phases. In comparison, the XRD of the 1:3 product detected only the Pb(OH)Cl phase (figure S6). This strengthens the suggested mechanism that an increase of OLA content enhance the formation of Pb(OH)Cl, repelling Rb-oleate species in the growth processes. For a better insight into this issue, the interaction of the Pb-terminated (001) surface with the oleic acid molecules were simulated. A shorter molecule than the OA molecule was used for the simulation (see figure S7), since the COOH group is the functional group, which attached to the NCs surface. Three plausible geometric configurations were assumed (figure S8) and their atomic structures were optimized. Two of these reactions end up with the oxygen atom on top of Rb from a cavity of the triangular shape set by three Pb surface atoms. The formation energy is -2.88 eV in a case when the acid molecule swaps the -OH termination into =O and -H, attached directly to the C atom which lost =O (see figure S7). The -OH group can also build the surface; if it takes the position between two Pb atoms, then the formation energy is -2.59 eV (see figure S8). Before the reaction, no charge transfer was observed to the surface, thus the band structure was not affected by a proximity with the acid (see figure S9). In contrast, the adsorption of O or OH affects the band gap, as expected (see band structures in figure S10). Both cases cause the red shift; it is about 0.4 eV for the oxygen adsorption case, and it seems to be a multi-excitation between many impurity states for the surface reaction with -OH. However, the oscillator strengths need to be further investigated with more advanced methods, in order to find which optical transitions are active.



**Figure 3.** HR-TEM images of obtained NCs with volume ratio of 1:2 (a) and 1:3 (b) of oleic acid (OA) and oleylamine (OLA), respectively (OA:OLA). (c) Absorbance spectra of the NCs in both cases. (d) An XRD pattern of the NCs with 1:2 ratio of OA:OLA that corresponds to a main orthorhombic phase of Pb(OH)Cl. The spectrum of the NCs with ligands ratio 1:3 OA:OLA is similar to the one presented in (d) and can be found in the SI section, figure S6.

In addition, the opposite case was examined to further understand the ligands' roles. Accordingly, syntheses with ligands ratios of 2:1 OA:OLA and 3:1 OA:OLA (**figures 4a,b**) were performed. In figure 4a, the obtained NCs have a distorted shape, compared to the 1:1 OA:OLA NCs. According to literature, the oleate ligands are effective in the control of the size of more isotropic structures<sup>26</sup>, as seen in figure 4a, and in contrast to the case of OLA excess. In the case of 1:3 OA:OLA ratio, as presented in figure 4b, the NCs did not form at all. The reason for that can be insufficient amount of OLA which can severely affect the stabilization of the forming NCs. The concentration of OLA is probably too small in order to form free-standing NCs due to less coordinative bonding of oleylammonium ligands to the metal cations on the surface.



**Figure 4.** HR-TEM images of rubidium lead chloride NCs with volume ratios of (a) 2:1 and (b) 3:1 of oleic acid (OA) and oleylamine (OLA) ligands.

## Conclusions

This paper reports the synthesis of rubidium lead chloride NCs as a novel UV-active material with intriguing features and complicated structure. HR-TEM analysis revealed some speckled square-like shaped NCs and XRD determined the symmetry of tetragonal  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  phase. Theoretical calculations of electronic and structural properties were correlated with the experimental data. Different ligands ratios appeared to change the morphology and crystal structure of the NCs into a main phase of  $\text{Pb}(\text{OH})\text{Cl}$  with an optical

red shift. The suggested mechanism indicates that a high content of OLA relative to OA can affect the crystallization process by insufficient oleylammonium species to stabilize the Pb cations. In this case there is more coordinative bonding of unprotonated OLA ligands to the Pb cations on the surface, which minimizes the interaction of Rb-oleate species with the growing surface. The result was a main Pb(OH)Cl phase without any Rb cations in the lattice. A work by Shu et al.<sup>29</sup> suggests that Pb(OH)Cl material can function as an anode for lithium-ion batteries, which can be very attractive in the nanometric scale as well. Moreover, it can function as a precursor in the synthesis of PbSe nanocrystals.<sup>31</sup> Future experiments will focus on synthesis modifications in order to achieve the perovskite phase of RbPbCl<sub>3</sub> in the nanoscale, as well as in the bulk form. The UV optical properties of the as-synthesized NCs can be utilized for ultra violet light emitting diodes (UV-LED) or lasing applications.

## Experimental

**Chemicals.** Rubidium carbonate (Rb<sub>2</sub>CO<sub>3</sub>, 99%, Sigma-Aldrich), lead (II) chloride (PbCl<sub>2</sub>, 98%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), oleylamine (OLA, 70%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), trioctylphosphine (TOP, 97%, Strem), 2-propanol (≥99.8%, Sigma-Aldrich), and hexane (not pure, Gadot) were purchased and used as received, without any further purification.

**Preparation of Rb-oleate.** Rb-oleate precursor was prepared according to previous published procedure by Protesescue et al.<sup>2</sup> 0.138 g of Rb<sub>2</sub>CO<sub>3</sub> were mixed with 625 μL of oleic acid (OA) and 7.5 mL of 1-octadecene (ODE) in a 100 mL 3-neck flask. The solution was degassed for 1h under vacuum at 120 °C and then heated to 150 °C under Ar flow.

**Synthesis of Rb<sub>6</sub>Pb<sub>5</sub>Cl<sub>16</sub> NCs.** The NCs were synthesized according to Protesescue et al.<sup>2</sup> 0.052 g of PbCl<sub>2</sub> were mixed with 0.5 mL of OA, 0.5 mL of OLA, 1 mL of TOP, and 5 mL of ODE in an additional 100 mL 3-neck flask. The mixture was degassed for 1h under vacuum at 120 °C and then heated to 150 °C under Ar flow. The reaction was carried out by injection of 0.4 mL of the Rb-oleate precursor solution into the PbCl<sub>2</sub> precursor solution. The reaction was quenched using an ice bath after a few seconds. Isopropanol was added to the crude solution in a volume ratio of 1:1 and the NCs were centrifuged at 6000 rpm

for 10 min. The last stage was repeated once and then the purified NCs were dispersed in hexane for further characterization.

**Transmission Electron Microscopy (TEM).** Morphology and elemental composition of NCs were analyzed with HR (S)TEM (High Resolution Scanning Transmission Electron Microscope) Tecnai F20 G2 (FEI Company, U.S.A.). Samples preparation was performed as follows: 3.5  $\mu\text{L}$  of the NCs dispersion were dropped on a copper grid coated with amorphous carbon film, then the solvent was evaporated using a vacuum chamber. Elemental analysis of NCs was done with EDAX EDS (Energy Dispersive X-Ray Spectroscopy) when the microscope was operated in STEM mode at accelerating voltage 200 kV.

**X-ray Diffraction (XRD).** Powder X-ray diffraction measurements were performed on the D8 Advance Diffractometer (Bruker AXS, Karlsruhe, Germany) with a secondary graphite monochromator,  $2^\circ$  Soller slits, and 0.2 mm receiving slit. The powder samples were placed on low background quartz sample holders. XRD patterns within the range  $3\text{--}65^\circ 2\theta$  were recorded at room temperature using  $\text{CuK}\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) with the following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of  $0.02^\circ 2\theta$ , and counting time of 1 s per step.

**Absorption Measurements.** Absorption spectra were recorded using Jasco V- 670 spectrophotometer.

**X-ray photoelectron spectroscopy (XPS).** The electronic structure and chemical state of the  $\text{Rb}_6\text{Pb}_5\text{Cl}_{16}$  NCs were characterized by the X-ray photoelectron spectroscopy (XPS). The XPS measurements were done using a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, U.K.). Spectra were acquired using an Al  $\text{K}\alpha$  monochromatic radiation source (1486.7 eV) with  $90^\circ$  take-off angle (normal to analyzer). The vacuum pressure in the analyzing chamber was maintained at  $2 \times 10^{-9}$  Torr. The XPS spectra were collected with pass energy 20 eV and step 0.1 eV. The binding energies were calibrated relative to the C 1s peak energy position as 285.0 eV. Data analyses were done using Casa XPS (Casa Software Ltd.) and the Vision data processing program (Kratos Analytical Ltd.).

**Surface photovoltage spectroscopy (SPS).** Work function (WF) measurement was performed using the SKP5050-SPS040 system. The contact potential difference (CPD)

between the sample and the vibrating tip was measured by the Kelvin probe technique. The sample was measured in a Faraday cage under air environment in three different points. Before the measurement, the sample was stabilized with a tip for about 15 minutes. The scan direction was from long to short wavelength. The WF was calculated according to:  $WF_{sample} = WF_{tip} + CPD$ . The WF function of the tip was calibrated above the gold stage.

**Density functional theory (DFT).** The pseudopotential based plane-wave code, named Quantum ESPRESSO<sup>32</sup>, was used for the DFT calculations. We have our pSIC implementation<sup>33</sup> in the above package. The band structures were accurately interpolated via the matrix elements of the Hamiltonian between the maximally-localized Wannier functions<sup>34</sup> obtained with the wannier90 code<sup>35</sup>. The formation energies were calculated from the total energies of the substrates and the final atomic configuration, via the formula:  $E_{form} = E_{total}(\text{surface+adsorbate}) - E_{total}(\text{surface}) - E_{total}(\text{adsorbate})$ . The hole and electron effective masses were estimated from the densely interpolated bands at the VBT and CBM, respectively, via the equation  $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}$ . The dielectric function was calculated with the epsilon.x code from the Quantum ESPRESSO suite. Thus, the excitonic parameters were obtained from the relations:  $\alpha_0 = \frac{4\pi\hbar^2 \epsilon \epsilon^{vac}}{m^* e^2}$  and  $E_b = \frac{m^*}{m_e \epsilon^2} 13.61 \text{ eV}$ . Further details are given in SI.<sup>36</sup>

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### Competing financial interests

The authors declare no competing financial interests.

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