Dehydration process in 1D ammonium lead halide and mixing of organic cations in hybrid perovskites through mechanosynthesis

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Abstract

Organic-lead halide perovskites have attracted much attention as a promising material for optoelectronic and photovoltaic applications. However, the broad commercial use of such materials is hindered by their chemical instability. The detrimental processes of degradation often involve the occurrence of hydrated compounds. However, the knowledge of some aspects related to the thermal stability of hydrated lead halides compounds is still very limited. In this work, we report the structural study dealing with the formation of NH₄PbI₃ obtained by removing crystallization water from NH₄PbI₃ (H₂O)₂ with thermal treatment. The hydrated compound is prepared by solvent-free grinding applied on a mixture of NH₄I and PbI₂ powders. Upon heating, the structural evolution of the de-hydration process, monitored by powder x-ray diffraction, consists in the rearrangement of the 1D chains of octahedral PbI₆ units throughout rotations around a specific crystallographic axis. Besides, the fabrication of the solid solution (CH₃NH₃)₁₋ₓ(NH₄)ₓPbI₃ with x = 0, 0.05, 0.10, 0.20 is attempted with different conditions of mechanosynthesis. The experimental results confirmed the limited solubility of the NH₄⁺ group in the methylammonium lead iodate perovskite with a maximal substitution limit of 5%.

Introduction

In the last years, mesoscopic organic-inorganic perovskites ABX₃ with X = Cl, Br or I gathered increasing attention owing to their outstanding photovoltaic performance with power conversion efficiency reaching 25.2% [1, 2]. The growing interest in the use of these hybrid perovskites is due to their unique combination of crucial properties for the massive employment in the photovoltaic (PV) technology: wide band gap tunability with an appropriate choice of metals, halogens and organic cations; a high dielectric coefficient; absorption in the visible spectrum [3, 4]. The semiconductor CH₃NH₃PbI₃, methylammonium lead iodide (MAPbI₃), represents the prototypical benchmark showing a series of positive aspects mainly related to the sustainable fabrication of solar cells [5–7].

Nevertheless, dispositive based on PV perovskites have life-time extremely low, barely achieving few months even if protected by physical barriers [8, 9]. The degradation of halide perovskite materials mainly rely on the presence of organic cations sensitive to ambient conditions, such as the intensity of the radiation to which the device is exposed, temperature and atmosphere (as a variation in the content of atmospheric oxygen) [10–12]. For instance, after exposure to humidity, MAPbI₃ turns into MAI and PbI₂ causing the substantial degradation of the device with a complete suppression of the optoelectronic properties. Actually the identification of the products obtained by humidity-induced decomposition of MAPbI₃ and the relative degradation pathway is still matter of debate [13]. The exposure to humidity contributes to the formation of hydrate products such as MAPbI₃(H₂O)₂ or (MA)₂PbI₄(H₂O)₂ that cause negative effects on the morphology of the thin films and consequent degradation of the PV properties [2, 14, 15]. Solid solutions of formamidium lead iodide (FAPbI₃)
and MAPbI$_3$ are indicated as one of the most promising material for the design of the new generation PV devices. In contrast, it has been demonstrated that the FAPbI$_3$ is subjected to the transformation into NH$_4$PbI$_3$ in conventional ambient conditions [16, 17]. The gradual formation of hydrated compounds is also observed in mixed halide perovskites such as Cs$_x$FA$_{1-x}$Pb(Br$_x$I$_{1-x}$)$_3$ wherein the degradation proceeds with intermediate different byproducts depending on the diverse experimental conditions [18]. The ammonium based NH$_4$ compound plays also an important role in the conversion of porous NH$_4$PbI$_3$ polycrystalline deposition into MAPbI$_3$ thin film with stunning morphological properties [19]. The starting hydrated compound is converted in MAPbI$_3$ with the exposure to CH$_3$NH$_3$ gas at ambient conditions, opening the avenue to the affordable production of thin films showing enhanced mesoscopic properties [19].

As recent literature highlights, the hydrated compounds in the halide lead-based compounds are observed in limited number of compositions but, they play a crucial role in many aspects of the chemistry of such materials [15–19]. In this perspective, we investigated the decomposition of the hydrated compound NH$_4$PbI$_3$(H$_2$O)$_2$ with the progressive structural transformation into NH$_4$PbI$_3$ during heat treatment. We documented the structural evolution triggered by the release of crystallization water molecules involving the concerted rotation of the edge-sharing ribbons composed by octahedral Pb$_6$ units.

Then, we pursuit the fabrication of solid solutions with nominal (CH$_3$NH$_3$)$_{1-x}$(NH$_4$)$_x$PbI$_3$ $x = 0, 0.05, 0.10, 0.20$ composition following different mechanosynthesis procedures. The experimental results confirmed the limited solubility of NH$_4$ in the perovskite lattice with a maximal amount of 5%. Our findings are in agreement with what suggested by the empirical approach related to the application of the tolerance factor for perovskite structures [20].

**Experimental methods**

The synthesis of NH$_4$PbI$_3$(H$_2$O)$_2$ was carried out by manual grinding. The compound is obtained by adding a 1:1 mix of PbI$_2$ and NH$_4$I powders in a mortar. The powders were ground for 6–5 min sessions for a total of 30 min of grinding. The reaction was attempted by adding few drops of different solvents as lubricant; we tried acetone and water in separated synthesis processes. However, it was found that the addition of such solvents avoided the phase formation by promoting the decomposition and return to the starting reagents, disadvantaging the formation of NH$_4$PbI$_3$(H$_2$O)$_2$. It was therefore found that the best way to obtain the compound was a solvent-free route that earns 100% yield of single phase.

The mechanosynthesis sessions was carried out by using two planetary ball milling systems: (a) Pulverisette 7 Classic Line (Fritsch) planetary ball milling machine, (b) Retsch planetary mill 100. Both milling systems was used with agate pots and a variable number of agate balls. Specially by using the Retsch milling system, we checked different conditions in terms of run per minute (RPM) and duration of milling. All the mechanosynthesis procedures was attempted without the use of solvent or surfactants.

The structural analysis was performed by powder x-ray diffraction PXRD with the Thermo XTRA diffractometer working with a Cu K$_\alpha$ radiation and equipped with a solid state detector Si(Li) suited to suppress the K$_\beta$ radiation. The XRD measurements collected at different temperatures was undertaken by using a TTK450 Anton Paar camera in the temperature range from room temperature RT to 90 °C. Rietveld and fitting refinements was carried out by using Jana2006 suite [21].

Thermal analysis on the hydrated compound was carried out with Perkin Elmer DSC 6000 and TGA 8000 instruments. Differential scanning calorimetry is performed in N$_2$ atmosphere from 20 to 100 °C wherein the thermogravimetric analysis was made from RT to 130 °C.

UV–vis diffuse reflectance spectroscopy was carried out using a UV–vis spectrophotometer (U-3900).

**Results and discussion**

The hydrated form of NH$_4$PbI$_3$ is prepared after few minutes of simple grinding of the PbI$_2$ and NH$_4$I salts in stoichiometric ratio. The pale yellow microcrystalline powder obtained by mechanosynthesis is analyzed by powder x-ray diffraction.

The collected diffraction pattern corresponds to the sequence of reflections typical of NH$_4$PbI$_3$(H$_2$O)$_2$ in agreement with the PDF 00-074-0397 phase from ICDD (International Center for Diffraction Data) database confirming the absence of secondary phases or residual reagents.

The orthorhombic structure is isostructural with KPbI$_3$(H$_2$O)$_2$ and RbPbI$_3$(H$_2$O)$_2$ whose crystal data was firstly reported by D. Bedlivi et al. [22] and determined by single crystal x-ray diffractionetry. The ammonium-based system NH$_4$PbI$_3$(H$_2$O)$_2$ crystallizes in space group $Pmn\alpha$ [20, 21], and forms thin pale yellow needles very similar to the anhydrous CsPbI$_3$ crystals [23]. Therefore, the Rietveld refinement performed on the XRD pattern confirms for the fabricated hydrated ammonium lead iodide the main structural features resumed in the former
study. Crystal data and agreement factors of the Rietveld analysis, illustrated in figure 1, are summarized in table 1 and selected interatomic distances are listed in table S1. The crystal structure is formed by double chains of edge-sharing PbI$_6$ octahedra intercalated with NH$_4^+$ cations. The two symmetrically independent H$_2$O molecules are longitudinally accommodated along the c axis, between the adjacent 1D lead iodide PbI$_6$ infinite stripes as it is shown in figure 2. Since the starting structural model used for the Rietveld refinement pertains the crystal structure of the counterpart KPbI$_3$(H$_2$O)$_2$,[23, 24] the fractional coordinates omits hydrogens for both ammonia group and water molecules (not determined in all the previous structural studies concerning the hydrated lead-based halide compounds). Thus, the analysis of hydrogen-bonds likely occurring in the lattice framework is bypassed. Nevertheless, the O1…O2 distance around 2.72(14) Å is consistent with the occurrence of intermolecular hydrogen bond. Moreover, the N1…O1 length ranging 2.80(9)Å corresponds to a single weak hydrogen bond. The distorted octahedral environment of Pb$^{2+}$ is featured by a long apical Pb–I distance of 3.49 Å (see table S2) exceeding the average of the remaining bond lengths.

To determine the decomposition temperature of the hydrated compound, a complete thermal characterization was carried out. The combined DSC/TGA runs, shown in figure 3, indicate the presence of a sharp transition at 78.4 °C with additional broad peak observed at higher temperatures.

Figure 1. Rietveld plot for the compound NH$_4$PbI$_3$(H$_2$O)$_2$. The ticks indicate the calculated position of the reflections related to the orthorhombic structure. (red line–calculated, black cross–experimental data).

Table 1. Crystal data of NH$_4$PbI$_3$(H$_2$O)$_2$ from Rietveld refinement on x-ray diffraction data collected at RT.

| Chemical composition | NH$_4$PbI$_3$(H$_2$O)$_2$ |
|---------------------|--------------------------|
| Symmetry            | Orthorhombic             |
| Space group         | P n m a                  |
| a(Å)                | 10.2589(5)               |
| b(Å)                | 4.6115(1)                |
| c(Å)                | 22.613(1)                |
| Z                   | 4                        |
| Rp, Rwp             | 0.0426, 0.0469           |
| Atom type           | Wck                      |
| Pb                  | 0.544(2)                 |
| I1                  | 0.416(1)                 |
| I2                  | 0.755(1)                 |
| I3                  | 0.661(2)                 |
| NH4                 | 0.136(6)                 |
| O1                  | 0.042(5)                 |
| O2                  | 0.363(4)                 |
| x                   | 0.25                     |
| y                   | 0.25                     |
| z                   | 0.405(3)                 |
|                      | 0.283(2)                 |
|                      | 0.868(3)                 |
|                      | 0.550(2)                 |
|                      | 0.302(7)                 |
|                      | 0.354(8)                 |
|                      | 0.474(5)                 |
The TGA scan reports the marked decrement of weight corresponding to the removal of water molecules from the crystalline phase in the range 68 °C–90 °C. The global weight decrement of 5%, is in agreement with the expected mass of the de-hydrated NH₄PbI₃. Such a temperature transition essentially agrees with the typical thermal conditions found for the dehydration process in other compounds like RbPbI₃(H₂O) [21, 23]. Nevertheless, the relatively low temperature necessary to trigger the transformation is explained by the absence of strong interactions between NH₄⁺ and H₂O.

In order to deepen the structural evolution of the de-hydration process we carried out PXRD experiments in the temperature range from RT to 90 °C. To determine the unit cell parameters for both hydrated and de-hydrated NH₄PbI₃ phases the collected diffraction patterns was analyzed by Rietveld method. The dehydrated form is isostructural with NH₄CdCl₃ and the fitting of the unit cell parameters was obtained by adopting the structural model published in [24]. From RT to 60 °C no evident changes are observed in the collected diffraction patterns, in turns by approaching the limit of 68 °C we noticed the rise of a new series of peaks readily attributed to the NH₄PbI₃ orthorhombic phase (see figure S1 available online at stacks.iop.org/MRX/7/115503/mmedia). The figure 4 illustrates the evolution of the unit cell parameters for both phases in the selected 50 °C–90 °C temperature interval. Interestingly, at the first stages of the growth of the stoichiometric NH₄PbI₃ the hydrated phase exhibits a pronounced shortening of the c lattice parameter. This likely indicates a progressive, rather that sudden, release of water molecules predominantly impacting on the longest unit cell constant. Further, the whole structure is progressively distorted as the hydrated phase rapidly decomposes.
The removal of water molecules induces the rotation of the double PbI$_6$ chains around the a crystallographic axis of about 45°, whilst the NH$_4^+$ ions shift to occupy interstices originated by the new arrangement of the chains. The double chain located at the origin of the unit cell exhibits an anti-clockwise rotation symmetrical to the clockwise motion involving the second PbI$_6$ ribbon. Thus three new shorter bonds takes place whereas the longest NH$_4^+$–I bond (NH$_4^+$–I$_{11} = 4.00$ Å) is broken.

The figure 2 illustrates the main differences of the two structures emphasizing the combined rearrangement of the structural units during the phase transformation.

With the purpose to test the compatibility of NH$_4^+$ ion in the 3D lead iodate PbI$_6$ perovskite framework we attempted the fabrication of the solid solution (MA)$_{1-x}$(NH$_4$)$_x$PbI$_3$ with $x = 0, 0.05, 0.1$ and $0.2$. Mechanosynthesis is a solid state method of preparation for nanocrystalline and bulk polycrystalline materials suitable for the achievement of metastable solid solutions that are not attained with classical heat treatments [25, 26]. This unconventional approach is also a powerful tool for activating RT solid state synthesis of inorganic compounds very promising in the field of photovoltaics e.g. Cu–In chalcogenides [25]. For instance, several authors have reported the facile production of optical active lead-based perovskites by mechanochemical procedures [27–29]. The adjustment of some parameters such as milling instrument, energy (rounds per minute RPM), balls-to-powder ratio (BPR) and time requires much attention because they correlate each other [26]. In this work we used two planetary milling systems with a combination of different mechanosynthesis parameters (see table S3). The evolution of the phase formation with time was monitored by collecting small portions of the milled sample at selected moments. In the figure 5, the PXRD patterns for the compounds obtained by the same duration of milling treatment are displayed. The tetragonal MAPbI$_3$ perovskite was obtained as single phase with high-crystallinity degree and their unit cell parameters are listed in the table S4. This systematic study indicated that, irrespectively to the energy of the process, the crystallinity is enhanced as the milling time increases.
Conversely, the mixing of MA$^+$ and NH$_4^+$ in the same phase was possible only for minute amount of the NH$_4^+$ ion.

As it is evidenced in figure 5, as the critical limit of $x = 0.05$ is exceeded, XRD patterns display the presence of the two separated phases namely tetragonal MAPbI$_3$ and hydrated NH$_4$PbI$_3$. Indeed, the maximal content of NH$_4^+$ substituting MA$^+$ in lead iodate based perovskite is very limited. To evaluate the theoretical stability of the perovskite framework for rational mixing of organic cations, we adopted the tolerance factor approach implemented by G. Kieslich et al [30]. The estimation of the tolerance factor indicated as $\alpha = r_x + r_I / [\sqrt{2}(r_{\text{Pb}^6^+} + r_I)]$ is based on the effective ionic radius for organic cations listed in [30]. The empirical approach based on the geometrical requirements ruling almost close-packed structures indicates that perovskite structure is observed when $\alpha$ parameter corresponds to a value within the 0.91–0.89 range. Considering the MAPbI$_3$ and NH$_4$PbI$_3$ endmembers the calculated factor is 0.91 and 0.79 respectively, demonstrating that the ammonium ion NH$_4^+$ does not possess the size necessary to stabilize the perovskite lattice. If the effective radius is considered with regards to the nominal ratio MA$^+$/NH$_4^+$, the maximal amount of NH$_4^+$ that perovskite can tolerate might be comprised in the 0.1%–8% range. Indeed, for $x = 0.05$, the tolerance factor (0.904) is included in the aforementioned range. In this new compound both $a$ and $c$ unit cell constants of the tetragonal lattice (see table S3) characterizing MAPbI$_3$ [7, 20, 31] show a significant decrease with a global volume contraction of 1%, clearly indicating the inclusion in the A site of NH$_4^+$ with respect MA$^+$.

Further, the successful mechanosynthesis of the (MA)$_{0.95}$(NH$_4$)$_{0.05}$PbI$_3$ compound is also corroborated by band gap (BG) measurements. Figure 5 reports the BG for pure MAPbI$_3$ is 1.52 eV which is in agreement with the previous reported values [32, 33]. Among the series of mixed compounds, we noticed a consistent shift of the band gap for the $x = 0.05$ composition. The widening of the band gap could be related to the structural distortion seemingly involving octahedra tilting. The tuning of the band gap mediated by tilting of octahedral framework and related to the substitution of organic cations was already envisaged by different authors in systematic studies of lead halides based perovskites [34, 35]. As the critical value of $x$ is exceeded, the BG does not show further shift toward higher energy indicating that, irrespective to the nominal composition, the substitution of MA$^+$ with NH$_4^+$ is essentially the same for all the mixed compounds.

Furthermore, our study on the replacement of MA$^+$ with NH$_4^+$ in agreement with the results reported by G Wu et al on the same system [35]. The authors report the presence of a stable perovskite phase obtained with the incorporation of NH$_4^+$ in MAPbI$_3$ accompanied by a shift of the observed BG but without indicating the effective degree of substitution achieved [35]. Our findings allow to assess that the limit of substitution of MA$^+$ with NH$_4^+$ is closely around 5% and well agrees with the expected constraint indicated by the tolerance factor approach.

**Conclusions**

The de-hydration process of NH$_4$PbI$_3$ was investigated by the combination of thermal and structural characterizations. The removal of water molecules from the orthorhombic structure was investigated giving valuable insights concerning the conversion mechanism from hydrated to anhydrous form. The formation of MA$_{0.95}$(NH$_4$)$_{0.05}$PbI$_3$ perovskite solid solution was undertaken by mechanosynthesis defining a systematic study of the role played by several parameters such as system of milling, rotation speed and duration of treatment. We demonstrated that the NH$_4^+$ ion is tolerated by perovskite structure with a maximal limit of solubility of around 5%. This result is in line with what predicted by the tolerance factor approach modified for hybrid perovskites [20, 30]. Therefore, in the frame of hybrid organic–inorganic perovskites, our findings point out that this phenomenological approach is a reliable tool for the design of stable solid solutions in hybrid systems.

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