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Communications

Coordination Chemistry Dictates the Structural Defects in Lead Halide Perovskites

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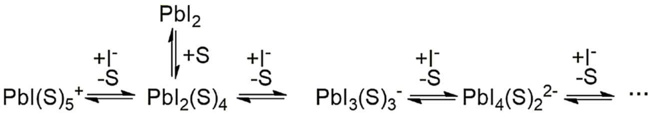
We show the influence of species present in precursor solution during formation of lead halide perovskite materials on the structural defects of the films. The coordination of lead by competing solvent molecules and iodide ions dictate the type of complexes present in the films. Depending on the processing conditions all $PbIS_5^+$, PbI_2S_4, $PbI_3S_3^-$, $PbI_4S_2^{2-}$, $PbI_5S_2^{3-}$, $PbI_6^{4-}$and 1D $(Pb_2I_4)_n$ chains are observed by absorption measurements. Different parameters are studied such as polarity of the solvent, concentration of iodide ions, concentration of solvent molecules and temperature. It is concluded that strongly coordinating solvents will preferentially form species with a low number of iodide ions and less coordinative solvents generate high concentration of PbI_6^-. We furthermore propose that all these plumbate ions may act as structural defects determining electronic properties of the photovoltaic films.

Photovoltaic devices based on lead halide perovskites have erupted as strong candidates to compete with already commercially available technologies.[1] Significant efforts have been devoted towards the achievement of high efficiencies, leading to 21.0% using derivatives of methylammonium lead triiodide perovskites.[2,3] Solvent engineering has proved key to obtain increased crystallinity of the perovskite layer with a low presence of grain boundaries and impurities, both factors limiting the device performance.[4] In spite of the great advances in this technology very little information is available on the species present in the crystallizing perovskite layer, connected with the electrical defects existent in the photovoltaic devices. Deep investigations of the species present during formation of the films are important toward the understanding of the photophysics in devices as electrical defects are known to limit the device performance.[5]

Methyl ammonium lead iodide perovskite ($MAPbI_3$) is synthesised by the reaction of PbI_2 with methyl ammonium iodide (MAI) using highly polar solvents such as dimethylsulphoxide (DMSO), *N*,*N*-dimethylformamide (DMF) or γ-butyrolactone (GBL).[6,7] During this chemical reaction an equilibrium like that shown in Scheme 1 dominates the species present in solution, where S is a generic solvent. This equilibrium expands the equilibrium proposed by Kamat et al. who focused on the photophysic effect of having $PbI_3S_3^-$ and $PbI_4S_2^{2-}$ species in films.[8] For simplicity generation of 1D $(Pb_2I_4)_n$ chains are not included in the equilibrium but these type of species are also expected to form during perovskite crystallization.[9] In this work we show that the coordination ability of the solvent plays a very important role and depending on the processing conditions all $PbIS_5^+$, PbI_2S_4, $PbI_3S_3^-$, $PbI_4S_2^{2-}$, $PbI_5S_2^{3-}$, PbI_6^{4-} and 1D intermediate crystals may be present in both solution and films.



Scheme 1. Dissolution of PbI_2 in a generic solvent (S) and competitive reaction between iodide ions and solvent molecules leading to different plumbate ions.

The coordination ability of the solvent can be probed by monitoring the species present using absorption measurements of diluted PbI_2 solutions (i.e. 0.5 mM). Figure 1a shows absorption spectra of PbI_2 in a series of solvents with different coordination abilities: Water, DMSO, DMF and GBL. Depending on the solvents different proportions of plumbate ions are detected such as $PbIS_5^+$ ($\lambda_{max} = 286$ nm), PbI_2S_4 ($\lambda_{max} = 325$ nm) or $PbI_3S_3^-$ ($\lambda_{max} = 370$ nm). This is a clear evidence that the solvent is readily competing with iodine atoms to fill the octahedral coordination sphere, see for example the diagram in the inset of Figure 1a. Water is included in the series as it is known to be a key player during crystallization kinetics.[10] Absorption measurements show that H_2O readily coordinates to Pb producing mostly $PbIS_5^+$ and some PbI_2S_4. The low intensities of the bands can be taken as a clear sign that the solvent is able to fully dissociate PbI_2 generating Pb^{2+}. Similar results are observed for DMSO with higher concentration of PbI_2S_4 and

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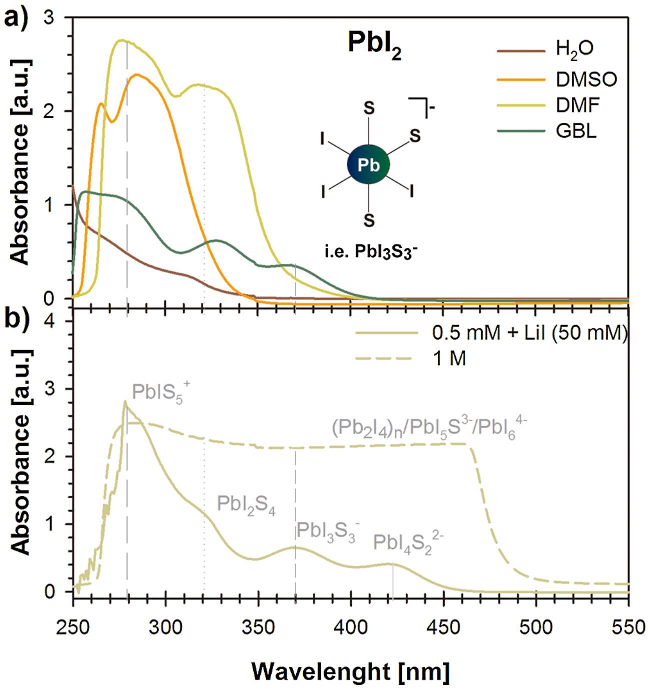

Figure 1. Absorption spectra of solutions containing PbI_2 a) in a range of different solvents at a concentration of 0.5 mM and b) at two different concentrations in DMF. The dashed line contains 100 eq. of LiI. Each plumbate ion is marked with a vertical line defined by their λ_{max}.

some formation of $PbI_3S_3^-$. In DMSO covalent character between the DMSO and Pb has been described in the literature which would explain the observed λ_{max} shift and a similar effect is observed using H_2O as solvent.[2] Alternatively, in DMF higher concentration of PbI_2S_4 and $PbI_3S_3^-$ are detected than in the previous two solvents. Finally, when a less coordinating solvent such as GBL is used all three species $PbIS_5^+$, PbI_2S_4 and $PbI_3S_3^-$ are observed with comparable intensities. Therefore we can state that the affinity to coordinate Pb of the studied solvents is as follows: $H_2O > DMSO > DMF > GBL$.

The equilibrium proposed in Scheme 1 can be further validated in Figure 1 b by modifying the concentration of either iodide ions or solvent molecules using PbI_2 solutions in DMF. As expected for this equilibrium, increasing the proportion of I^- ions using a large excess of LiI (100 eq) shifts the equilibrium towards the presence of polyiodide plumbates like $PbI_4S_2^{2-}$ ($\lambda_{max} = 428$ nm). Alternatively, increasing the PbI_2 concentration to 1 M decreases the number of solvent molecules and the absorption curve is further red shifted to reach wavelength close to $\lambda_{max} = 490$ nm, where PbI_2 films show the absorption onset due to the presence of PbI_6^{4-} moieties in the absence of the methyl ammonium cation (see supporting information).[11] We also note that 1D $(Pb_2I_4)_n$ chains have also been reported to form and the actual absorption maximum of these type of species have not been ambiguously identified.[9,12]

Addition of MAI to PbI_2 in these highly concentrated solutions using different solvents (Figure 2 a) also show a continuous absorption band covering the whole range from 250 nm to 520 nm, indicating that all the different multiodide plumbate species described before are present in solution ($PbIS_5^+$,

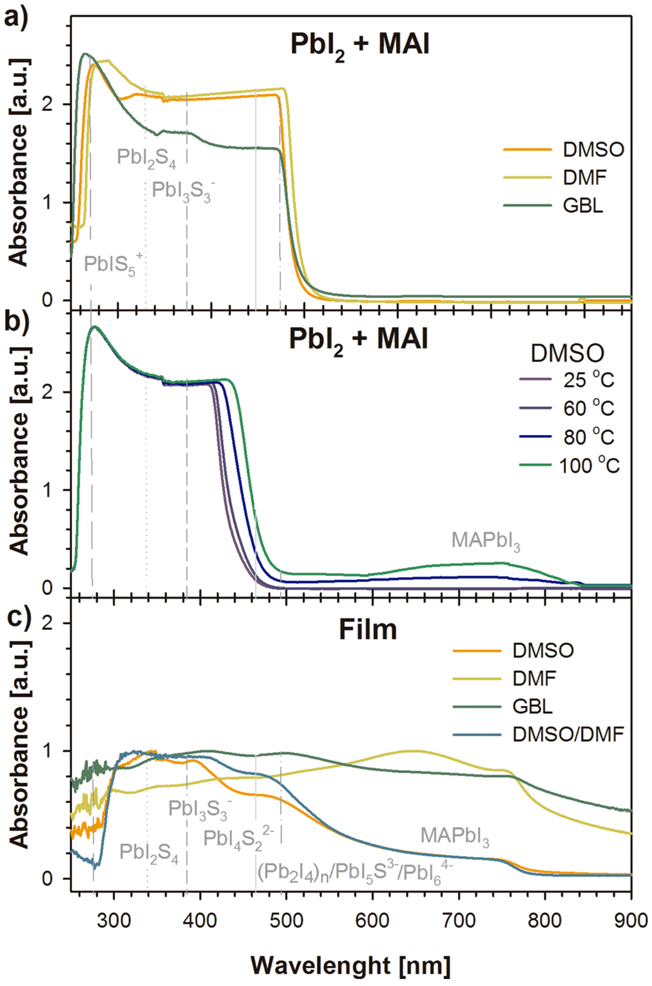

Figure 2. Absorption spectra of a) solutions containing PbI_2 and MAI (ratio 1:1) in concentrated solution (1 M) using a range of different solvents. b) Solutions containing PbI_2 and MAI in DMSO (0.05 M) as a function of the temperature. c) $MAPbI_3$ films on FTO prepared from different solvents. The signal has been normalized to the maximum value. Each plumbate ion is marked with a vertical line defined by their λ_{max}.

PbI_2S_4, $PbI_3S_3^-$, $PbI_4S_2^{2-}$, $PbI_5S_2^{3-}$, PbI_6^{4-} and 1D $(Pb_2I_4)_n$ chains. Although we note that the signal is saturated and the response is not linear we observe that some bands are more prominent than others depending on the solvent. For example, whilst the band due to $PbIS_5^+$ is present in all solvents, the band from PbI_2S_4 is more noticeable for DMSO in good agreement with generation of the DMSO complex during film formation.[6] Similarly, using GBL the $PbI_3S_3^-$ complex is more intense as expected for a less nucleophilic solvent than DMSO or DMF. Absorption spectra of solutions containing PbI_2 and MAI under different concentrations and solvents are shown as supporting information (Figure SI2). The generation of multiodide species containing higher proportion of I^- atoms as the amount of solvent molecules decreases is observed.

The effect of the temperature on the competition between iodide ions and solvent was also studied as it will have important implications for the crystallization of bulk material. Figure 2 b shows the absorption spectra of a solution containing PbI_2 and MAI (ratio 1:1, 0.05 M) in DMSO as a function of the temperature. When the temperature is increased we observe a red-shift in the absorption band onset due to the presence of iodide plumbate ions containing a higher number of iodine ions. This result is in agreement with the DFT calculations shown as Supporting Information for DMSO where the Gibbs free energies for successive replacement of solvent molecules by iodide to obtain plumbates with a higher number of iodide ions is an endergonic process requiring energy. Then, plumbate species with high content of iodide ions will only be favoured at high temperatures. We note that the process is reversible as cooling the solution to room temperature recovers the initial spectra (Supporting Information). In addition, a new band appears at a $\lambda_{max} = 690$ nm which belongs to $MAPbI_3$ species in solution as compared to the observed bands in $MAPbI_3$ films (Figure 2 c).

So far the basics of the coordination chemistry of the lead atom has been fully described in solution and now we proceed to the preparation of bulk perovskite material to understand if the acquired knowledge can be extrapolated to the synthesis of pure material. It is important to recall that in the $MAPbI_3$ crystal structure Pb is at the centre of an octahedron surrounded by six iodine atoms, one at each vertex of the octahedron. Then, the presence of PbI_6^{4-} is desired as it provides the correct environment for generation of the perovskite phase. An inverse temperature crystallization model has been proposed for crystallization of single $MAPbI_3$ crystals.[7] The model considers different solubility of the final perovskite material depending on temperature and solvent but does not account for possible variation in concentrations in the species present during crystallization. Absorption measurements shown in Figure 2 b and DFT calculations suggest that the species present in solution will depend on the temperature. Therefore, the use of high precursor concentrations and high temperatures is needed for maximize the presence of PbI_6^{4-} and 1D $(Pb_2I_4)_n$ chains.

The synthesis of the bulk material is carried out by slow evaporation of the solvent in a well ventilated oven at temperatures 20 °C below the boiling point of the solvent to maintain similar evaporation kinetics amongst the solvents. Full details can be found in the methods section in the Supporting Information. Interestingly, synthesis carried out in this manner provides materials with very different morphology and structure. Synthesis from DMSO (Figure 3 a) generates a mixture of yellow and black powders with different morphologies as observed by SEM: black domains are needle-like and yellow domains are highly amorphous. Interestingly, the perovskite formed from DMF show crystallites with dispersion in size containing macroscopic (up to 1–2 cm) and microscopic crystallites. In general these are composed by highly aligned needles as those shown in Figure 3 b. Alternatively, when GBL is used, generation of large cubic-like crystallites is evident (Figure 3 c). Overall the crystallinity is enhanced by using less coordinative solvents like GBL where the presences of octahedral PbI_6^{4-} moieties are favoured. On the other hand, XRD analysis (Figure 3 d) shows for DMSO a blend of PbI_2(DMSO) complex (Supporting Information) and $MAPbI_3$, with crystallographic planes (110), (220), (312) and (224). The additional PbI_2(DMSO) complex clearly indicates that the DMSO molecule is tightly bound to the lead.[13] On the other hand, synthesis from DMF and GBL provides quantitative yield of highly crystalline material in the tetragonal phase as compared with simulated data using monocrystalline XRD data.[14] Very importantly, crystalline defects are minimized using GBL as observed by measuring the full width at half maximum of the peaks as compared to DMSO and DMF.

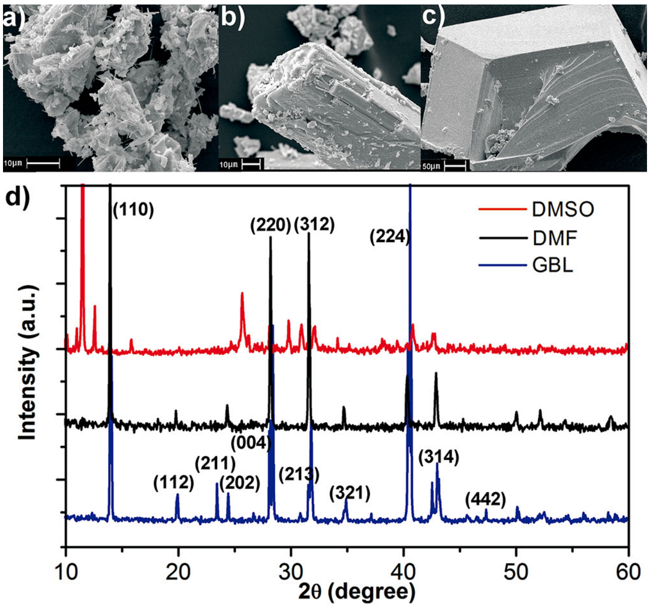

Figure 3. Representative SEM image of crystallites generated from three different solvents a) DMSO, b) DMF and c) GBL. d) XRD powder pattern of samples prepared in three different solvents. Diffraction peaks are assigned similarly to previously published results.[7]

We finalize the study with the analysis of $MAPbI_3$ films as they are representative to understand the type of structural defects present in photovoltaic devices. Figure 2 c shows normalized absorption spectra of films prepared using different solvents followed by a heat treatment at 100 °C. The use of DMSO leads to films containing $MAPbI_3$ and a large proportion of all plumbate species $PbIS_5^{+}$, PbI_2S_4, $PbI_3S_3^{-}$, $PbI_4S_2^{2-}$, $PbI_5S_2^{3-}$, PbI_6^{4-} and 1D $(Pb_2I_4)_n$ chains. The proportion of some of these plumbate ions can be modified by using the method reported by Ahn et al. in which diethyl ether is used during the spin-coating process to wash out part of the DMSO and generate the PbI_2:MAI:DMSO complex.[6] Using this modification the proportion of PbI^{+} and PbI_2 is reduced and PbI_3^{-}/PbI_4^{2-}/PbI_5^{3-}/PbI_6^{4-} are increased as expected by reducing the concentration of DMSO. The use of less coordinative solvents such as DMF and GBL favour formation of the $MAPbI_3$ perovskite and this is observed in the absorption spectra with the presence of a low proportion of plumbates and by the rather flat profile of the band. We note that absorption beyond 800 nm does not reach the baseline due to voids filled with air (pinholes) inducing generation of artefacts by light scattering in the films.[15] We also highlight that the reported absorption spectra of $MAPbI_3$ single crystals are rather flat in the region 400–820 nm.[7,16] Depending on the solvent used here films show bands of different intensities at λ_{max} of 286 nm, 325 nm, 370 nm, 428 and 490 nm. Therefore, we propose that several multiodide plumbate species remain in the films.

The presence of these structural defects lead to important implications connected with the nature of electrical defects generated in photovoltaic devices, which may limit the device performance. Indeed, unintentional doping like Pb, I, and MA vacancies have been reported for $MAPbI_3$.[17,18] It has also been proved that the *n*-/*p*-type can be efficiently manipulated by controlling the growth processes.[19] For example, an excess of MAI produces *p*-type character defects and excess of PbI_2 induces generation of *n*-type defects. In this respect Kamat et al. have detected the photoluminescence signature of PbI_3^- and PbI_4^{2-} defects in perovskite films but generation of other 1D plumbate ions chains are also expected following our absorption measurements.[8–9] Discrepancies found in the nature of the doping (*n*/*p* type) could also be the result of different presence of plumbate species. For example, it is expected that positively and negatively charged species (i.e. PbI^+ and PbI_4^{2-}) will have a completely different electrical effect in devices. In this respect our current work will need further investigations to separate the effect of each of the plumbate species and morphology of the films. It is known, for example, that DMF provide films with fibre-like morphology with a large presence of pinholes leading to shunt pathways, which has a negative effect on device performance.[20]

In summary, this communication shows that coordination of lead, by competing solvent molecules and iodide ions, dictates the species present in the precursor solution and in the final perovskite layer for photovoltaic applications. Highly polar solvents are required to dissolve the precursors but must permit the generation of PbI_6^{4-} species to provide the correct environment for perovskite crystallization. The presence of impurities is minimized by decreasing the polarity of the solvent leading to crystallization reaction into the perovskite tetragonal phase. Here we propose that all these plumbate ions may act as structural defects and these are present in films using state-of-the-art processing conditions, indicating that there is still some more room to improve device efficiencies.

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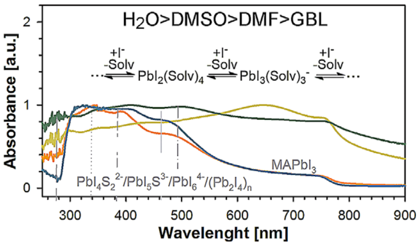
Coordination needed: Structural defects are created during crystallization of perovskite materials depending on coordination ability of the solvents.



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