Synthesis of organo tin halide perovskites via simple aqueous acidic solution-based method

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A B S T R A C T

Organometal halide perovskites have been studied extensively during the last ten years for their interesting applications in solar cells and optoelectronics. One drawback of these materials is the presence of lead inside the compound, thus limiting their practical applications. Replacing lead with tin has been one of the implemented approaches for lead-free perovskites. In this paper, we report on the synthesis of organo tin mixed halide perovskites CH$_3$NH$_3$SnBr$_x$Cl$_{3-x}$ at room temperature in an aqueous acidic mixture between HCl and H$_3$PO$_2$ without the need of protecting perovskites against moisture. X-ray diffraction patterns show that the tin mixed halide perovskites adopt the trigonal phase. A detailed analysis of Raman scattering measurements has identified several low frequency Sn-Cl and Sn-Br modes of these perovskites. These results show that the high-quality CH$_3$NH$_3$SnBr$_x$Cl$_{3-x}$ crystals have been successfully synthesized by this aqueous solution-based method, demonstrating a low-cost approach to replace lead in organo metal halide perovskites for photovoltaic and optoelectronic applications.

1. Introduction

Organometal halide perovskites so far have attracted a lot of attention in the academic community, and their excellent properties in solar cells have been proved due to high absorption, long balanced carrier diffusion length, tuneable energy gap and relatively simple fabrication processes [1–3]. The photovoltaic properties of solar cells depend strongly on the fabrication process, hole transport layers, electron transport layers, nanoporous layers, interfacial microstructures and crystal structures of perovskites [4,5]. There are still several key challenges that need to be carefully addressed before organo-metal halide perovskites become feasible for practical application in solar cells. One of these challenges is to synthesize lead-free perovskites with good stability because it is well known that lead is harmful to human’s health. For example, lead interferes with a variety of body processes and is toxic to many organs and tissues; including heart, bones, intestines, kidneys, reproductive and nervous systems [6]. Candidates for the replacement of Pb in the perovskites include elements in the same group 14 of the periodic table, such as Sn or Ge [7–10]. However, it is well known that the stability of the Z lead oxidation state decreases when going up the group 14, thus the major problem with the use of these metals is their chemical instability in the required oxidation state. Sn-based perovskites have shown excellent mobility in transistors [11], but can also be intentionally or unintentionally doped to become metallic [12,13]. It has been demonstrated that when the Sn$^{2+}$ ion is oxidized to Sn$^{4+}$, the Sn$^{4+}$ acts as a p-type dopant within the material in a process referred to as “self-doping” [12]. The first report of completely Pb-free and Sn-based perovskite (CH$_3$NH$_3$SnI$_3$) in solar cells was done by Noel and co-workers in 2014 and showed efficiencies of over 6% under one sun illumination [14]. A recent study by Ogomi et al. reported a mixed metal, Sn-Pb, perovskite which allowed the tunability of the band gap of the perovskite...
absorber by varying the Sn:Pb ratio, thus indicating that Sn could be a good choice for metal cation, especially for having lower band gap solar cells [15]. Another approach for replacing lead was the anion splitting method in order to obtain “mixed metal halide-chalcogenide” [16]. The halogen anions (X = Cl, Br, I) were partially substituted by chalcogenides (Ch = S, Se, Te), i.e. one atom per formula unit, to obtain I−−III−−VII2−−type semiconductors with the formula CH3NH3BiChX2 such as CH3NH3BiSe2 and CH3NH3BiS2I2 [17]. The cation splitting approach have been also reported in double perovskites such as Cs2InAgCl6 [18] and A2BiXO6 (A = Ca, Sr, Ba; X = Br, I) [19]. These approaches were more or less limited because of the chemical stability of these new quaternary perovskites. Recently, chloride-based two-dimensional perovskite has drawn huge attention for yielding broadband white photoluminescence [20]; thus tin chloride based perovskites may exhibit interesting properties for opto-electronic applications.

Here, we have attempted to synthesize Sn-based perovskites starting with CH3NH3SnPb1−xI3 for comparison purposes, and then arriving to the synthesis of CH3NH3SnBrxCl3−x. The highlight of this paper is the simple synthesis of CH3NH3SnBrxCl3−x in acidic aqueous solution at room temperature by using the low-cost tin (II) chloride dihydrate precursor. According to our understanding, there exist very few reports of organo tin halide perovskites utilizing an acidic aqueous solution as a reaction environment since Sn2+ is easily oxidized to Sn4+. For CH3NH3I under a moisture condition. The acidic solution was composed of a mixture between HCl and H3PO2, which had remarkable advantages, such as affordable cost and availability, compared to other organic solvents, such as dimethylformamide (DMF), gamma-Butyrolactone (GBL) and dimethyl sulfoxide (DMSO) [21], in synthesizing Sn-based perovskites.

2. Experimental

2.1. Synthesis of precursors

CH3NH3Br was synthesized by putting 45 ml of CH3NH2 (25%) into a 2-neck round bottom flask and 67 ml of 4.5 M HBr into a dropping funnel. The reaction was taken place under a nitrogen environment at 0 °C. When the temperature of methylamine in the round bottom flask was cooled down to 0 °C, the dropping funnel was slowly opened to let HBr drop into the round bottom flask. The reaction was kept at 0 °C for 150 min. After the reaction had completely taken place, the solution was transferred to an evaporating. Then 0.340 g of CH3NH3Cl (for synthesizing CH3NH3SnCl3) was boiled and stirred until the solution was completely transparent. Then 0.340 g of CH3NH3Cl (for synthesizing CH3NH3SnCl3) was added and kept for 30 min. After the reaction had taken place, the solvent was evaporated until about 4 ml of solution left. Cooling down the solution allowed CH3NH3SnBrCl3 crystals to grow gradually in 24 h. Finally, white rod-shaped crystals appeared and the product was filtered and dried under vacuum at 60 °C.

For comparison purposes, the synthesis of CH3NH3Sn0.5Pb0.5I3 was carried out as follows: A mixture of solution of SnI2 and PbI2 (the molar ratio of SnI2: PbI2 = x:(1-x)) and CH3NH3I in gamma-Butyrolactone (GBL) was heated to 130 °C under nitrogen environment for 2.5 h. After the reaction had taken place, the obtained solution exhibited high viscosity and the perovskite black powder precipitation was observed by adding dichloromethane (DCM) into the solution. Then the powder was filtered and finally dried at 100 °C under vacuum for 24 h.

2.2. Synthesis of perovskites

The synthesis of CH3NH3SnBrCl3−x was carried out as follows: 6 ml of distilled water were put into a 2-neck round bottom flask, followed by 4.3 ml of concentrated HCl and 1.3 ml of H3PO2 (50%) to form an aqueous solution of HCl and H3PO2 with the molar ratio of HCl:H3PO2 = 3:1. This acidic mixture was heated to 100 °C under nitrogen environment before 1.128 g of tin (II) chloride dihydrate (SnCl2.2H2O) was added and stirred until the solution was completely transparent. Then 0.340 g of CH3NH3Cl (for synthesizing CH3NH3SnCl3) or 0.560 g of CH3NH3Br (for synthesizing CH3NH3SnBrCl2) was added and kept for 30 min. After the reaction had taken place, the solven was evaporated until about 4 ml of solution left. Cooling down the solution allowed CH3NH3SnBrCl3−x crystals to grow gradually in 24 h. Finally, white rod-shaped crystals appeared and the product was filtered and dried under vacuum at 60 °C.

For comparison purposes, the synthesis of CH3NH3Sn0.5Pb0.5I3 was carried out as follows: A mixture of solution of SnI2 and PbI2 (the molar ratio of SnI2: PbI2 = x:(1-x)) and CH3NH3I in gamma-Butyrolactone (GBL) and dimethyl sulfoxide (DMSO) [21], in synthesizing Sn-based perovskites.

3. Results and discussion

Fig. 1a shows X-Ray diffraction (XRD) patterns of the synthesized CH3NH3Sn0.5Pb0.5I3 powder sample in comparison with those previously reported in the literature, for CH3NH3SnI3 with cubic structure [22] and for CH3NH3PbI3 with tetragonal structure [23]. These results from the literature suggest that the crystalline structure of CH3NH3Sn0.5Pb0.5I3 perovskite would change from cubic to tetragonal when the ratio of Sn:Pb (or the parameter x) decreases from 1 to 0. Therefore, determining the phase structure of the synthesized product could be considered as an indirect method to confirm the existence of tin in the perovskite compound. The most obvious feature that helps us distinguish CH3NH3PbI3 (tetragonal structure H/mmm) from CH3NH3SnI3 (cubic structure Pm3m) is to investigate XRD peaks with diffraction angle around 28°. Fig. 1b shows high-resolution XRD patterns of the same sample CH3NH3Sn0.5Pb0.5I3, in comparison with CH3NH3PbI3 and CH3NH3SnI3. For CH3NH3PbI3, as previously reported [23], we observed two peaks, corresponding to the reflection planes 004 and 220. For CH3NH3SnI3, our simulated XRD pattern shows only one peak, corresponding to the planes 200 [22]. There are two remarks that we could draw from the XRD shown on Fig. 1. Firstly, tin does contribute to the perovskite structure with a concentration value being lower than the intended Sn:Pb ratio of 1:1, as described in the synthesis section above; so the structure is tetragonal. Secondly, the synthesized powder has the crystalline structure of CH3NH3PbI3 and tin atoms do not contribute to the perovskite compound. Hence, the presence of mixed metal cation Sn-Pb perovskite
requires more advanced techniques. In this study, a small and very expensive quantity of SnI₂ has been provided, thus limiting our further characterization. Still from the XRD pattern, our calculation of lattice parameters of tetragonal structure of CH₃NH₃Sn₀.₅Pb₀.₅I₃ shows that a = 8.832 Å and c = 12.598 Å.

Fig. 2 shows the energy-dispersive X-ray spectrum (EDX) and SEM micrographs of the synthesized CH₃NH₃Sn₀.₅Pb₀.₅I₃ powder. The existence of tin in the obtained product is clearly confirmed. Another noticeable feature on Fig. 2 is that the oxygen peak found in the EDX spectrum, indicating that a part of the synthesized powder has been oxidized. It is highly likely that tin has been oxidized. On the other hand, we also attempted to synthesize CH₃NH₃SnₓPb₁₋ₓI₃ with different values of x such as 0.3, 0.75 and 1. However, in the case of x = 0.75 and of x = 1, the synthesized

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![Figure 1](image1.png)

**Fig. 1.** (a) XRD patterns of the synthesized CH₃NH₃Sn₀.₅Pb₀.₅I₃ compared with those of the reported CH₃NH₃SnI₃ [22] and CH₃NH₃PbI₃ [23]; (b) High resolution XRD patterns from 27 to 30 degrees of the synthesized CH₃NH₃Sn₀.₅Pb₀.₅I₃, CH₃NH₃SnI₃ [22] and CH₃NH₃PbI₃ [23].

![Figure 2](image2.png)

**Fig. 2.** (a) EDX spectrum and (b,c) SEM micrographs of the synthesized CH₃NH₃Sn₀.₅Pb₀.₅I₃ powder.
powder was degraded so quickly by oxidation that on XRD patterns we obtained only the signature of amorphous tin oxide. In the case of $x = 0.3$, the synthesized powder’s XRD pattern had similar feature in comparison with the case $x = 0.5$ shown on Fig. 1. This suggests that $\text{CH}_3\text{NH}_3\text{Sn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite with high tin concentration ($x \geq 0.75$) is very sensitive and easily decomposed when exposed to air, thus tin iodide perovskites need extremely special conditions for applications.

In contrast with the instability of tin iodide perovskite, tin mixed Br-Cl ($\text{CH}_3\text{NH}_3\text{SnBr}_x\text{Cl}_{3-x}$) crystals were very stable after being synthesized from a tin (II) chloride dehydrate precursor and methylammonium halide ($\text{CH}_3\text{NH}_3\text{X}$, $\text{X} = \text{Cl}$, Br) in an acidic aqueous solution of $\text{HCl/H}_3\text{PO}_4$. Fig. 3, and respectively Fig. 4, show SEM micrographs, EDX spectra and elemental analysis of perovskite powder of preparation formula $\text{CH}_3\text{NH}_3\text{SnCl}_3$, and respectively of $\text{CH}_3\text{NH}_3\text{SnBrCl}_2$, after gradually crystallized from the solution for 24 h. A photograph taken on an optical microscope of $\text{CH}_3\text{NH}_3\text{SnCl}_3$ powder is illustrated on Fig. 2S of the supporting information, showing obtained crystals with transparent appearance and an elongated shape. For the sample corresponding to the preparation formula $\text{CH}_3\text{NH}_3\text{SnBrCl}_2$, an elemental analysis revealed 28.4 w% of Cl and 29.2 w% of Br, corresponding to a molar halide ratio Br:Cl of about 0.94:2.06, or a deduced formula $\text{CH}_3\text{NH}_3\text{SnBr}_{0.94}\text{Cl}_{2.06}$. This composition will be further discussed with XRD powder refinement in the next part.

Fig. 5 shows experimental XRD patterns of $\text{CH}_3\text{NH}_3\text{SnCl}_3$, the tin (II) chloride dehydrate precursor $\text{SnCl}_2.2\text{H}_2\text{O}$ and $\text{CH}_3\text{NH}_3\text{Cl}$, in comparison with the simulated XRD pattern of $\text{CH}_3\text{NH}_3\text{SnCl}_3$
SnCl₂·2H₂O and CH₃NH₃Br with an equimolar ratio, the synthesized CH₃NH₃SnCl₃ is transferred to the triclinic phase [22] or to the trigonal phase [24]. Since we let CH₃NH₃SnCl₃ crystallize at room temperature, we expected that the structure of the product would be triclinic or trigonal. A comparison between CH₃NH₃SnCl₃ with the precursors’ halogen atoms. The refinement of the trigonal phase yielded following parameters \( a = 5.7316 \text{ Å}, b = 8.2538 \text{ Å}, c = 7.9227 \text{ Å}, \alpha = 90.3608^\circ, \beta = 93.0415^\circ, \gamma = 90.2468^\circ \) whereas the refinement of the trigonal phase gave \( a = b = c = 5.7173 \text{ Å} \) and \( \alpha = \beta = \gamma = 92.1060^\circ \). Details of the trigonal parameters are shown on Table 1, and the corresponding Rietveld analysis can be found on Figure S2 from the provided supplementary information. The XRD pattern of the synthesized CH₃NH₃SnCl₃ crystals was perfectly matched with the pattern based on the reference [24], which implies the trigonal structure of the synthesized CH₃NH₃SnCl₃ powder. For further XRD powder Rietveld analysis, we chose the trigonal phase as it possesses higher crystalline order than the triclinic one.

For CH₃NH₃SnBrCl₃₋ₓ, after 24 h of crystallizing, obtained crystals also had an elongated shape but its colour is slightly different in comparison to CH₃NH₃SnCl₃. While CH₃NH₃SnCl₃ crystals were rather transparent, CH₃NH₃SnBrCl₃₋ₓ exhibited pale yellow appearance, as shown in Figure S1. Since we have mixed SnCl₂·2H₂O and CH₃NH₃Br with an equimolar ratio, the synthesized perovskites formula is expected to be CH₃NH₃SnBrCl₂. As shown on Fig. 6, the experimental XRD pattern of CH₃NH₃SnBrCl₂ is similar to that of CH₃NH₃SnCl₃. A perfect match between the experimental and simulation of CH₃NH₃SnBrCl₂ trigonal structure indicating that the material, with the preparation formula CH₃NH₃SnBrCl₂, is in the trigonal phase. The performed refinement of the preparation formula CH₃NH₃SnBrCl₂ by adjusting also the halide site occupation factor (SOF) of Br and Cl, gave \( a = 5.7833 \text{ Å} \) and \( \alpha = 91.5462^\circ \) (as shown on Table S1, and the corresponding Rietveld analysis is illustrated on Figure S4). We can see that the unit size of experimental formula CH₃NH₃SnBrCl₂ is higher than that of CH₃NH₃SnCl₃. This is due to the presence of Br atoms, replacing Cl atoms in the lattice of the synthesized crystals, which causes the lattice parameter to increase when increasing the ion radii of the halogen atoms. The refinement figured out also that the SOF of Cl was 0.6493, and the SOF of Br was 0.3507. This corresponds to a molar halide ratio Br:Cl of 1.05:1.95, or a refined formula CH₃NH₃SnBr₁.₀₅Cl₁.₉₅. We performed supplementary refinement of XRD powder pattern of the preparation formula CH₃NH₃SnBrCl₂ by using: (i) an isoelectronic dummy (V) for the average of BrCl₂ yielding \( a = 5.7827 \text{ Å} \) and \( \alpha = 91.571^\circ \) (as shown on Table S1, and the corresponding Rietveld analysis is illustrated on Figure S5), (ii) an isoelectronic dummy (Cu) for the average of BrCl yielding \( a = 5.7832 \text{ Å} \) and \( \alpha = 91.5610^\circ \) (as shown on Table S1, and on Figure S6).

We can see a very slight difference of the obtained unit size (\( a \)) and the angle (\( \alpha \)) of the trigonal structure of both three different choices of refinement parameters for the halide site. If we compare the values of \( a \) and of \( \alpha \) with the one in the literature, for example in the reference [24], we see that a combination of \( a = 5.783 \pm 0.001 \text{ Å} \) and \( \alpha = 91.56^\circ \pm 0.01^\circ \) should be corresponded.

### Table 1

<table>
<thead>
<tr>
<th>Preparation formula</th>
<th>Atom/Unit</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>a (Å)</th>
<th>( \alpha ) (degree)</th>
<th>Site occupation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₃SnCl₃</td>
<td>CH₃NH₃⁺</td>
<td>0.017 (4)</td>
<td>−x</td>
<td>−x</td>
<td>5.717 (3)</td>
<td>92.106 (0)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0.517 (4)</td>
<td>−x</td>
<td>−x</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.460 (6)</td>
<td>−x</td>
<td>−0.017 (4)</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CH₃NH₃SnBrCl₂</td>
<td>CH₃NH₃⁺</td>
<td>−0.034 (7)</td>
<td>−x</td>
<td>−x</td>
<td>5.783 (3)</td>
<td>91.546 (2)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0.575 (6)</td>
<td>−x</td>
<td>−x</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.502 (4)</td>
<td>−x</td>
<td>0.069 (5)</td>
<td></td>
<td>0.649 (3)</td>
<td>0.350 (7)</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Isoelectronic K (19) was used as a dummy.
to a chemical formula CH$_3$NH$_3$SnBrCl$_2$ (or $x = 1$ for CH$_3$NH$_3$SnBr$_x$Cl$_{3-x}$). The Rietveld analysis that we used in this report may not be sensitive enough when changing the halide Br:Cl composition. On the contrary, we had proved that the halide composition had been quite sensitive when refining XRD of single crystals of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ [25]. In this study, we observed that the values of $a$ and $a$ could reveal the halide composition when comparing with similar results. So we decided to use a value $x = 1$, which is in agreement with the EDX elemental analysis giving CH$_3$NH$_3$SnBr$_0.94$Cl$_{2.06}$ and with the SOF refinement giving CH$_3$NH$_3$SnBr$_{1.05}$Cl$_{1.95}$, for the subsequence of this report.

![Fig. 7. Raman spectra of CH$_3$NH$_3$SnBrCl$_2$ and CH$_3$NH$_3$SnCl$_3$. The inset shows the superposition of the normalized peak at about 70 cm$^{-1}$ for both CH$_3$NH$_3$SnBrCl$_2$ and CH$_3$NH$_3$SnCl$_3$.](image)

Table 2
Details of Raman modes obtained after multi Gaussian peaks adjustment of Raman spectra.

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$NH$_3$SnCl$_3$ (Relative adjustment error 0.04)</th>
<th>CH$_3$NH$_3$SnBrCl$_2$ (Relative adjustment error 0.005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (cm$^{-1}$)</td>
<td>114.8 ± 0.7</td>
<td>140.2 ± 0.2</td>
</tr>
<tr>
<td>FWHM (cm$^{-1}$)</td>
<td>69.5</td>
<td>12.9</td>
</tr>
<tr>
<td>Relative height</td>
<td>4.0</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$SnBrCl$_2$ (Relative adjustment error 0.005)</td>
<td>CH$_3$NH$_3$SnCl$_3$ (Relative adjustment error 0.04)</td>
</tr>
<tr>
<td>Frequency (cm$^{-1}$)</td>
<td>100 ± 1</td>
<td>115 ± 3</td>
</tr>
<tr>
<td>FWHM (cm$^{-1}$)</td>
<td>67</td>
<td>18</td>
</tr>
<tr>
<td>Relative height</td>
<td>10.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Mode description</td>
<td>Sn-Br symmetrical stretching [29]</td>
<td>Sn-Cl rocking [26]</td>
</tr>
<tr>
<td></td>
<td>a The relative adjustment error is equal to the adjustment value of $\chi^2$ divided by total peaks area.</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion

The paper shows various processes for synthesizing different types of perovskite containing tin. Apart from using organic solvent-based methods for obtaining CH$_3$NH$_3$Sn$_{0.5}$Pb$_{0.5}$I$_3$, we illustrated that lead-free tin halide perovskites CH$_3$NH$_3$Sn$_{1-x}$Br$_x$Cl$_x$ ($x = 0$ and 1) have been successfully synthesized via an acidic aqueous solution at room temperature from the low-cost tin (II) chloride dehydrate precursor. The structural properties of the
obtained perovskites have been investigated and characterized by XRD and Raman spectroscopy. Raman spectroscopy results show the existence of tin in the perovskite structure with clear fitted results of Sn-C1 and Sn-Br rocking, bending, and stretching modes. XRD patterns show that CH$_3$NH$_3$SnBr$_3$$_5$Pb$_2$S$_3$I$_3$ adopts the tetragonal structure, while CH$_3$NH$_3$SnC1$_3$ and CH$_3$NH$_3$SnBrC1$_2$ crystals adopt the trigonal phase. These results pave the way for our future study for applications of organo tin halide perovskites in optoelectronics as well as in solar cells.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jsamd.2018.08.004.

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