Mechanochemical synthesis of the lead-free double perovskite Cs$_2$[AgIn]Br$_6$ and its optical properties

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Abstract

Hitting hard on the binary halides yields in the formation of Cs$_2$[AgIn]Br$_6$. The lead-free double perovskite marks, although not usable itself, a further step forward in finding sustainable and durable perovskite materials for photovoltaic applications. Cs$_2$[AgIn]Br$_6$ is one of the prominent examples of double perovskites materials that have been suggested to circumvent the use of lead compounds in perovskite solar cells. We herein report the successful synthesis of the material as bulk powder using a mechanochemical approach. It crystallises in an elpasolite-type structure, an ordered perovskite superstructure, with a cell parameter of $a = 11.00$ Å. However, the compound exhibits a relatively large optical bandgap of 2.36 eV and is unstable under illumination, which impedes its use as solar absorber material at this early stage. Still, substitution of lead and the potential of this synthesis method are promising as well as the fruitful combination of theoretical considerations with experimental materials discovery.

1. Introduction

Hybrid organic–inorganic perovskite solar cells are clearly one of the most intriguing developments within the field of energy materials in recent years [1]. Their quick development is, however, in stark contrast to some their inherent problems, which are most prominently the comparably low stability under working conditions as well as the toxicity of lead [2]. Additionally, lead is not only a scientific hurdle, for instance due to the complicated modelling of the organic cation orientation [3], but also a legal one. The use of lead is strictly limited for electrical devices in most countries, for instance through the RoHS directive in the European Union [4], and similar regulations in other countries. Therefore, considerable efforts have been invested in the development of lead-free and all-inorganic perovskite materials to overcome both the toxicity as well as the stability issue related to hybrid organic–inorganic lead halides [5]. An intriguing class of compounds that are bearing these properties are double perovskites of the general formula A$_3$[B$^+$B$^{3+}$]X$_6$. In this material class, the B position in AIBIX$_6$ is substituted by equal amounts of single and triple charged cations. A number of stable double perovskites with B$^+$ = Bi have been successfully synthesised [6], but they generally have an indirect bandgap [7], which gives them a considerable disadvantage in performance versus direct bandgap materials. Materials with B$^+$ = In, on the other hand, have also been proposed through theoretical considerations [7], but have proven to be more challenging to synthesise. Cs$_2$[AgIn]Br$_6$, for instance, was found to be thermodynamically stable but only in a very narrow region of the chemical potential [7]. Other calculations did actually predict an instability of the material compared to ternary compounds in the system [8]. It is hence expectable that the formation of this compound is challenging, and was in fact claimed unlikely to be achieved based on Goldschmidt tolerance factor considerations [9]. It should be noted that a number of recent publications report on the synthesis Cs$_2$[AgIn]Cl$_6$ [9, 10], but its bromide analogue has, to the best of our knowledge, not been reported so far.
obtained a bright yellow powder, which was treated in a nitrogen atmosphere. Using a planetary ball mill with a stoichiometric mixture of the binary metal halides as starting materials, we were able to obtain Cs₂AgInBr₆. This technique is advantageous for the formation of compounds with narrow existence region [16]. First, the confined space of the reaction avoids loss of starting material and hence allows to control the final composition by the overall composition of the starting materials. Second, the reactions take place near ambient conditions and without any solvent. This prevents the formation of undesired phases through differences in solubility of the different starting materials or intermediate compounds as in a high temperature synthesis.

2. Results and discussion

Using a planetary ball mill with a stoichiometric mixture of the binary metal halides as starting materials, we obtained a bright yellow powder, which was treated in a nitrogen-filled glovebox due to its anticipated sensitivity towards moisture. Further details of synthesis and characterisation may be found in the supplementary information.

2.1. Crystal structure

The x-ray diffraction pattern of the reaction product showed a pattern of mediocre quality (figure 1(a)), which is mainly due to the small coherent domain size, as is characteristic for mechanochemical syntheses [17]. It should also be noted, that the synthesis of this compound using other methods proved difficult as it was reportedly not possible to obtain Cs₂AgInBr₆ through solution synthesis [9] or solid state reaction [18]. Therefore, the disadvantages of a mechanochemical approach for further synthesis, namely the low crystallinity of the obtained product, are outweighed by the fact that this method is the only one so far to produce this compound. To evaluate the approximate crystallite size, we have used a Williamson–Hall type relationship [19] between the refined Lorentzian peak shape function and the crystallite size. This yielded in an approximate crystallite size of 10 nm (figure S5 is available online: stacks.iop.org/JENERGY/1/025003/mmedia). Attempts to anneal the product at temperatures up to 200 °C were unsuccessful and hence, an increase of the crystallinity could not be achieved. This was further confirmed in a temperature-dependent x-ray diffraction measurement, where the sample was heated under nitrogen gas flow (figures S6–S8). It is evident that the double perovskite phase decomposes between 140 °C and 160 °C with a further phase change at 220 °C (figure S7). Given the complex powder diffraction pattern, we were not successful to distinguish the exact composition of the decomposition product, yet. However, the powder pattern does neither match to the starting materials, nor to the phases identified as competing phases within the system [7, 8]. Nevertheless, we were able to perform a Rietveld refinement of the compound in an elpasolite type structure (figure 1(b)) using Jana2006 [20], which is also adopted by the analogous chloride compound Cs₂AgInCl₆ [9]. The full details of the Rietveld refinement may be found in the ESI (figures S1 and S2 and tables S1–S14). Our refined cell parameter of a = 10.997(5) Å is larger than the one found for Cs₂AgInCl₆ (a = 10.47 Å) [9], which is in line with the differences in ionic radii for Br⁻ and Cl⁻.
In fact, the difference in cell parameters $\Delta a = 0.52 \, \AA$ between the bromide compound reported here and the chloride compound synthesized by Volonakis et al. [9] coincides very closely with the difference in atomic radii (taking into account that two anions sit on each cell edge) $2\cdot\Delta d = 4\cdot\Delta r = 0.6 \, \AA$. Given the poor crystallinity of the powder pattern and the background introduced from the airtight sample holder, the Rietveld refinements yield relatively large uncertainties. The excellent agreement of our found cell parameters with the values expectable based on the chloride analogue therefore add another level of confidence in the findings presented herein. In order to reach a stable refinement, the isotropic displacement parameters of In$^{3+}$ and Ag$^+$ were constrained to a common value, since both ions are isoelectronic and hence indiscernible from x-ray diffraction.

The elpasolite-type structure can be thought of as a perovskite-type derived structure, where the octahedral, corner sharing, B-sites are alternately occupied by Ag and In atoms. Corner-sharing [InBr$_6$] and [AgBr$_6$] octahedra form the backbone, in the voids of which the Cs atoms occupy cuboctahedrally (12-fold) coordinated positions. Since In$^{3+}$ and Ag$^+$ are indiscernible from x-ray diffraction, the question whether the B-cations are ordered alternately in the elpasolite-type structure, or disordered in the perovskite-type structure (with $2\cdot d_{\text{perovskite}} = d_{\text{elpasolite}}$) cannot be answered directly from x-ray diffraction (figures 1(a)–(c), see ESI for Rietveld refinements in both structural models). While the differences in neutron scattering lengths ($b_{\text{Ag}} = 5.922$ fm, $b_{\text{In}} = 4.065$–0.0539 fm) should, in principle, suffice to make a clear distinction between the ordered and disordered structural model, the low crystallinity of our samples and the consequently large peak widths, prevented any conclusion on the ordering of the structure with this method (figures S3 and S4).

Nevertheless, we are confident to attribute the structure to the ordered elpasolite type, due to another characteristic of this structure, as compared to the perovskite type structure. While the bromide positions in the undistorted perovskite-type are fixed by symmetry to be exactly in the middle between two metal positions, and hence only allow one M–Br distance, no such restriction exists in the elpasolite-type structure, were the Br atom can be distorted from the symmetrical position between two edge-sharing octahedra. This supplementary degree of freedom allows the formation of two distinct sorts of [MBr$_6$] octahedra with different M–Br distances. When refining this site, the Br atom shifts away from the symmetrical position at ¼ towards one of the metal sites yielding in a larger octahedron with $d_{\text{Ag-Br}} = 2.845(5)$ Å and a smaller octahedron with $d_{\text{Ag-Br}} = 2.665(5)$ Å. Given the comparably large difference in ionic radii between Ag$^+$ ($r = 1.15 \, \AA$) and In$^{3+}$ ($r = 0.8 \, \AA$) in octahedral coordination [21], it is only logic to assume an ordered elpasolite-type structure with Ag$^+$ in the larger octahedra and In$^{3+}$ in the smaller octahedra. Applying the bond-valence concept to these compounds ($R_{\text{In-Br}} = 2.41, R_{\text{Ag-Br}} = 2.22$ and $b = 0.37$ taken from Brese and O’Keeffe [22]), the valence sums of In and Ag in these octahedra of 3.05 and 1.12 are close to their charges. In other words, the expected bond lengths from trivalent Indium $d_{\text{In-Br}} = 2.666$ Å and monovalent silver $d_{\text{Ag-Br}} = 2.883$ Å are very close to the values observed in the structure. In fact, the very same shift is observed in Cs$_2$AgInCl$_6$ where the distances are $d_{\text{Ag-Cl}} = 2.85$ Å and $d_{\text{In-Cl}} = 2.38$ Å [9]. The situation for Cs$_2$AgBiBr$_6$ is less clear as the differences in size between the Bi–Br and Ag–Br octahedra are less distinct. As a matter of fact, two of the three structures reported in the ICSD report the Ag–Br distance to be smaller than the Bi–Br distance [22, 23], while the third reports the inverse situation [6]. The second case appears more plausible at first sight, since the Shannon radius for Bi$^{3+}$ (1.03 Å) is smaller than the one for Ag$^+$. To further confirm the physicality of this anion shifting, we performed a structure optimisation of the elpasolite-type structure. Firstly, we note that the cell parameters of the optimised structure are slightly larger than the observed cell parameters (table S14). Using the PBE exchange–correlation potential often produces slightly overestimated cell parameters [25], but the optimised cell parameters do correlate very well with the ones prior obtained using more expensive calculation methods [7, 8]. Herein, we observe a significant shift of the Br atoms away from the symmetrical position towards the In atoms. The M–Br distances in the optimised structure of $d_{\text{Ag-Br}} = 2.869$ Å and $d_{\text{In-Br}} = 2.738$ Å are slightly longer than our observed values, which is mainly due to the fact that the optimised unit cell parameters are approximately 2% larger than the observed ones. However, the increase is nearly isotropic and the ratio $d_{\text{Ag-Br}}/d_{\text{In-Br}}$ (DFT) = 1.048 is close to the observed one ($d_{\text{Ag-Br}}/d_{\text{In-Br}} = 1.068$).

### 2.2. Optical properties

While our findings confirm the general conclusion of prior theoretical work that the compound should be stable, we find an optical bandgap of $E_g = 2.36$ eV from diffuse reflectance measurements (figure 2). The optical bandgap was obtained by treating the diffuse reflectance data with the Kubelka–Munk function $F(R) = (1-R)^2/2R$ (where $R$ is the reflectance of the sample) to obtain a calculated absorption combined with a Tauc-plot treatment, as successfully applied on halide semiconductors previously [26]. Plotting the data as for a direct forbidden transition with $[F(R)\cdot h\nu]^{2/3}$ gives a very good linear fit over a wide region above the optical bandgap. This optical bandgap is significantly higher than predicted from theoretical calculations ($E_g$ in the range of $r = 1.96$ Å and $r = 1.81$ Å) [21].
1.33–1.5 eV) [7, 8]. It is remarkable that the same effect is observed for the chloride analogue, where the bandgap error is $E_g(\text{expt.}) - E_g(\text{theor.}) = 0.9$ eV [7–9]. In a recent theoretical study, this behaviour was explained by parity-forbidden transitions that make excitations at the bandgap level unlikely [27]. When zooming on the onset of the Tauc function below the optical bandgap, one finds an increase of the absorption at about 1.7 eV and hence much closer to the theoretically calculated bandgap (figure S10). This discrepancy may be taken as a hint for a parity-forbidden transition in this material as predicted by Mitzi et al [27].

Not only that the observed optical bandgap of 2.36 eV is probably too large for direct use of this material in a solar cell, we further observed another problematic characteristic that will prevent this material from being used as solar absorber. When exposing the compound to light, a rather quick degradation of the material can be observed, clearly visible through a darkening of the illuminated area (figure S11). To quantify the effect of light on Cs$_2$[AgIn]Br$_6$, we performed long-term spectrally resolved reflectance measurements with a broadband light source on the sealed sample. The decay of the reflectance below the band gap of Cs$_2$[AgIn]Br$_6$ (2.3 eV $\approx$ 540 nm) shows that the compound degrades quickly under light illumination (figure 3, S12–S14). One can quantify that approximately half of the relative change happening in the first $\approx$40 min (figure 3). While the illuminated area is clearly darkened after the light exposure, the rest of the sample preserved its colour during the measurement, showing that the degradation was caused by the light, rather than being an intrinsic effect of the material (figure S13). The stability in dark conditions is also supported by prior diffuse reflectance measurements of freshly prepared material and after 2 h of storage in in the dark (figure S9). The light-induced decomposition of the material might happen in analogy to AgBr, which decomposes into elemental silver nanoparticles and Br$_2$ [28]. A similar effect of light on the analogous Bi-containing double perovskite Cs$_2$AgBiBr$_6$, but not with the same severity, has been observed [6, 24]. Further studies on nanocrystals of the

Figure 2. Tauc-plot for a direct forbidden transition (red line) with a linear fit in the region of 2.6–3.25 eV (black line, $f(x) = 5.187 \times 11.858$). The horizontal black line give the base line as $g(x) = 0.36$.

Figure 3. Integrated reflectance signals over the 400–1100 nm range versus light exposure time. The measurement over 7 h (red curve) is shifted by 2.5 in intensity for a better comparison with the measurement over 16 h (black curve).
material showed the formation of silver nanoparticles during the degradation [29]. We would expect that the decomposition process in Cs$_2$[AgIn]Br$_6$ would work through a similar pathway. The degradation of the material results in a notable change of the reflectance in the region below the bandgap (500–900 nm) (figures S14–S17). Furthermore, we observed that the irradiated spot appeared less dark after a period of time (figure S13), which could rather be a consequence of an overall sample degradation than a ‘healing effect’ but a more detailed study would clearly be beneficial to understand the light degradation of this material.

3. Conclusion

We present the successful mechanochemical synthesis of Cs$_2$[AgIn]Br$_6$, which is of great interest due to its predicted suitability as potential solar absorber material. However, the measured optical bandgap of the compound is 2.36 eV and is approx. 1 eV larger than predicted by theory. This relatively large bandgap and the observation of a light-induced degradation are significant challenges for the application of Cs$_2$[AgIn]Br$_6$ in photovoltaics and should be addressed in further studies. Overcoming the instability under light will, in fact, be the most important step on the way to produce long term stable solar cell devices with double perovskites. From the comparison of Cs$_2$[AgIn]Br$_6$ with the Bi$_3^+$ containing analogues, it is to be anticipated that Ag$^+$ is the limiting factor in the light stability and a replacement of Ag$^+$ will be highly beneficial for the production of stable solar absorber materials in this class. We are currently following this direction and will combine an experimental materials discovery approach with in-depth structural and physical characterisation to identify more promising candidate materials. Still, the proof of existence of Cs$_2$[AgIn]Br$_6$ as presented in this work is a powerful demonstration of the possibilities of in silico materials discovery and their targeted synthesis to screen the chemical space in the most efficient way.

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