Journal of Hazardous Materials 447 (2023) 130829

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Organic solvent free PbI_2 recycling from perovskite solar cells using hot water

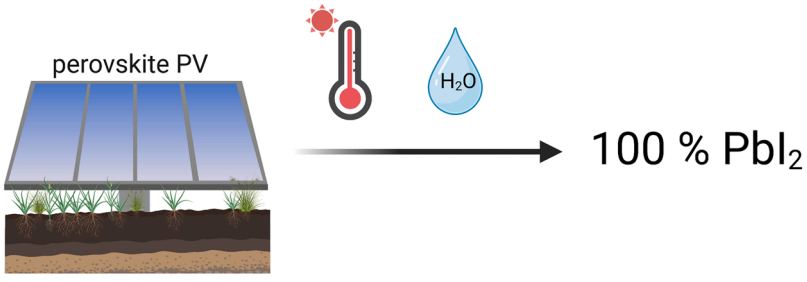
Felix Schmidt [a,b,1], Meret Amrein [a,1], Sebastian Hedwig [a,c], Manuel Kober-Czerny [d], Adriana Paracchino [e], Ville Holappa [f], Riikka Suhonen [f], Andreas Schäffer [b], Edwin C. Constable [c], Henry J. Snaith [d], Markus Lenz [a,g,*]

[a] Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Hofackerstrasse 30, 4132 Muttenz, Switzerland
[b] Institute for Environmental Research, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany
[c] Department of Chemistry, University of Basel, Mattenstrasse 24a, Basel 4058, Switzerland
[d] Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK
[e] PV-Center, CSEM, Jaquet-Droz 1, 2002 Neuchâtel, Switzerland
[f] Printed materials systems, VTT Technical Research Centre of Finland Ltd., Kaitoväylä 1, Oulu 90570, Finland
[g] Department of Environmental Technology, Wageningen University, 6708 WG Wageningen, the Netherlands

HIGHLIGHTS

- Water solubility of PbI_2 is highly temperature dependent, which was exploited for Pb recycling from perovskites.
- Pb was fully extracted from different perovskites and PbI_2 recovered in pure form was made into a new perovskite layer.
- The extracted perovskite residues were sufficiently depleted in metals to not qualify as hazardous materials.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Edward Burton

Keywords:
Perovskite solar cells
Recycling
Environment
Recovery
Lead pollution

ABSTRACT

Perovskite solar cells represent an emerging and highly promising renewable energy technology. However, the most efficient perovskite solar cells critically depend on the use of lead. This represents a possible environmental concern potentially limiting the technologies' commercialization. Here, we demonstrate a facile recycling process for PbI_2, the most common lead-based precursor in perovskite absorber material. The process uses only hot water to effectively extract lead from synthetic precursor mixes, plastic- and glass-based perovskites (92.6 – 100% efficiency after two extractions). When the hot extractant is cooled, crystalline PbI_2 in high purity (> 95.9%) precipitated with a high yield: from glass-based perovskites, the first cycle of extraction / precipitation was sufficient to recover 94.4 ± 5.6% of Pb, whereas a second cycle yielded another 10.0 ± 5.2% Pb, making the recovery quantitative. The solid extraction residue remaining is consequently deprived of metals and may thus be disposed as non-hazardous waste. Therefore, exploiting the highly temperature-dependent solubility of PbI_2 in water provides a straightforward, easy to implement way to efficiently extract lead from PSC at the end-of-life

* Corresponding author at: Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Hofackerstrasse 30, 4132 Muttenz, Switzerland.
E-mail address: markus.lenz@fhnw.ch (M. Lenz).
[1] These authors contributed equally.

https://doi.org/10.1016/j.jhazmat.2023.130829
Received 24 November 2022; Received in revised form 12 January 2023; Accepted 17 January 2023
Available online 18 January 2023

and deposit the extraction residues in a cost-effective manner, mitigating the potential risk of lead leaching at the perovskites' end-of-life.

Environmental implications

Novel perovskite photovoltaics are promising for renewable energy production, but can contain lead (Pb) in their perovskite layers. So far, Pb recycling mostly relied on selective dissolution in organic solvents. We exploited the temperature dependence of PbI_2 solubility in water instead and used hot water to fully extract Pb from different perovskites, producing pure PbI_2 upon cooling. The recovered PbI_2 was successfully re-manufactured into a new perovskite layer. The extracted perovskite residues were sufficiently depleted in Pb so that they did not longer classify as hazardous materials. Relying only on water, our approach offers an environmentally benign possibility for recycling.

1. Introduction

Perovskite solar cells (PSCs) are considered a potential breakthrough technology for sustainable energy [1,2]. Vast research and development efforts have led to large improvements in power conversion efficiencies, up to 25.7% [3]. These improvements have, along with straightforward solution-based processing methods, paved the way towards the technologies' commercialization [4]. However, the use of lead (Pb) represents a possible environmental and social acceptance concern for the industrial-scale application of perovskite solar cells [5–7]. Lead is a prominent metal pollutant due to its formerly widespread use in various consumer goods (paint, gasoline and household plumbing) and is highly regulated. Pb recycling is mandatory for the commercialization of Pb-containing products [8–12] and any new technology is required to limit Pb use, to prevent Pb leaching [13,14] and/or develop suitable Pb recovery and re-use schemes[15,16]. Avoidance of Pb in PSC is possible via substitution with Sn or by using Pb-free double perovskites such as $Cs_2AgBiBr_6$ [17–19]. However, the resulting photovoltaic devices are neither as efficient nor as stable compared to their Pb-based counterparts [3]. Therefore, utility-scale commercialization with Pb-based perovskites is probable.

During the early stages of PSC development, initial efforts towards Pb recycling have been carried out. Binek et al. (2016) and Kadro et al. (2017) used selective dissolution in different organic solvents to recover all components of the PSC device stack layers [20,21]. After these initial studies, further methods used molten-salt electrolysis and subsequent electrochemical recovery [22], and leaching followed by ion exchange resins and / or composite materials to concentrate Pb sufficiently for recovery [23,24]. Despite successful in recovering Pb, the methods used so far have potential for optimization with regard to their demand for chemicals (organic solvents, eluents), materials (ion exchangers), energy (high-temperature processes) as well as occupational health and safety requirements (regulated chemicals, acids). Further, the methods used so far were partly based on mechanical handling that may proof difficult to upscale (i.e., the use of adhesive tape to remove electrodes).

Therefore, this study investigated a novel recycling route based solely on the strong temperature dependence of PbI_2 solubility in water. The process consists of simple mechanical pre-treatment for breaking the PSC structure (either cutting of the plastic PSC by scissors or shattering of glass cells by a hammer), hot aqueous extraction of the perovskite layer, separation of plastic or glass residues from Pb dissolved in hot water and crystallization of PbI_2 upon cooling. Extraction conditions were optimized using a design-of-experiment approach and extraction efficiency was determined by triple-quadrupole inductively coupled plasma mass spectrometry (QqQ-ICP-MS) for synthetic PSC mixtures as well as real plastic- and glass-based PSC. The elemental mass flow as well as purity of the precipitates was studied by QqQ-ICP-MS and total organic carbon (TOC) measurements. The starting materials as well as the residues after extraction were evaluated in relation to their possible classification as hazardous wastes.

2. Methods

2.1. Chemicals and materials

A synthetic PSC mixture was prepared based on the composition of a stack of indium tin oxide (ITO) / TiO_2 / (methylammonium lead triiodide) (MAPI) / 2,2′,7,7′-Tetrakis[N,N-di(4-methoxyphenyl)amino]−9,9′-spirobifluorene (spiro-OMeTAD)/Al commonly used [55]. ITO nanopowder, TiO_2 (nanopowder, < 100 nm), spiro-OMeTAD and PbI_2 (all Sigma-Aldrich, Basel, Switzerland) and methylammonium iodide (MAI, TCI Chemicals, Tokyo, Japan) were dissolved in deionized water (18.2 MΩ/cm). HNO_3 (67%, trace metals grade, Sigma-Aldrich, Basel, Switzerland) was used for sample acidification and digestion. The amounts dissolved were based on typical material thicknesses in PSC (Table S1, Supporting Information) and the final concentration of PbI_2 corresponded to 1 g/L.

For extraction experiments, glass substrate samples (ITO / poly(4-butyl-N,N-diphenylaniline) (poly-TPD) or [2-(3,6-Dimethoxy-9 H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz) / $FA_{0.83}Cs_{0.17}PbI_{0.83}Br_{0.17}$ / LiF / C_{60} / SnO_2 / ITO / Ag) were shattered with a hammer and the fragments (6–9 cm^2) were processed without any further size reduction. Polyethylene terephthalate (PET) substrate samples (ITO / SnO_2 / $FA_{0.83}Cs_{0.17}PbI_3$ / poly(3-hexylthiophene-2,5-diyl) (P3HT) or spiro-OMeTAD / Ag) were cut into pieces of 0.5 cm^2. Based on the sample area, the water volume was calculated using an area-equivalent concentration of 1 g PbI_2 per m^2. Total concentrations in the samples were verified after microwave-assisted acid digestion (see Section 4.2). This included waste glass cells (~1.1 × 1.4 cm^2) used to establish the mass balances.

2.2. Analytical methods

All metal analyses were performed on an ICP-MS system (8800 QqQ-ICP-MS, Agilent, Basel, Switzerland) using general-purpose operational settings. Quantification was performed via external calibration from multi-element standards using $^{103}Rh^+$ as an internal standard to account for matrix effects. For extraction experiments, $^{107}Ag^+$, $^{115}In^+$, $^{118}Sn^+$, $^{133}Cs^+$, $^{197}Au^+$, and $^{208}Pb^+$ were used for quantification and the ICP-MS was operated using helium as a collision gas (5 mL/min), whereas $^{47}Ti^+$ and $^{27}Al^+$ were measured in mass-shift mode using O_2 as a reaction gas (30%). Total metal content after extraction was determined by microwave-assisted acid digestion (MARS 6, CEM GmbH, Kamp-Lintfort, Germany). The samples were placed into 55 mL Teflon vessels and 5 mL 67% HNO_3 was added. The temperature was then ramped to 200 °C in 15 min and kept at 200 °C for 10 min before cooling to room temperature.

Scanning electron microscopy (SEM) images were recorded with a GeminiSEM (Zeiss, Oberkochen, Germany) operating at 20 kV. The investigation of the elemental composition was performed by energy dispersive X-ray diffraction (EDX) analysis using an ultra-dry EX470–299100 detector (Thermo-Scientific, Basel, Switzerland) operating at 20 kV. Crystalline PbI_2 samples were applied onto an Au-coated nuclear pore filter (0.2 μm pore size, APC GmbH, Eschborn, Germany) and air dried.

2.3. Design of experiments and extraction process

Process conditions for PbI_2 extraction were optimized using a design-of-experiments approach (STAVEX software, AICOS, Basel, Switzerland). In short, the added amount of PbI_2, temperature and exposure time was investigated using a central composite design matrix (Table S2, Supporting Information). The measured response variables were the maximal dissolved Pb^{2+} concentration and the minimal energy requirement. The energy requirement was based on water mass, temperature increase and the specific heat capacity of water (detailed in Section S4, Supporting Information). The experiments were performed in batches of 100 mL. Heating was carried out on a heating plate under stirring. Samples were taken after 5, 15, 30, 60 and 120 min and immediately diluted into 3% HNO_3 for ICP-MS measurements.

After the design-of-experiment, the optimized extraction process consisted of the following: after heating of the synthetic PSC solution for one hour at 50 °C, the solid residue was removed by vacuum microfiltration using an MN-GF 5 filter (0.4 µm, Macherey-Nagel, Düren, Germany). The filtration was performed with heated glassware (> 50 °C) to minimize losses by early crystallization on colder surfaces. The hot permeate was then left to cool down to room temperature. The crystalline precipitate was separated from the supernatant by vacuum microfiltration and dried under reduced pressure.

2.4. Calculations

The extraction yield, Y_E [%] was defined as the amount of element dissolved at 50 °C divided by the total amount of element in the experiment × 100. The precipitation yield, Y_P, [%] was defined as the amount of element dissolved at 50 °C minus the amount of element dissolved at 20 °C divided by the total amount of element in the experiment × 100.

3. Results

3.1. Pb extraction

Optimal process parameters (i.e., minimal energy input and exposure time, maximal dissolved Pb^{2+} concentration) were determined by a design-of-experiments approach to be 50 °C, 1.05 g/L PbI_2 loading and 62.5 min exposure time (full details in Table S2, supporting information). Based on these parameters, high PbI_2 extraction yields were achieved and ranged between 87 ± 11% (synthetic perovskite mixture, Fig. 2A), 87 ± 4% (plastic substrate, Fig. 2B) and 91 ± 3% (glass substrate, Fig. 2C). After separation of PbI_2 by crystallization, the same aqueous phase was subjected to another extraction cycle and total Pb extraction could be increased to 93 ± 11% using the synthetic perovskite mixture (Fig. 2A), 96 ± 6% using a plastic substrate (Fig. 2B) and 100 ± 6% using a glass substrate (Fig. 2C).

Importantly, other non-perovskite layer-derived elements (Ti, In, Sn, Al, Ag) were not extracted. The maximal extraction was seen for Ti (6.3%, synthetic perovskite mixture, Fig. 2 A) and Sn (0.03% and 1.6%, plastic and glass substrate, respectively, Fig. 2B-C), whereas the other elements were not detected via ICP-MS. The respective limits of detection were lower than 0.0001% for Ag, Al and In. This was consistent with the mass flow determined for glass PSCs (Table 1), that showed quantitative Pb recovery and little other element recovery after two extractions (max 1.9% In). The low residual Pb concentrations that were still observed in the extracted glass residues (Table 2) may be either due to an (mathematical) overestimation of elemental yields (compare the standard deviations in Table 1) and / or to Pb present in the original glass not being extracted by water. Other possible components that will be extracted at 50 °C and may thus interfere with the recovery of pure PbI_2 are BrI_2, MAI, FAI and CsI. However, all these compounds are highly soluble at 20 °C as well (supporting information, section S4), so that PbI_2 is the only component which is expected to precipitate upon cooling due to the significant difference in solubility at 20 °C and 50 °C (supporting information, Fig. S3). This was reflected by the crystallinity and high purity of the precipitates obtained (see next section).

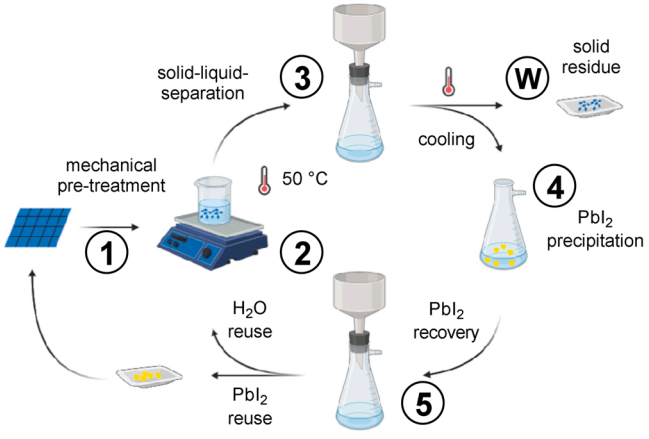


Fig. 1. Scheme of the facile recycling process developed. The process includes mechanical pre-treatment (cutting or shredding) (1), hot aqueous extraction(2), solid-liquid separation (filtration) (3), PbI_2 precipitation (cooling) (4) and recovery (5). PbI_2 can be reused in new perovskites; solid waste (W) is deprived of Pb.

3.2. Characterization of recovered PbI_2

Precipitates from the synthetic PSC mixture were visible as hexagonal platelets (size variation between a few µm and 10–15 µm up to 100–150 µm) in SEM, which corresponded to typical morphology of PbI_2 [25]. Elemental analysis of different platelets the crystalline product via EDX spectroscopy showed that Pb and I were present in a weight ratio of 25.0 ± 0.7 wt% Pb: 29.5 ± 0.3 wt% I, corresponding to a molar ratio of 1 ± 0.03 mol Pb: 1.95 ± 0.02 mol I Fig. 3C). The high value for Au (29.5 ± 0.9 wt%) originated from the gold nuclear pore filter on which the crystals were deposited, and Cu possibly originated from the sample holder. XRD measurements have shown that the crystallinity of the product was comparable to the starting material (supporting info, Fig. S5). The purity of the precipitates was determined by QqQ-ICP-MS and TOC and higher than 95.9% (supporting information, Table S4). The obtained PbI_2 was successfully incorporated in a new perovskite layer with optoelectronic properties (band gap, visible absorption behaviour and carrier lifetime) similar to commercial PbI_2 (supporting information, section S8). For fabrication of most efficient PSCs, however, one may still need to recrystallize PbI_2 (either in water or organic solvent) and finetune its stoichiometry (e.g. [25,26]), which will result in some environmental impacts (compare e.g. [11]).

4. Discussion

4.1. PSC recycling by hot aqueous extraction

Binek et al. (2016) achieved PbI_2 recovery by first hydrolysing the perovskite layer and extracting MAI in water, followed by quantitative extraction of PbI_2 in DMF [20]. The PbI_2-DMF solution was then re-used for the fabrication of fresh perovskite layers. A residual concentration of Pb in the aqueous phase (after MAI extraction) of 4 mg/L was reported. Similarly, Kadro et al. (2017) demonstrated a two-step approach for PbI_2 recovery by perovskite conversion using EtOH (for MAI extraction) and subsequent PbI_2 extraction using DMF [27]. Despite PbI_2 can be selectively dissolved in DMF, the use of DMF in industrial processes is highly regulated (e.g., EU Commission Regulation 2021/2030) due to its reproductive toxicity. Therefore, both studies routes would need to include efficient solvent recovery to ensure a safe Pb management [28],

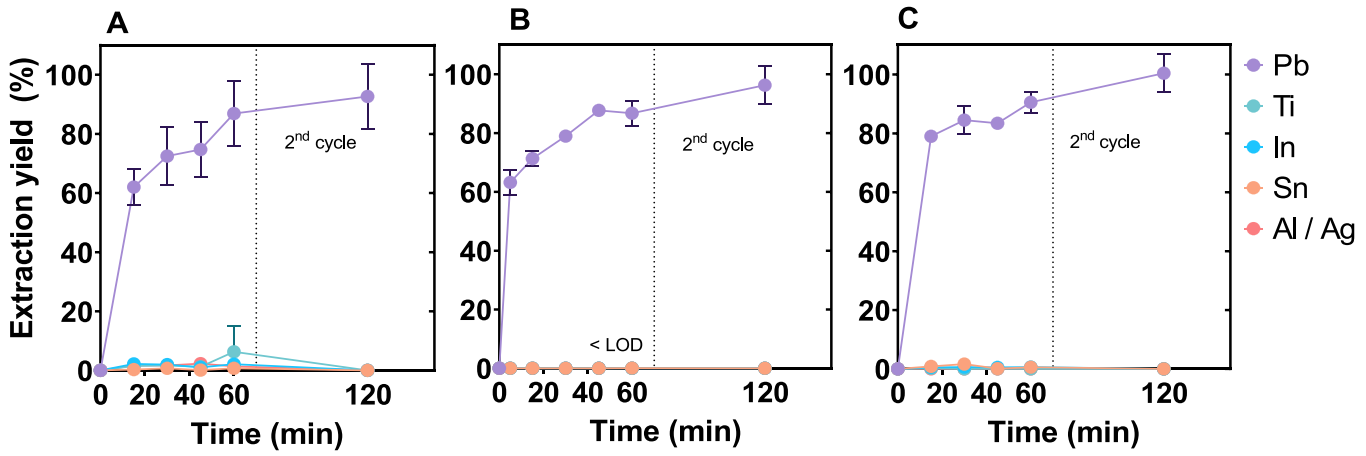


Fig. 2. Metal extraction of a synthetic PSC mixture (A), a plastic-based PSC (B) and a glass-based PSC (C) during two consecutive extraction cycles (for details on composition see supporting information).

Table 1
Mass flow during glass-based PSC recycling.

		Extraction 1		Extraction 2		total
	Initial [%]	Y_E [%]	Y_P [%]	Y_E [%]	Y_P [%]	Y_P-SUM [%]
Pb	100	97.3 ± 5.4	94.4 ± 5.6	12.6 ± 5.1	10.0 ± 5.2	104.3
Ti		0.1 ± 0.2	-0.1 ± 0.4	0.8 ± 0.8	0 ± 1.6	-0.1
In		2.0 ± 0.8	1.8 ± 0.8	0.1 ± 0.1	0.0 ± 0.1	1.9
Sn		0.5 ± 0.7	0.5 ± 0.7	0 ± 0	-0.2 ± 0.3	0.3
Al		0 ± 0	0 ± 0	0 ± 0	0 ± 0	0.0

Table 2
Metal content in glass PSC before and after extraction versus maximally allowed concentration in solid (regulated in the US "Resource Conservation and Recovery Act", see supplementary information).

	Max. Conc. solid [mg / kg]	Conc. PSC initial [mg / kg]	Conc. PSC residue [mg / kg]
As	100	21.1 ± 2.3	< 1.8
Ba	2000	< 2.0	92.9 ± 18.0
Cd	20	< 3.9	< 2.0
Cr	100	< 1.0	< 1.0
Pb	100	360 ± 51.5	37.2 ± 3.6
Hg	4	< 1.0	< 1.0
Se	20	3.4 ± 0.7	1.1 ± 0.1
Ag	100	< 5.8	< 2.0

certainly adding to the costs. Recently, more than a dozen different recycling options mainly relying on selective dissolution with organic solvents were compared by life-cycle-analysis [29], demonstrating that most had a higher environmental and toxicological impact than the materials themselves due to the use of high amounts of solvents. Though technically possible, other approaches of Pb recycling may prove too energy intensive (e.g. molten-salt electrolysis and subsequent electrochemical recovery [22]) or costly (ion exchange resins and composite materials to eluents to regenerate these) [23,24].

Here, we present a simple procedure using hot water as the only extractant and means to concentrate PbI_2 by precipitation (Fig. 1). The recovered PbI_2 was crystalline (Fig. 3 and supporting information, Fig. S5) and pure (supporting information, Table S5) and successfully re-used in new perovskite films, with no considerable negative effect on optoelectronic properties in comparison to commercial PbI_2 (supporting information, Fig. S6). The necessary pre-treatment is easy to implement technically (shredder for plastic PSC, hammer mill or else for glass PSC).

Perovskite hydrolysis leads to the immediate dissolution of various inorganic and organic halide salts (e.g. CsI, MAI, FAI, CsCl), depending on the perovskite composition [30]. These salts are highly water soluble even at 20 °C (supporting information, section S4), and thus remain in solution upon cooling of the perovskite aqueous extractant (confirmed by purity and crystallinity of the PbI_2 produced). Contrary, PbI_2, the most common starting material for perovskite absorber layer fabrication, has a strongly temperature-dependent water solubility (supporting information, Fig. S3) [31]. This behaviour is leveraged here to recover PbI_2 selectively. Process optimization showed full dissolution after 15 min (supporting information, Fig. S2) at moderate temperatures (50 °C, 97% dissolution) after two extraction steps. Even higher temperatures may be used to ensure high PbI_2 extraction when off-heat from another process is used as a heating source [32]. Water reuse for another recovery cycle (see Fig. 2) represents a simple method to increase PbI_2 recovery. Critically, while aiding PbI_2 dissolution in initial cycles, gradual build-up of iodide (one molar equivalent per cycle) would limit Pb^{2+} solubility at very high iodide concentrations; by the presence of

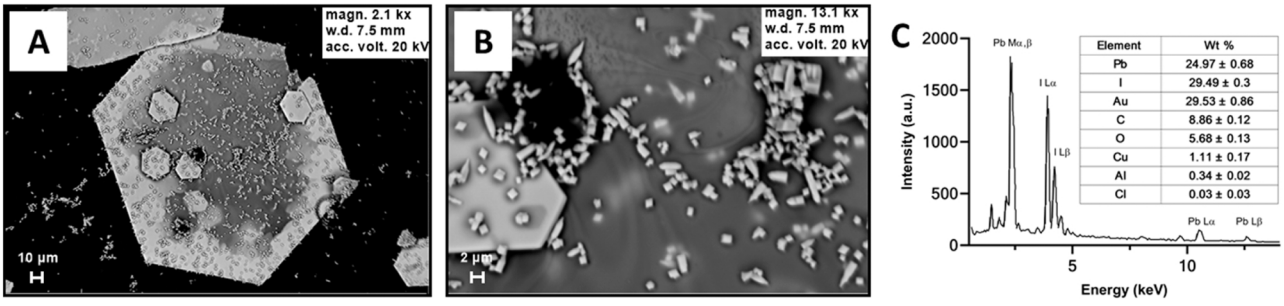


Fig. 3. SEM micrographs showing hexagonal crystals of PbI_2 recovered at 2100 × (A) and 13100 × (B) magnification and EDX spectra with elemental composition (C).

excess iodide in a common ABX_3 composition, the thermodynamic equilibrium for PbI_2 precipitation ($APbI_3 \rightleftarrows A^+_{(aq)} + Pb^{2+}_{(aq)} + 3\ I^-_{(aq)} \rightleftarrows PbI_{2\ (s)} + A^+_{(aq)} + I^-_{(aq)}$) is shifted and favours the precipitation based on "Le Chatelier's principle" and the "common ion effect". Addition of excess iodine (e.g. by KI addition) thus offers an opportunity to further increase the yield of Pb, limiting emissions with the spent aqueous phase and minimizing Pb impacts [26]. In this study, the extraction with hot water was conducted twice since this was sufficient to recover Pb quantitatively (Table 1). In practise, one would probably use the same extraction medium for further extraction steps until the Pb extraction is no longer quantitative and the solution has been saturated. After that, either the dissolved materials can be recovered from the concentrate or the liquid needs to be disposed of (by means of conventional or advanced wastewater treatment; or by incineration). How often the extraction can be repeated (as well as how much cost / environmental impact is associated with the respective treatment) remain questions for future research.

Extraction at high pulp densities decreases water (and thus heat) use as well as necessary footprint per area of PV recycled. Applying optimized extraction conditions to real PSC samples, pulp densities (i.e., substrate mass per volume of water) ranged from 250 to 270 g/L (for PET substrate) to 1′300–1′500 g/L (for glass substrate). Despite these high pulp densities, efficient extraction was achieved (see Fig. 2B–C). These pulp densities were considerably higher compared to other published PV recycling routes; Chakankar et al. (2019) leached various metals from end-of-life solar cells (glass substrate) using microbes at a low pulp density of 10 g/L [33]. Zhang et al. (2020) reported efficient recovery of Te from (glass-based) CdTe PV by acid leaching employing a pulp density of 40 g/L [34]. Additionally, two recycling methods concerning recycling processes of CdTe and CIS modules (glass substrate) employ pulp density between 10 and 300 g/L, which, for PET substrate PSCs, is similar to the process described here [35,36].

4.2. Roadmap to future solid waste management of PSCs

Waste disposal costs (via landfilling) are commonly determined on a by-weight basis [37], and different categories of wastes are associated with distinctive costs. In particular the deposition of "hazardous waste" is costly: it has been estimated that deposition of such waste can cost ~ 3´300 $USD/t compared to 40 $USD/t for municipal waste [11]. Previously, it has been noted that the value of recovered materials may be a driver for recycling. For instance, Binek et al. determined FTO to be one of the most expensive layers in the stack (with a price of ~18 USD/m^2 for industrial scale), whereas the perovskite layer is relatively inexpensive (1.1 $ USD/m^2). Considering the weight of the glass PSCs used here (~5.6 kg / m^2 for the cell alone, without frame, wiring etc.), the deposition of 1 m^2 PSC as hazardous waste would cost an estimated 18.5 $ USD/m^2, with a cost saving of 18.3 $ USD / m^2 if it can be deposited at the price of 40 $ USD /t. In the USA, for instance, there is a number of elements that will determine, if a waste is considered hazardous or not (compare section S6, supporting information) [11], amongst them Pb. Therefore, Pb extraction needs to be sufficiently efficient to qualify the residual waste for standard disposal and WEEE compliance [38]. Using hot water applied here indeed resulted in sufficiently low residual Pb concentration in the glass residues (Table 2). If the glass fraction is sufficiently depleted in metals, it may not be deposited at all (but re-used for the manufacture of new glass), so that cost savings would be the full 18.5 $ USD/m^2. Although these are rough estimations, they clearly underline that avoidance of deposition costs at the end-of-life will be a major driver for recycling, and the value of recovered PbI_2 will not be. In any case, end-of-life waste management will thus strongly influence LCOE [39], in particular that of glass based PSCs, since glass can account for more than 90% of total PSC weight [40].

Next to fulfilling the requirements regarding hazardous waste, Pb recycling is also mandatory from the point of complying with Waste from Electrical and Electronic Equipment (WEEE) regulations. The European Unions' Waste from Electrical and Electronic Equipment (EU WEEE) directive, for instance, defines recycling rates based on weight. Thus, successful glass recycling is therefore the prerequisite for achieving specified recycling rates. Decommissioning of glass-based perovskites in rooftop or solar park installations may proceed similarly than for first-and second-generation PV and glass recycling may proceed in the same way (reviewed in [41,42]), with the exception of materials exclusively present in PSCs. Tandem solar cells (e.g. perovskite-on-silicon or all-perovskite tandems) have the potential to become the first PSC product to enter the market [2,43]. The low reactivity of silicon active layers towards aqueous treatment should enable the development of processes similar to those presented here.

Next to costs, there are considerate social and environmental impacts associated with the use of some materials in PSC, most prominently with Pb, Ag and/or ITO (e.g. [16]). One the one hand, impacts are generated during the production (through primary mining and refining of raw materials), on the other hand, negative impacts may originate during the use and end-of-life phase upon e.g. leaching (see [44,45]). Recycling and re-use of PSC components thus also contributes to the mitigation of these negative impacts. In addition, it may lessen supply risks associated (in particular In is a critical raw material[39]). Augustine et al. (2019) recently published a straightforward procedure to recover ITO glass using mild alkaline treatment and demonstrated the re-usability of PSC substrates [46]. Li et al. (2011) showed In recovery from ITO targets via acid leaching and selective precipitation to quantitatively recover In [47,48]. Ag recovery may be envisioned via acid extraction (see [49]). All approaches can be considered compatible with the PbI_2 recovery scheme development and would use the solid residue ("W" in Fig. 1) as a starting material for extraction of elements. For applications envisioned for plastic-based PSCs, such as consumer electronics and internet-of-things [50] one can apply energy recovery via incineration with prior or subsequent element recovery (as demonstrated for Ag and organic photovoltaics by Søndergaard et al., 2014, 2016 [49,51]). Alternatively, plastic waste (after elemental recovery) may be used as an aggregate in building and construction materials [52,53]. Lastly, recycling may also facilitate technology acceptance[54], in particular considering that Pb is such a "prominent" contaminant.

Funding Sources

This project has received funding from the European Union's Horizon 2020 framework programme for research and innovation under grant agreement no 763977 of the PerTPV project.

CRediT authorship contribution statement

Felix Schmidt: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization. **Meret Amrein**: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization. **Sebastian Hedwig**: Methodology, Investigation. **Manuel Kober-Czerny**: Resources, Investigation. **Adriana Paracchino**: Resources, Writing – review & editing. **Ville Holappa**: Resources, Writing – review & editing. **Riikka Suhonen**: Resources, Writing – review & editing. **Andreas Schäffer**: Writing – review & editing, Supervision. **Edwin C. Constable**: Writing – review & editing, Supervision. **Henry J. Snaith**: Resources, Writing – review & editing, Supervision. **Markus Lenz**: Conceptualization, Investigation, Writing – review & editing, Visualization, Supervision.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Markus Lenz reports financial support was provided by European Commission.

Acknowledgements

The authors thank Stefan Lehmann for support during the extraction experiments.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.130829.

References

[1] Christians, J.A., Habisreutinger, S.N., Berry, J.J., Luther, J.M., 2018. Stability in perovskite photovoltaics: A paradigm for newfangled technologies. ACS Energy Lett 3, 2136–2143.
[2] Sutherland, B.R., 2020. Perovskite-silicon tandems edge forward. Joule 4, 722–723.
[3] Green, M.A., Dunlop, E.D., Hohl-Ebinger, J., Yoshita, M., Kopidakis, N., Hao, X., 2020. Solar cell efficiency tables (version 56). Prog Photovolt Res Appl 28, 629–638.
[4] Wang, P., Wu, Y., Cai, B., Ma, Q., Zheng, X., Zhang, W.-H., 2019. Solution-processable perovskite solar cells toward commercialization: progress and challenges. Adv Funct Mater 29, 1807661.
[5] Rong, Y., Hu, Y., Mei, A., Tan, H., Saidaminov, M.I., Il Seok, S., McGehee, M.D., Sargent, E.H., Han, H., 2018. Challenges for commercializing perovskite solar cells. Science 361.
[6] Jeong, D.-N., Yang, J.-M., Park, N.-G., 2020. Roadmap on halide perovskite and related devices. Nanotechnology 31, 152001.
[7] Chatterjee, S., Pal, A.J., 2018. Influence of metal substitution on hybrid halide perovskites: towards lead-free perov-skite solar cells. J Mater Chem A 6, 3793–3823.
[8] McConnell, J.R., Wilson, A.I., Stohl, A., Arienzo, M.M., Chellman, N.J., Eckhardt, S., Thompson, E.M., Pollard, A.M., Steffensen, J.P., 2018. Lead pollution recorded in Greenland ice indicates European emissions tracked plagues, wars, and imperial expansion during antiquity. Proc Natl Acad Sci 115, 5726–5731.
[9] Njati, S.Y., Maguta, M.M., 2019. Lead-based paints and children's PVC toys are potential sources of domestic lead poisoning–A review. Environ Pollut 249, 1091–1105.
[10] Boskabady, M., Marefati, N., Farkhondeh, T., Shakeri, F., Farshbaf, A., Boskabady, M.H., 2018. The effect of environmental lead exposure on human health and the contribution of inflammatory mechanisms, a review. Environ Int 120, 404–420.
[11] Moody, N., Sesena, S., deQuilettes, D.W., Dou, B.D., Swartwout, R., Buchman, J.T., Johnson, A., Eze, U., Brenes, R., Johnston, M., et al., 2020. Assessing the regulatory requirements of lead-based perovskite photovoltaics. Joule.
[12] M. Aboughaly, H.A. Gabbar, Recent Technologies in Electronic-Waste Management, in: E-Waste Recycl. Manag., Springer, 2020: pp. 63–80.
[13] Wu, P., Wang, S., Li, X., Zhang, F., 2022. Beyond efficiency fever: Preventing lead leakage for perovskite solar cells. Matter 5, 1137–1161. https://doi.org/10.1016/j.matt.2022.02.012.
[14] Ren, M., Qian, X., Chen, Y., Wang, T., Zhao, Y., 2021. Potential lead toxicity and leakage issues on lead halide perovskite photovoltaics. J Hazard Mater, 127848. https://doi.org/10.1016/j.jhazmat.2021.127848.
[15] Jung, B., Park, J., Seo, D., Park, N., 2016. Sustainable system for raw-metal recovery from crystalline silicon solar panels: from noble-metal extraction to lead removal. ACS Sustain Chem Eng 4, 4079–4083.
[16] Kim, H.-S., An, Y.-J., Kwak, J.I., Kim, H.J., Jung, H.S., Park, N.-G., 2022. Sustainable green process for environmentally viable perovskite solar cells. ACS Energy Lett 7, 1154–1177. https://doi.org/10.1021/acsenergylett.1c02836.
[17] Ke, W., Kanatzidis, M.G., 2019. Prospects for low-toxicity lead-free perovskite solar cells. Nat Commun 10, 965.
[18] Wu, C., Zhang, Q., Liu, Y., Luo, W., Guo, X., Huang, Z., Ting, H., Sun, W., Zhong, X., Wei, S., et al., 2018. The dawn of lead-free perovskite solar cell: highly stable double perovskite Cs2AgBiBr6 film. Adv Sci 5, 1700759.
[19] Diau, E.W.-G., Jokar, E., Rameez, M., 2019. Strategies to improve performance and stability for tin-based perovskite solar cells. ACS Energy Lett 4, 1930–1937.
[20] Binek, A., Petrus, M.L., Huber, N., Bristow, H., Hu, Y., Bein, T., Docampo, P., 2016. Recycling perovskite solar cells to avoid lead waste. ACS Appl Mater Interfaces 8, 12881–12886. https://doi.org/10.1021/acsami.6b03767.
[21] Kadro, J.M., Hagfeldt, A., 2017. The end-of-life of perovskite PV. Joule 1, 29–46.
[22] Wang, H., Chen, X., Li, X., Qu, J., Xie, H., Gao, S., Wang, D., Yin, H., 2022. Recovery of lead and iodine from spent perovskite solar cells in molten salt. Chem Eng J 447, 137498. https://doi.org/10.1016/j.cej.2022.137498.
[23] Ren, M., Miao, Y., Zhang, T., Qin, Z., Chen, Y., Wei, N., Qian, X., Wang, T., Zhao, Y., 2021. Lead Stabilization and Iodine Recycling of Lead Halide Perovskite Solar Cells. ACS Sustain Chem Eng 9, 16519–16525. https://doi.org/10.1021/acssuschemeng.1c07083.
[24] Chen, B., Fei, C., Chen, S., Gu, H., Xiao, X., Huang, J., 2021. Recycling lead and transparent conductors from perovskite solar modules. Nat Commun 12, 5859. https://doi.org/10.1038/s41467-021-26121-1.
[25] Tsevas, K., Smith, J.A., Kumar, V., Rodenburg, C., Fakis, M., bin Mohd Yusoff, A.R., Vasilopoulou, M., Lidzey, D.G., Nazeeruddin, M.K., Dunbar, A.D.F., 2021. Controlling PbI2 stoichiometry during synthesis to improve the performance of perovskite photovoltaics. Chem Mater 33, 554–566.
[26] Lee, C., Shin, Y., Jeon, G.G., Kang, D., Jung, J., Jeon, B., Park, J., Kim, J., Yoon, S. J., 2021. Cost-efficient, Effect of Low-Quality PbI2 Purification to Enhance Performances of Perovskite Quantum Dots and Perovskite Solar Cells. Energies 14, 201.
[27] Kadro, J.M., Pellet, N., Giordano, F., Ulianov, A., Müntener, O., Maier, J., Grätzel, M., Hagfeldt, A., 2016. Proof-of-concept for facile perovskite solar cell recycling. Energy Environ Sci 9, 3172–3179.
[28] Park, S.Y., Park, J.-S., Kim, B.J., Lee, H., Walsh, A., Zhu, K., Kim, D.H., Jung, H.S., 2020. Sustainable lead management in halide perovskite solar cells. Nat Sustain 3, 1044–1051.
[29] Rodriguez-Garcia, G., Aydin, E., De Wolf, S., Carlson, B., Kellar, J., Celik, I., 2021. Life cycle assessment of coated-glass recovery from perovskite solar cells. ACS Sustain Chem Eng 9, 15239–15248. https://doi.org/10.1021/acssuschemeng.1c05029.
[30] Hailegnaw, B., Kirmayer, S., Edri, E., Hodes, G., Cahen, D., 2015. Rain on methylammonium lead iodide based perovskites: Possible environmental effects of perovskite solar cells. J Phys Chem Lett 6, 1543–1547.
[31] Condeles, J.F., Martins, T.M., Dos Santos, T.C., Brunello, C.A., Mulato, M., Rosolen, J.M., 2004. Fabrication and characterization of thin films of PbI2 for medical imaging. J Non-Cryst Solids 338, 81–85.
[32] Grillo, R.J., 2014. Energy recycling–landfill waste heat generation and recovery. Curr Sustain Energy Rep 1, 150–156.
[33] Chakankar, M., Su, C.H., Hocheng, H., 2019. Leaching of metals from end-of-life solar cells. Environ Sci Pollut Res 26, 29524–29531.
[34] Zhang, X., Xu, W., Wang, S., Liu, D., Deng, P., Deng, J., Jiang, W., 2020. Research status of recovery of tellurium from cadmium telluride photovoltaic modules. In: Conf, I.O.P. (Ed.), Ser. Mater. Sci. Eng., p. 22024.
[35] Taylor, P., DeFilippo, M., 2012. Process to recycle end of life CDTE modules and manufacturing scrap. US 8821711, B2.
[36] W.F. Drinkard, M.O. Long, R.E. Goozner, Recycling of CIS photovoltaic waste, US577 98 77A, 1997.
[37] Nanda, S., Berruti, F., 2021. Municipal solid waste management and landfilling technologies: a review. Environ Chem Lett 19, 1433–1456.
[38] Walther, G., Steinborn, J., Spengler, T.S., Luger, T., Herrmann, C., 2010. Implementation of the WEEE-directive—economic effects and improvement potentials for reuse and recycling in Germany. Int J Adv Manuf Technol 47, 461–474.
[39] Cai, M., Wu, Y., Chen, H., Yang, X., Qiang, Y., Han, L., 2017. Cost-performance analysis of perovskite solar modules. Adv Sci 4, 1600269.
[40] Directive 2912/19/EU of the European Parliament and of the council of 4 July 2021 on Waste electrical and electronic equipment (WEEE), 2012.
[41] Azeumo, M.F., Germana, C., Ippolito, N.M., Franco, M., Luigi, P., Settimio, S., 2019. Photovoltaic module recycling, a physical and a chemical recovery process. Sol Energy Mater Sol Cells 193, 314–319.
[42] Chowdhury, M.S., Rahman, K.S., Chowdhury, T., Nuthammachot, N., Techato, K., Akhtaruzzaman, M., Tiong, S.K., Sopian, K., Amin, N., 2020. An overview of solar photovoltaic panels' end-of-life material recycling. Energy Strategy Rev 27, 100431.
[43] Djurišić, A.B., Liu, F.Z., Tam, H.W., Wong, M.K., Ng, A., Surya, C., Chen, W., He, Z. B., 2017. Perovskite solar cells - An overview of critical issues. Prog Quantum Electron 53, 1–37. https://doi.org/10.1016/j.pquantelec.2017.05.002.
[44] Celik, I., Song, Z., Phillips, A.B., Heben, M.J., Apul, D., 2018. Life cycle analysis of metals in emerging photovoltaic (PV) technologies: A modeling approach to estimate use phase leaching. J Clean Prod 186, 632–639.
[45] Gong, J., Darling, S.B., You, F., 2015. Perovskite photovoltaics: Life-cycle assessment of energy and environmental impacts. Energy Environ Sci 8, 1953–1968.
[46] Augustine, B., Remes, K., Lorite, G.S., Varghese, J., Fabritius, T., 2019. Recycling perovskite solar cells through inexpensive quality recovery and reuse of patterned indium tin oxide and substrates from expired devices by single solvent treatment. Sol Energy Mater Sol Cells 194, 74–82.
[47] Schmidt, F., Schaeffer, A., Lenz, M., 2019. Renewable energy from finite resources: example of emerging photovoltaics. Chim Int J Chem 73, 874–879.
[48] Li, Y., Liu, Z., Li, Q., Liu, Z., Zeng, L., 2011. Recovery of indium from used indium–tin oxide (ITO) targets. Hydrometallurgy 105, 207–212.
[49] Søndergaard, R.R., Espinosa, N., Jørgensen, M., Krebs, F.C., 2014. Efficient decommissioning and recycling of polymer solar cells: justification for use of silver. Energy Environ Sci 7, 1006–1012.
[50] Polyzoidis, C., Rogdakis, K., Kymakis, E., 2021. Indoor perovskite photovoltaics for the internet of things—challenges and opportunities toward market uptake. Adv Energy Mater 2101854.
[51] Søndergaard, R.R., Zimmermann, Y.-S., Espinosa, N., Lenz, M., Krebs, F., 2016. Incineration of organic solar cells: efficient end of life management by quantitative silver recovery. Energy Environ Sci 9, 857–861.
[52] Goli, V.S.N.S., Mohammad, A., Singh, D.N., 2020. Application of municipal plastic waste as a manmade neo-construction material: issues \& wayforward. Resour Conserv Recycl 161, 105008.
[53] Saikia, N., De, J., 2012. Brito, Use of plastic waste as aggregate in cement mortar and concrete preparation: A review. Constr Build Mater 34, 385–401.
[54] Abate, A., 2017. Perovskite solar cells go lead free. Joule 1, 659–664.
[55] Shi, Z., Jayatissa, A.H., 2018. Perovskites-based solar cells: a review of recent progress, materials and processing methods. Materials 11, 729.