

Lead or No Lead? Availability, Toxicity, Sustainability and Environmental Impact of Lead-Free Perovskites Solar Cells

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Abstract

Hybrid halide perovskites have taken over the world of new generation photovoltaics (PVs) since their first implementation just a decade ago, thanks to their efficiency comparable to commercial solutions, ease of fabrication, flexibility and versatility. Despite the outstanding performances, the presence of lead represents a severe concern for their future commercialisation, due to the toxicity and the associated risks for health and environmental impact. Lead-free perovskite offer a potential avenue to circumvent the problem. However, parameters such as material abundance, toxicity and environmental impact of potential lead-substituents are too often neglected. In this review, we put forward a different perspective, focusing on concepts such as cost, availability, sustainability and eco-friendliness required to justify large-scale use of lead alternatives in PV industry. Furthermore, a comparative case study with existing toxic-based technology using lead zirconate titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, also known as PZT, and CdTe solar panels is provided. Finally, it is argued that the advantages of using lead in photovoltaic panels – when including proper encapsulation and recycling - outweigh the risks associated with its manufacturing.

Introduction

Hybrid Perovskite solar cells have caused a stunning revolution in PVs, rising from 4 to 25.5% in just over a decade, while it took more than 40 years for CdTe and CIGS to achieve the same improvement^{1,2}. Common Lead-based Hybrid perovskites rely on APbX_3 structure, where A is an organic or inorganic cation (e.g. methylammonium, formamidinium or Cs^+) and X is a halide (mainly I⁻ or Br⁻). Their remarkable optoelectronic properties such as high optical absorption coefficient^{3,4}, carrier diffusion lengths up to 1 μm ,⁵ low trap density of $10^{16} - 10^{17} \text{ cm}^{-3}$, shallow defect states⁶, and small exciton binding energy⁷ are behind such high performances. Coupled with the ease of processability from solutions at or near room temperature and an expected Energy PayBack Time (EPBT) of just a few months⁸ (compared to 1.5 – 4.4 years for Si solar panels⁹) made them one of the most attractive candidate for a new chapter in PVs and also in other opto-electronics applications such as lasers, LEDs, photodetectors and beyond¹⁰. However, almost since the beginning of their steep rise to fame, two issues have constantly been considered as potential obstacles to the large-scale deployment of this new technology: i) their instability towards heat, oxygen, moisture and other environmental factors¹¹, and ii) the presence of the toxic element Pb, whose use is highly regulated and restricted in many countries, due to its severe toxicity for human health and adverse effects on the environment.

While their instability is a real, serious problem that needs to be (and has been partially) mitigated, the toxicity issue is mainly addressed by proposing new alternative materials which can substitute lead. In this work we review the current lead-alternatives, but we also want to put forwards a different and complementary perspective, so far

neglected, questioning the effectiveness of the proposed alternatives in terms of toxicity and environmental impact. Are they really better than lead? To verify this hypothesis, several studies and data already available in the literature¹² – but often overlooked - will be presented, in the attempt to provide a 360° picture of the issue.

By analysing lead-based perovskite solar cell with different architecture in a cradle-to-gate LCA approach, different groups^{13–15} came to the same conclusion: lead is not the main concern in terms of toxicity or environmental impact. Zhang *et al.*¹⁵ for example calculated that $\text{CH}_3\text{NH}_3\text{I}$ accounts for 62.31% of Human Toxicity Potential (HTP), due to the larger amount of energy and solvents involved, whereas PbI_2 contributes only for 3.68% to the global HTP. In this work we would like to offer a broader perspective which takes into account the supply chain of raw metals currently proposed as alternative to lead. This must not be intended as an underestimation of the hazards of lead, but merely an assessment of the costs-vs-benefits trade-off. We must distinguish the inherent dangers due to lead for human health from the actual risks due to possible exposure. It is worth mentioning that extremely dangerous substances, such as asbestos, hydrazine, sulfuric acid, benzene - just to name a few - are currently applied in the manufacturing industry and safely managed in large quantities (thousands or millions of tonnes each year), because: a) they are effectively contained, and b) there are no economically viable alternatives to their use. In this work, a comparison with other existing technologies using toxic elements is discussed and a final perspective upon material abundance, costs and environmental impacts is given.

Lead-free perovskites: current candidates

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Table 1. Availability, cost and Global Warming Potential (GWP) of Pb versus some of the elements proposed for Pb-free perovskite solar cells.

Element	Price Average 2006-2010 ¹⁶ (USD/kg)	Global Production ¹⁶ in 2008 (t)	Main Source ¹⁶	GWP ¹⁶ (kg CO ₂ -eq/kg)
Pb	2.26	8'065'000	Pb ores (PbS)	1.3
Sb	6.24 ¹⁷	188'000	Sb ₂ S ₃	12.9
Sn	20.6 ¹⁷	333'000	SnO ₂	17.1
Bi	21.12	16'600	Pb ores	58.9
Te	150.40	140	Cu ores	21.9
Ag	481.36	21'350	Cu, Au/Ag and Pb ores	196
In	692.6	600	Zn ores	102
Ge	1172	59	Zn ores	170

In the search for alternative elements to substitute Pb, chemical compatibility suggests to look at its neighbours on the periodic table, which should share similar chemical and physical characteristics: proposed candidates includes Bi, Ge, Sb, In, Ag, Te and especially Sn¹⁸. However, the questions are: *are these elements a better choice than Pb?* And considering the need of more than 20 TW_p of global installations if we want to cut CO₂ emissions by 2050¹⁹, and the corresponding amount of materials required, *would their replacement be feasible?* In this Perspective, a global picture will be presented to try to answer to these questions, which are extremely important to design impactful new generation PV materials and devices.

As a first point, since efficiency is a key factor in LCOE (Levelised Cost Of Electricity) calculations²⁰, lead-free devices will first have to be able to compete with lead-based ones to be considered for replacement. To date, several papers reported certified efficiencies above 20% for Pb-based perovskites solar cells²¹⁻²⁴, whereas the highest efficiency for a lead-free device is 9.6% for Gua_{0.2}FA_{0.8}SnI₃, reported by Jokar *et al.*²⁵ in 2019. In fact, the most promising

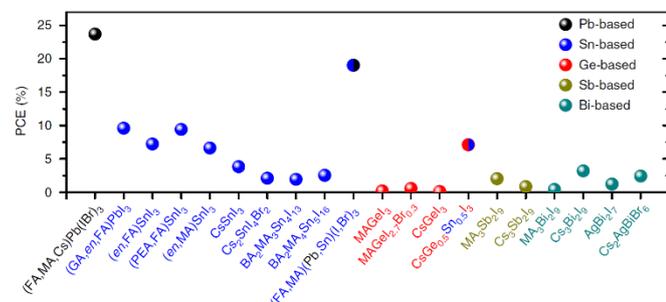


Figure 1. Highest efficiencies reported to date for lead-free perovskite solar cells compared to lead-based (FA,MA,Cs)Pb(I,Br)3 (black dot). Reproduced and adapted from ref. 26 under Creative Commons Attribution 4.0 International License.

candidate to replace Pb so far is Sn, due to the similar electronic configuration and the presence of a lone pair of electrons in the s orbital. MASnI₃ displays a smaller bandgap and a higher absorption coefficient than MAPbI₃, which would make it even more suitable for PV applications³; however, the high-energy 5s² orbitals of Sn are unstable and Sn(II) easily oxidizes to Sn(IV)²⁷: for this reason Sn-based perovskites react quickly with air and moisture, causing unwanted doping of the semiconductor properties and a catastrophic deterioration of photovoltaic efficiency²⁸. This spontaneous oxidation can be slowed by using additives or by careful encapsulation under inert atmosphere. However, this is likely to increase manufacturing costs and encapsulation is rarely 100% effective for the entire operational life of a device. For a comprehensive treatment of the opto-electronic properties of Sn-based perovskite solar cells, see the excellent reviews by Ke *et al.*²⁹ and Xiao *et al.*³⁰.

Other 3D analogs of CsPbI₃, MAPbI₃ and FAPbI₃ can be formed with Ge, however only CsGeI₃ display a suitable band gap (1.6 eV) for single junction applications³¹. Their PV performances are however worse than those of Sn-based perovskites, since the instability of the

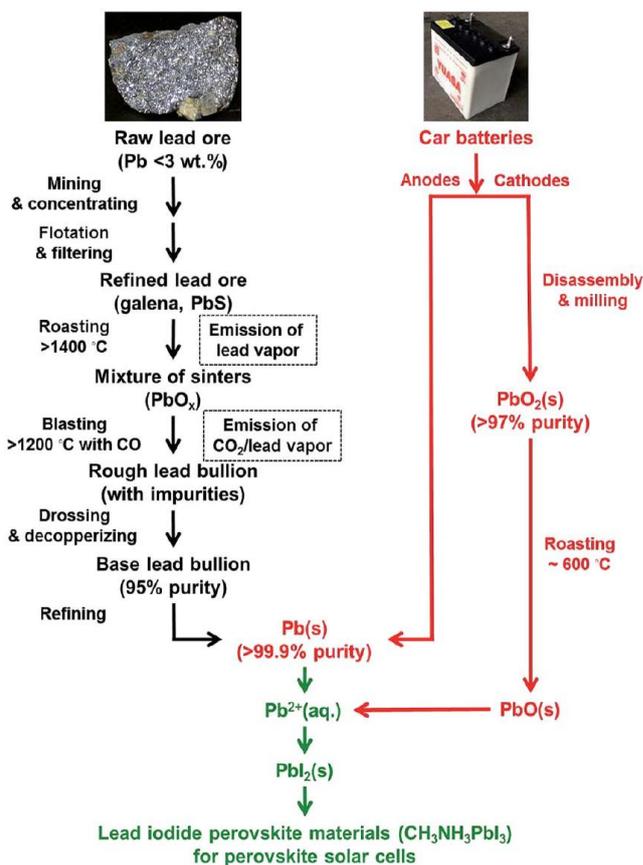


Figure 2. Comparison of lead production from raw lead ore vs recycling from exhausted lead-acid car batteries. Recycling requires far less energy and produces far less waste than mining (reproduced from Ref. 32 with permission from The Royal Society of Chemistry.)

+4 oxidation state increases with decreasing atomic number in the 14th group. Only a mixed Sn-Ge perovskite CsSn_{0.5}Ge_{0.5}I₃ reached

7.11% PCE and showed improved air stability, probably due to the formation of a thin GeO₂ layer³³.

Instead of substituting Pb(II) with another divalent metal, it is also possible to use a combination of a monovalent and a trivalent metal,

lowest GWP (global warming potential) of all metals (1.3 kg CO₂-eq/kg)¹⁶. As shown in **Figure 3**, all the aforementioned elements display one or two orders of magnitude greater environmental impact factors than Pb; they are also scarcer and therefore more expensive (**Table 1**). More importantly, the main source of all these

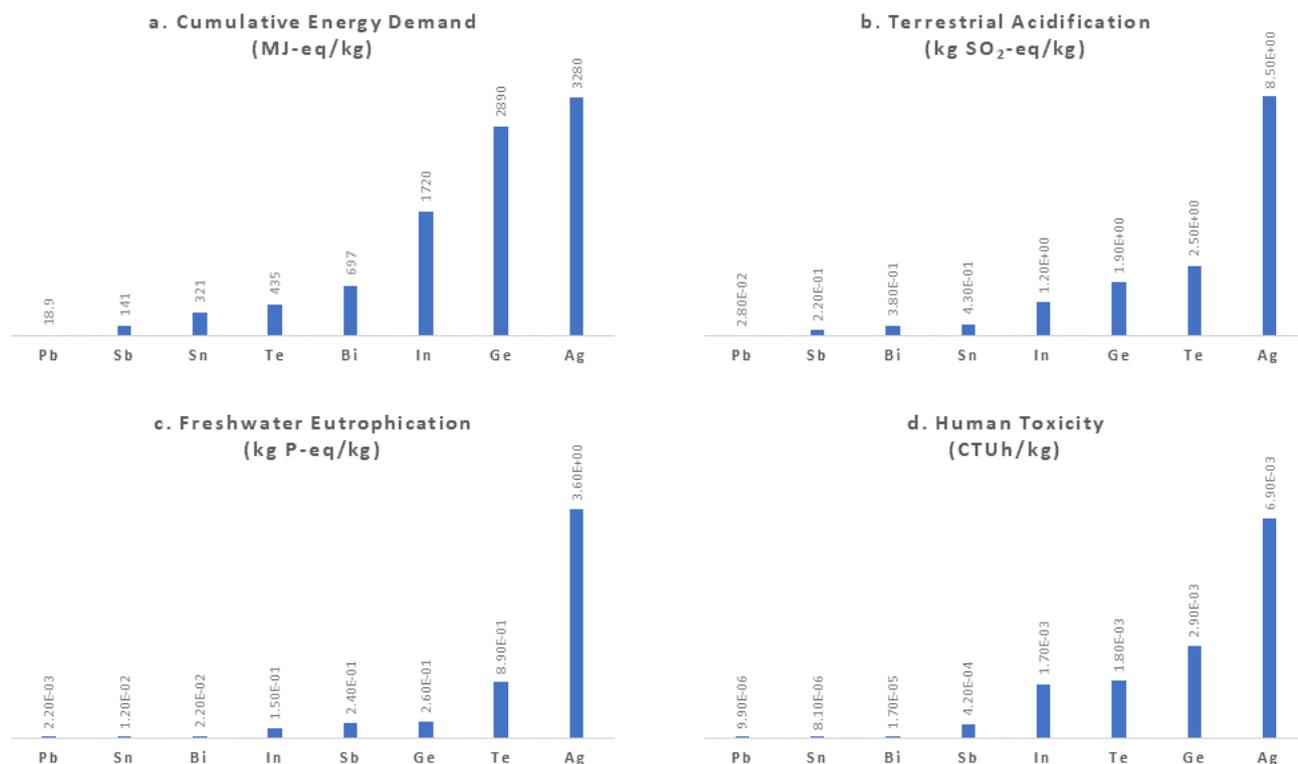


Figure 3. Environmental impact factors for Pb versus the elements proposed for Pb-free perovskites: a) cumulative energy demand (MJ-eq/kg), b) terrestrial acidification (kg SO₂-eq/kg), c) freshwater eutrophication (kg P-eq/kg) and d) human toxicity (cancer and non-cancer) (CTUh/kg), according to the USEtox model for LCA. Data retrieved from Nuss *et al.*²⁸.

such as Ag(I)/Bi(III) and In(I)/Bi(III), or a trivalent metal and vacancies, as in Cs₂AgBiBr₆, Cs₂AgSbCl₆, Cs₂CuInCl₆, Cs₂AgInBr₆, etc., some of them only proposed theoretically³⁰. Unfortunately, despite some interesting physical parameters³⁴, none of them has reached yet the performances of lead-based perovskites. Compounds like Cs₃Bi₂I₉, MA₃Bi₂I₉ and MA₃Sb₂I₉ possess a OD structure characterised by large exciton binding energy, high band gap and deep defect states, which makes them unsuitable for photovoltaic applications: the maximum PCE reported is 3.20%.³⁰

Material Abundance and Cost

In this paragraph we will describe how the production and availability of Pb differ from those of alternative elements. These elements are scarcer, in some cases extremely rare, and have already other uses. By a mere comparison of annual production, we can see that some of the proposed alternatives simply are not available in sufficient quantities to deploy PV panels on an industrial scale.

The global production of Pb in 2016 was 11'144'000 t (an increase of 38% from 2008), of which just 42% was extracted from its ores, while the rest came from secondary sources (recycling). In the US, the percentage of recycled Pb reaches 80%³⁵. Pb has therefore one of the

elements (except Sn and Sb) is the smelting of Pb and Zn ores or the electrorefining of Cu, therefore their price and availability depends on the production of these base metals, and their extraction in most cases is not commercially feasible on their own, but only as by-products of other metals. This poses severe limitations to an increase in production, should the demand increase.

In particular, Life Cycle Analysis (LCA) studies show that the environmental impact of Sn is 7 to 8 times higher than that of Pb¹²; 94.5% of Sn (as of 2008¹⁶) is extracted from its ore, cassiterite (SnO₂) and 82% of its production is concentrated in three countries: Peru, China and Indonesia. From 2000 to 2010 its price increased by 4 times just as a consequence of the actions of the Indonesian and Chinese governments¹⁷, and now Sn is 10 times more expensive than Pb. Furthermore, its global warming contribution and terrestrial ecotoxicity are more than 10 times greater than those of Pb.¹⁶ **Germanium** is scarce (1.6 ppm in the Earth's crust) and the most expensive among the proposed Pb substituents. It is found primarily in the mineral ore germanite (Cu₃(Ge,Fe)S₄), but it is not mined directly. The whole production of Ge depends on the refinement of Zn, in whose ores it is found in traces, accompanied by indium and gallium³⁶. The total world production of Ge was just 50 t in 2002,

averaging 41 t between 1998 and 2004^{37,38}. It is therefore safe to assume that Ge will never substitute Pb in mass-produced solar panels. Similarly, 95% of **bismuth** is obtained as by-product of Pb refining¹⁶ (400 to 700 t of Pb need to be produced for each ton of Bi³⁹) and almost 80% of the production is located in China. In 2008, the global Bi production was 16'600 t. The price of Bi is also approximately ten times that of Pb, 21.12 USD/kg¹⁶. Even though cost is not the primary issue - given that the perovskite layer contributes for less than 20% to the final cost of a device - mining Bi to substitute Pb cannot be logically justified, also considering that Pb can be recovered from other, more environmentally friendly sources than mining (**Figure 2**). **Indium** is recovered almost exclusively from Zn ores and in 2008 the global production of this rare metal was approximately 600 t¹⁶. The combined scarcity and high demand of In for electronics keep prices high (averaging almost 700 USD/kg). Already in 2011, Zuser and Rechberger⁹ estimated that in a realistic scenario the demand for In *just for photovoltaics* would be 1621 t/year until 2040, when total global reserves are estimated to be just 17490 t. Considering that In is in high demand also for LCD displays and other electronic applications, In-based PV cannot possibly be the basis for a significant fraction of the future electricity production. **Antimony**, on the other hand, is produced primarily from its ore (stibnite, Sb₂S₃), but 91% of the 188'000 t of Sb produced worldwide in 2008 came from China; the rest is recovered from the smelting of Pb, Au and Cu elsewhere. Therefore, despite being more abundant and less expensive than other candidates, its supply can be strongly influenced by geopolitical changes. Finally, 21'350 t of **silver** were produced in 2008, of which 34% came from Ag-Au ores, 28% from Pb ores, 17% from Cu electrorefining and 21% from recycling of electronic waste. Ag is 240 times more expensive (481.36 USD/kg) and has a greater GWP (196 kg CO₂-eq/kg) than Pb. Even assuming that the trend in the reduction of Ag content in conventional Si panels keeps decreasing, if by 2050 at least 25% of global electricity demand has to be provided by photovoltaics the PV industry would have to consume 30% to 53% of the world production of Ag⁹. That should discourage its further use in large-scale use for other photovoltaic technologies.

Toxicology Aspects

Beyond lead, many of the proposed alternatives also contains toxic elements, at different level. Regardless of the amount dispersed into the environment, these elements may present severe health issues as well.

Lead

Due to its widespread use since ancient times³⁵, the effects of acute and chronic Pb poisoning are well understood and documented: Pb compounds enter the soft tissues (liver, kidneys, etc.) through the bloodstream, interfering in the functions of enzymes and receptors by mimicry of essential elements such as Ca, Zn and Fe. It eventually deposits into the bones as lead phosphate with a half-life of 20-30 years. Pb poisoning causes neurological disorders (decreased intelligence and behavioural problems), especially in children but also in adults, upon exposure to values of 5 µg/dl or lower.⁴⁰ When exposed to the environment, the main degradation product of perovskite solar cells is PbI₂, which then transforms into Pb(OH)₂ and

HI. The acidification of the medium by HI is more harmful than the uptake of Pb(OH)₂, which is much smaller than typical organometallic lead compounds such as the infamous tetrabutyl lead¹.

Tin

The acute toxicity of **tin** is documented, whereas long term effects such as neurotoxicity and carcinogenicity are still under debate⁴¹. In the specific case of iodides, it has been found that *in vitro* SnI₂ is more toxic than PbI₂ due to increased acidification by formation of HI (LC₅₀ of 0.09 vs 0.83 mM⁴² for SnI₂ vs PbI₂, respectively), because SnI₂ is much less stable and decomposes quickly after release, even though SnO₂ is certainly less toxic than Pb(II) and Pb(IV) oxides.

Germanium

A positive aspect of **germanium** is its low toxicity (except for germanium tetrahydride): Ge compounds are not mutagenic nor carcinogenic: on the contrary, 5 ppm of sodium germanate in drinking water administered to rats for their entire life seems to have *decreased* the incidence of tumors, and some organic and inorganic Ge compounds have been reported to have anti-neoplastic activity in humans⁴³.

Bismuth

There is limited and conflicting amount of information on the toxicology of **bismuth** and Bi compounds. Although some have been used successfully as medicinal compounds, such as bismuth subcitrate and bismuth subsalicylate⁴⁴, chronic intake may result in encephalopathy^{45,46} and renal failure⁴⁷, since the highest concentration of Bi is found in kidneys. However, *in vitro* studies on cultured human proximal tubular (HPT) cells showed no toxicity of Bi from 1 to 100 µM, whereas Zn, Cd and Hg all showed various degrees of toxicity⁴⁷. A different study by Asakura *et al*⁴⁸. instead found evidence of genotoxicity of Bi (and Sb) in cultured mammalian cells. More in-depth studies therefore are required before Bi can be deemed safe for human health.

Indium

The adverse effects of **indium** have been investigated more extensively due to its widespread use as dopant in the production of the transparent conductive oxide ITO (Indium-doped Tin Oxide). It appears that In toxicity is linked to pulmonary inhalation of In compounds: two separate studies^{49,50} found evidence of severe toxicity and carcinogenicity for InP, suspected carcinogenicity for InAs, and pulmonary damage combined with increased cancer rates for ITO in rats. 6 cases of interstitial pneumonia (one of which fatal) caused by inhaled ITO were reported in Japan, with In concentration in serum ranged from 41 to 290 µg/L. Following a further study on 108 workers of an indium-processing plant, the Japanese Society for Occupational Health recommended a maximum occupational exposure of 3 µg/L of In in blood serum.

Antimony

The general population is already exposed to low levels of **antimony**, as this element occurs naturally due to volcanic activity, forest fires, sea spray, etc. Its concentration in soil has been measured to be 0.48 ppm on average, and the average intake was estimated to be approximately 5 µg/day. Potential risks therefore are connected to occupational exposure to Sb compounds like Sb₂O₃, stibine (SbH₃), Sb₂S₃, Sb₂O₅, SbCl₃, Sb₂S₅, as well as metallic Sb at production sites.

Chronic exposure to Sb_2O_3 and/or Sb_2O_5 resulted in pneumoconiosis, bronchitis, emphysema, and other conditions, however a clear causal relationship to Sb alone has not been established, because it is often handled in combination with Pb and As and it is difficult to separate individual effects. However, *in vivo* experiments showed teratogenic effects and lung tumours in rats upon exposure to Sb_2O_3 and Sb_2S_3 . One study found increased incidence of spontaneous abortions in women involved in Sb production, and Sb_2O_3 is classified as possibly carcinogenic to humans (IARC 2B). The US EPA established a maximum level of 0.006 ppm for Sb in drinking water⁵¹. In the environment, high levels of Sb are toxic to aquatic life and plants, where it has been shown to bioaccumulate⁵². These findings should not surprise, since Sb belongs to the same group of As and therefore shares many similar characteristics, including its toxicity.

Silver

Silver has also been used since antiquity, but, unlike Pb, it is unanimously considered harmless for human health, and it has been used for centuries for plates, cutlery and dental fillings without side-effects⁴⁸.

Toxicology is an extremely complex subject and it is hard to say if an element is more or less toxic than another, as it also depends on the chemical form to which humans are exposed. While some seems less problematic than Pb (Ge, Ag), for others we simply do not have enough information to make a conclusive assessment, and therefore it would not be justified to dismiss Pb solely on the basis of its known health effects.

A comparative Study: PZT and CdTe

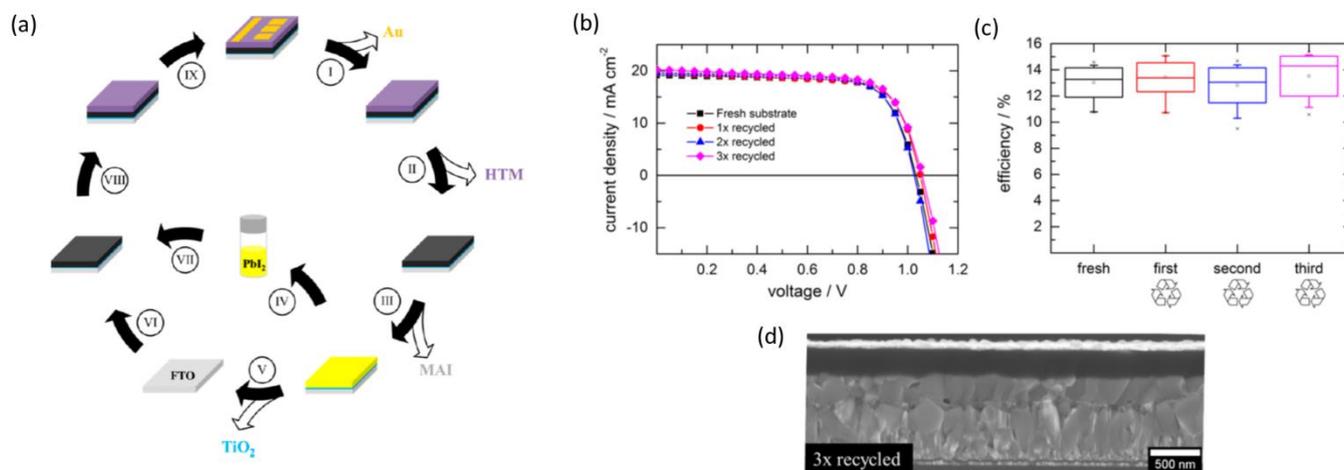


Figure 4. (a) Proposed recycling scheme for perovskite solar cells: each layer can be stripped apart by selective dissolution in appropriate (orthogonal) solvents and reused to fabricate new cells; (b) J-V characteristic of devices prepared on fresh and recycled substrates; (c) Bar diagram showing statistical data for 24 individual cells in each group; (d) cross-sectional SEM image of perovskite solar cell on a three-times recycled substrate. Reprinted (adapted) with permission from Binek *et al.*, "Recycling Perovskite Solar Cells to Avoid Lead Waste", *ACS Appl. Mat. Interfaces*, 2016, 8, 12881-12886. Copyright 2016 American Chemical Society.

Two useful analogies in the form of study-cases to support the central argument of this perspective come from lead zirconate titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, also known as PZT, and CdTe solar panels. In the following paragraph we will show how Pb and Cd in these materials, despite their intrinsic hazards, have been so far tolerated because the advantages outweigh the risks. Moreover, in the case of

CdTe solar panels, we will show how the constrained and small supply of Te severely limits the market share of this technology compared for instance to Si, which is much more abundant.

PZT, the most used piezoelectric material in the world, contains ~60 wt% of lead (II) oxide, PbO; it was discovered in the 1950s (together with BaTiO_3) and its annual production is ~ 5000 t, which might seem a large quantity, but it actually represents less than 0.03% of the global consumption of lead⁵³. The same health concerns raised nowadays for lead-based perovskites prompted extensive research into lead-free piezoelectrics to replace PZT: in over 20 years, no material has emerged which is able to compete against PZT in all aspects (stability, performances and cost). The most promising candidates are potassium-sodium niobate (KNN, $(\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3)$) and sodium bismuth titanate (NBT, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$). For the former, even though Nb poses no threat to human health (it is used in biocompatible alloys for metal implants), its extraction causes far more severe damages than that of Pb, which overall outweighs its advantage in terms of non-toxicity⁵⁴. For the latter, the almost complete reliance on Pb extraction for the supply of Bi and its low recyclability completely nullify any advantage that Bi might have over Pb, if we consider the broader picture⁵⁵. Therefore, despite the presence of Pb, PZT is still exempt, and will likely continue to be exempt, from European WEEE (Waste Electric and Electronic Equipment) and RoHS (Restriction on Hazardous Substances) regulations on Pb content³⁵ because, unlike solder and paints, there is no viable alternative to it.

Similarly, despite the fact that CdTe solar panels do not comply with RoHS 2 directive on the maximum content of Cd in consumer

products either, are also exempt because the advantages brought by the production of renewable energy outweigh the risks associated with the use of Cd³⁵. However, as it was quickly pointed out⁵⁶, the annual production and reserves of **tellurium** are not sufficient to provide a significant amount of PV capacity in the future, and CdTe has always represented a tiny fraction of the PV market, less than 5%

for the last 5 years⁵⁷. Tellurium has also been considered as replacement for Pb-free perovskites: Ju *et al.*⁵⁸ have reported on the potential for opto-electronic devices of Te-based double perovskites of formula A_2TeX_6 , where A is an organic cation (methylammonium, formamidineum or butylammonium) and X is a halide (iodide or bromide). This family of compounds displays a tunable band gap from 1.42 to 2.25 eV (calculated), trap densities and carrier diffusion lengths comparable to those of MAPbI₃, and good thermal stability. However, no photovoltaic devices were presented so far.

The supply chain of Te is an interesting case study as we have already seen the effects of the limited availability of Te on the market share of CdTe solar panels. Te is mainly obtained as by-product of Cu electrorefining in the anode sludges (>75% of the production⁵⁹), therefore its availability and price are related to those of Cu. It is a particularly rare element, with a crustal abundance of 1 ppb (1 µg/kg), similar to that of Pt and other precious metals⁵⁶. Te is much more abundant (50 ppm, or 50'000 times more concentrated) in ferromanganese nodules on the ocean floor⁶⁰, but its extraction from the sea bed would be antieconomic. Mining of Te itself from primary ores would be economically sustainable only in a few sites in Mexico, China, Norway and Sweden^{61–63}, but no definitive data are available. Besides Cu, approximately ~10% of Te is recovered from Zn and Pb, and ~12% from Au⁵⁹. The Global Warming Potential of Te is 21.9 kg CO₂-eq/kg, comparable with that of Sn (17.1), but, should its production from other sources increase, so will its environmental impact, especially from gold telluride (AuTe₂), since Au has the second highest GWP of all metals (12'500 kg CO₂-eq/kg).

Te has been for decades a cheap element with little or no market value and supply always exceeded demand. Its price oscillated between 20 and 90 USD/kg between 1970 and 2007. It has been used in steel, catalysts, rubber production and electronics. A sharp increase in price (200 USD/kg) occurred in 2007 due to increased production of CdTe solar panels and speculative buying fuelled by fear of limited supply¹⁷, which peaked at 350 USD/kg in 2011, when the production of CdTe solar panels was 2.4 GW/year. The latest figure is 40 USD/kg in 2017⁶⁴, but the price is rising. In 2005, 430 metric tons of Te were available, with a 33% recovery rates from Cu sludges. Recovery rates depends on price and current technologies allow for an 80% recovery rate (for example, for Au the recovery rate is >95%). Furthermore, most Te and Se are left in the mine tailing because they interfere with Cu production. Thus, there is potential for an increased extraction of Te. In 2009, Fthenakis⁶¹ estimated that in 2020 the annual production of Te would be 1450 t, assuming an 80% recovery rate and an annual increase of 3.1% in Cu production. In 2019, according to the Minor Metals Trade Association, Te global production was instead 835 t⁶⁵. Non-solar applications of Te uses approximately 420 t/year of Te, whereas solar PV already takes about 40% of the global Te consumption (**Figure 5**); First Solar (the world leader in CdTe solar panels) is planning to ramp up production to 7.6 GW per year, and other Chinese manufacturers to 1 GW; since each GW of CdTe panels needs 91 metric tons of Te, this would mean a deficit of 370 metric tons of Te. Since the main source of Te is Cu refining, there are physical limitations to increase the production if demand increases, hence an increase in price is inevitable. However,

if recovery rates increases, it should be possible in theory to meet the global demand⁶¹.

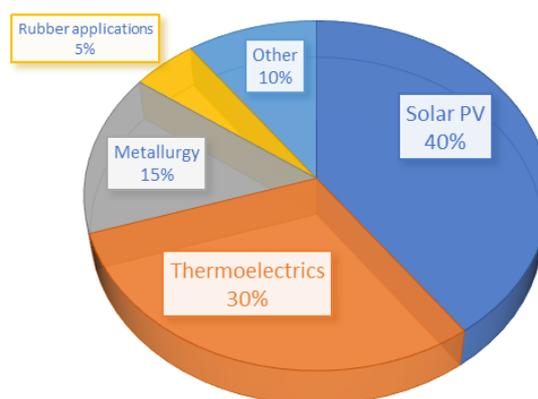


Figure 5. Global usage of Te per sector. Data from ref. ⁶⁶.

Interestingly, Te is one of the five elements never recorded in seawater but it is also the fourth most abundant element in traces in the human body after Fe, Zn and Rb, and unusually abundant in food⁶⁷. This might indicate that plants absorb Te from the soil much more efficiently than other trace element⁶⁷. Chemically speaking, Te exhibits similar properties to those of arsenic, selenium and antimony, all highly toxic. In experiments on rats, Te spreads virtually to every tissue (blood, spleen, heart, liver, kidneys, brain and bones, where it accumulates like Pb), and crosses the placental barrier causing birth defects (hydrocephaly). Acute toxicity of tellurite is higher than arsenite or selenite⁶⁸.

Further considerations: recycling

LCA studies on lead-based perovskite solar panels lack an assessment of their environmental impact after decommissioning, as there are no data available yet. It might be argued that they pose a risk at the end of their operational life if they are disposed of in a landfill. As electronic devices, they would have to be recycled according to EU laws. As a matter of fact, Si and CdTe panels are recyclable, but the process is expensive and it has become increasingly antieconomic as the content of precious metals decreased over time^{69–71}. The major cost of recycling in general is due to the energy required to separate mixed materials: hence, any procedure that can avoid high energy-intensive processes can make the recovery of useful materials economically attractive. It has been demonstrated^{8,72} that PSCs can be delaminated easily and effectively by selectively dissolve each layer with an appropriate solvent at room temperature, in which the other layers are not soluble; on the other hand, recycling Si and CdTe panels requires high temperatures and energy-intensive mechanical treatments. FTO-coated glass, PbI₂ and precious metal can be easily recovered (**Figure 4a**); and cells prepared with recycled materials do not show any decrease in performances after several cycles (**Figure 3b-d**).

Although it is obviously of utmost importance to avoid further leakage of Pb into the environment, it is very important to consider the quantities of lead emitted worldwide: the coal industry releases every year 80'000 metric tons of Pb into the atmosphere (in addition

to other heavy metals present in traces in coal, such as Cd and Hg); the global installed capacity of coal power plants is around 1.75 TW, of which 1 TW just in China; now, a 1 TW solar installation based on 20% efficient Pb-based solar cells would require approximately 0.8 g/m² of Pb, or 20'000 metric tons of Pb, which would be however immobilised in the panels and not dispersed into the environment⁷³. Furthermore, the natural concentration of Pb in soil is not zero, but as high as 36 mg/kg on average, due to years of use of Pb compounds (e.g. tetraethyl lead in gasoline) by mankind. Now, if all the lead contained in a 1 m² panel was to leak on the same area, it would increase the concentration of Pb by 4 mg/kg. As an example, the legal limit for lead in agricultural soil in China (one of the strictest in the world) is 250 mg/kg⁷⁴. This obviously does not mean we can safely dispose of Pb in the environment, but this leakage can occur only in extremely rare circumstances. Therefore, by using Pb-based PSCs to produce electricity instead of burning coal, and only in the case of catastrophic failure of the encapsulation (fire, hail, earthquakes, etc.), we are potentially leaking far *less* Pb into the environment. To strengthen the case for lead-based solar PV, it is estimated that there are approximately 250 million lead-acid batteries in the US alone³²; with continuous progress in the development of more efficient lithium-air and lithium-sulphur batteries, a growing number of lead-acid batteries will not be recycled into new ones, becoming a cheap source of lead for lead-based PSCs. It is also estimated that the amount of Pb recovered from a single car battery is enough to produce about 700 m² of perovskite-based PV panels. Hence using recycled lead instead of lead ores presents an obvious advantage in terms of costs and environmental benefits.

It is clear therefore how completely substituting Pb in perovskite solar cells with any of the proposed alternatives would have a much higher environmental impact, without at the same time a significant reduction of the global emissions of Pb; on the contrary, using unwanted and cheap Pb in photovoltaic panels could prevent it from being disposed of and potentially polluting the environment.

Conclusions

To qualify as sustainable, a technology must satisfy the needs of the present generation while at the same time ensuring that future generations can sustain their own growth. Renewable energy technologies such as photovoltaics can be truly sustainable if they are inexpensive to produce, are based on abundant and non-depletable materials, and are environmentally safe. So far, suggested replacements for Pb fail to meet one or more of these criteria, primarily because of either their scarcity and their reliance on the production of base metals such as Pb, Zn and Cu (Ge, Te, Bi, In and Ag), or their toxicity (Sb, Te, Bi, In). Only Sn shows some potential as a less toxic alternative to Pb, but its production is highly concentrated and Sn(II)-based solar cells suffer from intrinsic instability due to spontaneous oxidation to Sn(IV). As this perspective has hopefully made clear, the concept of “environmentally safe” needs to be understood in a wider framework that includes not only potential risks for human health but also global availability,

geographical distribution, processing costs, recyclability and overall emissions (including mining).

When trying to find a more environmentally friendly substitute for lead, one cannot ignore the results of Life Cycle Analysis studies on the availability and environmental impact of alternative elements. Even if Pb-free perovskite solar cells were to attain the same efficiency and stability of Pb-based ones, their cost and total environmental impact must be carefully analysed together with their effects on human health and global availability. Sn-based perovskite or other Pb-free perovskites show intrinsic limitations in terms of stability and efficiency, and do not offer substantial advantages in terms of cost, toxicity or environmental safety; on the other hand, Pb is an abundant and cheap element with a much smaller environmental impact, and it can be easily recycled from multiple sources. Nevertheless, Pb poses intrinsic health risks calling for further research on safer and more environmentally friendly elements to partially substituting Pb without neglecting cost, availability constraints and environmental impact. In conclusion, research and technology should really balance the advantages of using Pb for renewable energy generation with the risks associated with its manufacturing.

Conflicts of interest

There are no conflicts to declare.

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