



Safe or risk? Impact of lead from halide perovskites in the metabolism of living organisms

¿Seguro o peligroso? Influencia del plomo de las perovskitas de haluro en el metabolismo de seres vivos

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Resumen

Indiscutiblemente, las perovskitas de haluro y plomo (LHPs) han sido consideradas como materiales promisorios en la fabricación de nuevos y eficientes dispositivos optoelectrónicos, con el fin de mejorar la captación de luz del sol y convertir esta energía en electricidad a bajo costo. Sin embargo, el conocimiento actual acerca de la toxicidad del plomo proveniente de las LHPs y su impacto ambiental es aun desconocido. En esta revisión, nosotros establecemos estudios relevantes, en donde ha sido observado la toxicidad del plomo proveniente de las LHPs, y su potencial acción en el metabolismo humano. Este hecho considera la urgencia de substituir el plomo por otros metales menos tóxicos, manteniendo o mejorando la eficiencia de fotoconversión. Esto hace que la tecnología basada en LHPs sea más atractiva a futuro, sea comercialmente rentable y competitiva a otras fuentes de energías alternativas.

Palabras clave: perovskitas de haluro, plomo, metabolismo, transporte cationes.

Abstract

Indisputably, lead halide perovskites (LHPs) have been considered as promising materials in the fabrication of novel and efficient optoelectronic devices, with the purpose to improve the sunlight harvesting and transform this kind of energy in low-cost electricity. However, the actual knowledge about the lead toxicity from the LHPs and its environmental impact are unknown. In this review, we establish important studies where it has been observed the lead toxicity coming from LHPs, and its potential action in the human metabolism. This fact considers the urgency to substitute lead for other lower toxic metals, keeping or improving the photoconversion efficiency. This makes the LHPs-based technologies more attractive in the future, being commercially rentable and competitive with other alternative energy sources.

Keywords: halide perovskites, lead, metabolism, cation transport.

1 Introduction

Giving a deep view inside the material science looking for interesting alternatives to avoid the use of conventional energy sources, semiconductors have attracted the attention during the last years. In this line, studies performed by using halide perovskites (LHPs) have exponentially grown, due to important characteristics such as high light absorption capability, carrier mobility, facile and low-cost preparation and so on.[1-2] These characteristics become LHPs as promising materials to compete in commercial technologies for sunlight harvesting and electricity generation, as light-emitting diodes, solar cells and photodetectors.[3-7] In the case of photovoltaics, some main issues are considered to hinder the mass commercialization of devices based on LHPs (also denominated as perovskite solar cells, PSCs) such as their facile degradation under moisture, temperature, and lead (Pb) toxicity.[8-11]

Even although more toxic metals as cadmium (Cd) are used in established standard sunlight technologies as CdTe solar cells, these devices show a higher stability than PSCs, since the last ones are composed by organic-inorganic salts relatively soluble in polar solvents such as water.[12-13] This feature makes the Pb bioavailable or accesible to plants or another living species. Hence, diverse research groups have carried out different studies to replace Pb and incorporate less toxic metals as Sn, Ge, among others,[14-16] without changing the intrinsic properties of the LHPs. This is carried out to improve the availability of perovskite-based technologies to competitive in the topic of renewable energy sources. Unfortunately, the performance of the well-named “lead free LHPs” is lower than their Pb-counterparts, concluding that Pb is not so easy to substitute.[17] In this context, there is an urgency to know about the toxicity issues of this metal, but the panorama has not been widely elucidated to provide

valuable information about the risk to use Pb. Herein, in this review, we show diverse studies where it is described the real toxicity degree of Pb in living systems, focusing on the accumulation, metabolism and finally, potential alternatives to recycle or substitute Pb, for delivering safety and competitive perovskite technologies in the future.

1.1 Accumulation of Pb by metal segregation

It is well-known that PSCs have reached a photoconversion efficiency (PCE) near to 26%, generated precisely in small areas (less than 1 cm²). [18] This outstanding result has been the result of the facile chemical tunability and procesability of the components to synthesize LHPs. This fact has triggered the possibility to fabricate scaled devices, in order to enhance the generation of electricity keeping a similar PCE. Unfortunately, components of the LHPs can be easily dissolved in highly polar solvents such as water, alcohols, among others, which cause the unavoidable degradation of the light absorber, the damage of the device and finally, the decline of the energy transformation. [19-20] Mainly, one of the worst issues that the instability of the PSCs can provide, resides from the exposure to the moisture, rain or temperature, diffusing the species contained into the LHPs to the near ecosystems. [21] Specially, temperature has been the most important parameter to affect the stability of 3D iodide APbI₃ perovskites, where A= cesium, Cs⁺; formamidinium, FA⁺; methylammonium, MA⁺; X = Br and I. Through mass spectrometry measurements, it has been revealed that the thermal degradation of MAPbX₃ produces CH₃X + NH₃, where CH₄, HX and ethylene is produced from CH₃X. In the case of FAPbX₃, NH₄X, HCN and 2-aminomalononitrile are the main compounds obtained after degradation. [22-23] Interestingly, all-inorganic CsPbX₃ shows a higher stability due to CsX is a non-volatile compound that reduces the likelihood to negatively impact on the device performance. [22] Nevertheless, the black α -phase of these CsPbI₃ perovskite is converted to the yellow δ -phase, losing its intrinsic optical properties to be used as a light absorber. [24]

On the other hand, the dissolution of MAPbI₃ offers another decomposition pathway, producing CH₃NH₂, HI and finally PbI₂. [23] This lead precursor presents a high solubility constant in water (K_{ps}) around 10⁻⁸, which is higher than that of K_{ps} from other binary compounds as CdS, CdSe, PbS ranging between 10⁻²⁷ – 10⁻³⁴. [25] In this way, there would be a high likelihood to observe Pb in the effluents more than other toxic metals such as Cd, when the LHPs-based devices start to deteriorate. After estimating the composition of a PSCs based module, it is reported that a device based on MAPbI₃ with a 0.6 μ m thick shows 0.8 g Pb/m². If this amount of Pb is dispersed in a ground soil, this value will raise up to 4 mg/kg. In some countries like China, the maximum fraction allowed to satisfy the standards about Pb is around 250 mg/kg. [26] This fact indicates that the fraction

of Pb from the perovskite based devices is low to produce a high risk for ecosystem contamination.

With the purpose to observe how the Pb accumulated in the soil can affect some living organisms, Li and co-workers [13] have studied how the plants can grow in this kind of scenario. Plants are well-recognized to bioaccumulate heavy metals, which depends on the pH, metal transport capability between the roots and soil, concentration of the metal and so on. [27]

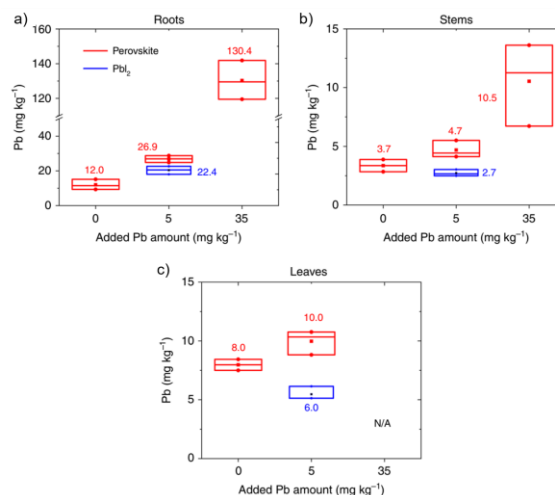


Figure 1. Accumulation of Pb from LHPs in roots, stems and leaves from mint plants. Reprinted with permission from ref. [13]. Copyright 2020 Springer Nature.

In the experiment, mint plants are grown under a relative Pb concentration around 36 mg/kg of Pb, which comes from the natural soil. Attending to this value, the Pb concentration in stems, leaves and roots are 3, 8 and 12 mg/kg, respectively (Figure 1). After adding 10% Pb from the perovskite sample, the Pb concentration in the abovementioned components from the plant increases up to 100%. These values are calculated to be 4.7, 8 and 26.9 mg/kg, respectively. The continuous incorporation of Pb (between 35.0 and 250 mg/kg) in the soil extremely surpass the Pb concentration in stems, leaves and roots ~210, 406 and 3906 mg/kg, observing the intoxication of the plant in form of blackening and rotting. These experiments were repeated by adding PbI₂, being this chemical one the precursors to prepare the LHPs, in order to observe if the organic cation from the perovskite has an influence on the Pb intoxication. As expected, the Pb accumulation by PbI₂ was lower in comparison with the metal segregated form LHPs, indication that the organic MA⁺ cation controls the pH of the natural soil, promoting a higher Pb accumulation.

On the other hand, Su and co-workers [28] have estimated the leaching toxicity from discarded PSCs in water after using through three different approaches in order to observe the behavior of the toxic metals contained into the device

components: (i) synthetic precipitation leaching procedure (SPLP) (Figure 2a), (ii) toxicity characteristic leaching procedure (TCLP) according with EPA method 13115 (Figure 2b) and (iii) water extraction test (WLT) (Figure 2c) at different solid:liquid ratio. By analyzing the leaching results, main metals such as Ni, Pb and Zn were detected by varying the number of leaching cycles. In all the cases, the concentration of the metals is higher than the subsequent ones, being representative the excessive fraction of Pb. According with these results, metals from PSCs can be easily segregated to the environment, which is harmful for the human health. Furthermore, the fraction of organic compounds from leaching are also estimated in water through total organic carbon (TOC) and chemical oxygen demand (COD) by varying the number of leaching cycles, with the purpose to verify the liquid quality. As seen in Figure 2d, TOC and COD are high after the first cycle, and decrease after the subsequent ones. This fact indicates that the metal segregation from PSCs produces releases a high fraction of CO₂ to the ecosystem, consuming a high amount of oxygen.

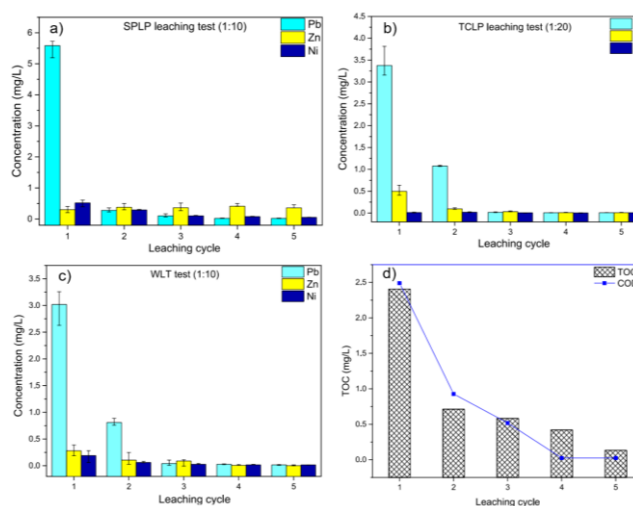


Figure 2. Determination of toxic metals from PSCs through different leaching processes: (a) SPLP, (b) TCLP and (c) WLT. (d) Concentration of TOC and COD in water after WLT leaching process from discarded PSCs. Reprinted with permission from ref. [28]. Copyright 2020 American Chemical Society.

By studying the release of Pb from the PSCs in hard environmental conditions (mainly moisture), devices were rinsed with water used as effluent at different pH values (4.8, 6.0 and 8.1) and also exposed to air vapor. The amount of MAPbI₃ from PSCs were estimated by thermogravimetric measurements, analyzing the difference in weight before and after water rinsing, and then the content of released Pb in the liquid was calculated by inductively coupled plasma mass spectrometry (ICP-MS).[25] As expected, A higher amount of Pb was found in the acidic media, which is associated to a higher dissolution of PbI₂ from the perovskite material. At this point, an 89 % Pb was calculated in the acidic water by ICP-MS. Furthermore, it is clear that the pH of rainwater can

vary, presenting more acidic characteristics, which can deteriorate the device fastly.[29] In this context, a higher amount of acid into the effluent can induce that the perovskite material release more Pb to the solution, reaching up to 92% Pb. Interestingly, PSCs only can segregate Pb if the device shows a broken encapsulation or is not well covered by the other components as conducting layers or metallic contacts. Thus, it can be concluded that there is a possibility that PSCs do not release lead to the ambient if the components from the device are stable enough to resist the environment itself.

1.2 Metabolism of Pb into the human organism

After Pb segregation to the environment and being absorbed mainly by plants, humans are the following step for the metal accumulation.[30] Here, some issues by lead intoxication are related to the decrease in the production of blood cells, hindering the haematopoiesis.[31] In this context, it has been reported that the amount of erythrocytes (red cells in charge to transport oxygen to all the complete body) decreases, indicative of high level of environment and occupational exposure. One erythrocyte can be contaminated by lead, and eventually exhibits the following biochemical processes:[32]

(i) Because the facility of Pb²⁺ (as result of its “d” orbital layer) to generate coordination complexes, this metal can be bonded to sulfhydryl, carboxyl and imidazole groups found in some enzymes and in fact proteins.

(ii) Attending to the fact that Pb²⁺ shows the same oxidation state than other main cations as Mn²⁺ and Zn²⁺, lead can be diffused through of a erythrocyte membrane and produce free radical reactions. By decreasing the concentration of erythrocytes, the activity of the erythrocyte enzyme is blocked, which is in charge to transform the available purine in erythrocytes.

According to the latter, purine nucleotides into the erythrocytes cannot be synthesized, and they can only be obtained through free purine bases or nucleosides. Moreover, the demand of cell energy increases, which produces the degradation of the bases and nucleosides. This cell disorder can produce big issues in human organisms such as hypertension, cardiomyopathy and in fact, male infertility at middle-long term.[32]

Regarding to the cation transport into the human metabolism, Gramigni and co-workers[33] have established that Pb²⁺ exhibits an effect on the cycle transport of the Na⁺, K⁺-ATPase. It is well-known that Na⁺, K⁺-ATPase is an enzyme presented into the plasmic membrane from the all animal cells, which uses the energy released during the ATP hydrolysis to transport Na⁺ out and K⁺ into the cell against their corresponding electrochemical gradients. This process

is pivotal for carrying out main cellular functions such as keeping the membrane potential, controlling the cell volumen, mediating the transport of solutes, and signal transduction. Therefore, with the aim to analyze the impact of the presence of Pb^{2+} on the different partial reactions during the transport cycle of Na^+ and K^+ mediated by the Na^+ , K^+ -ATPase, electrical currents provided by this enzyme were measured by depositing purified membrane fragments containing this ion pump on a solid-supported membrane (SSM). The SSM is a system composed by a bilayer lipid membrane, which shows a high stability that the solutions can be fastly exchanged with the surface (Figure 3a).[34] The electrical reponse obtained by the protein transport after following its chemical activation is essential to provide information about the protein functions, besides to provide main details such as modulation performed by drugs, peptides, and small proteins.[35]

With the aim to achieve valuable information about the chemical activity of the Na^+ , K^+ -ATPase, concentration jumps of diverse activating substrates such as Na^+ , K^+ and ATP, in presence and absence of Pb^{2+} were performed. As is shown in Figure 3b, by varying the ATP concentration jumps, in presence of Na^+ and K^+ cations (filled squares), a higher amount of Pb^{2+} cause the lowering of the performance in the charge movement promoted by the enzyme. The decrease of the protein activity was reached in the 0.01-10 μM Pb^{2+} concentration rango, which was corroborated through biochemical measurements of the ATPase activity under the same experimental parameters (empty circles). Surprisingly, the phosphorylation step, which is carried out by nutrients oxidation for producing ATP, is inhibited after increasing the concentration of Pb^{2+} higher than 1 μM in absence of K^+ cations (Figure 3c). Here, it is clear the eventual loss of the hydrolytic activity of the enzyme. At this point, it was concluded that Pb^{2+} serves a to stabilize the enzyme conformation that can be phosphorylated, but blocking the possibility to catalyze the hydrolysis of the enzyme phosphate. This fact unavoidably inhibits the dephosphorylation reaction of the Na^+ , K^+ -ATPase.

In general and considering the influence of the protein transporters in the performance of cellular activity, ionic channels, cellular adhesion proteins, metabolic enzymes and ADN-attached proteins are the principal molecular target for the Pb^{2+} coupling.[30, 36] Differences in the way that lead interacts with the coordinating groups from the proteins with respect to native ions, can conduct to the adoption of abnormal conformations in the proteins to which lead binds, which directly affects their functioning. Among the binding sites for polyvalent cations occupied by lead, Ca^{2+} sites appear to play a major role in its toxicity, being important for the cell physiology. The majority of issues provided by Pb^{2+} corresponds to the Ca^{2+} metabolism and several cell processes depending on it.[37] This fact could be the origin

of main neuropsychological disorders present by lead poisoning.

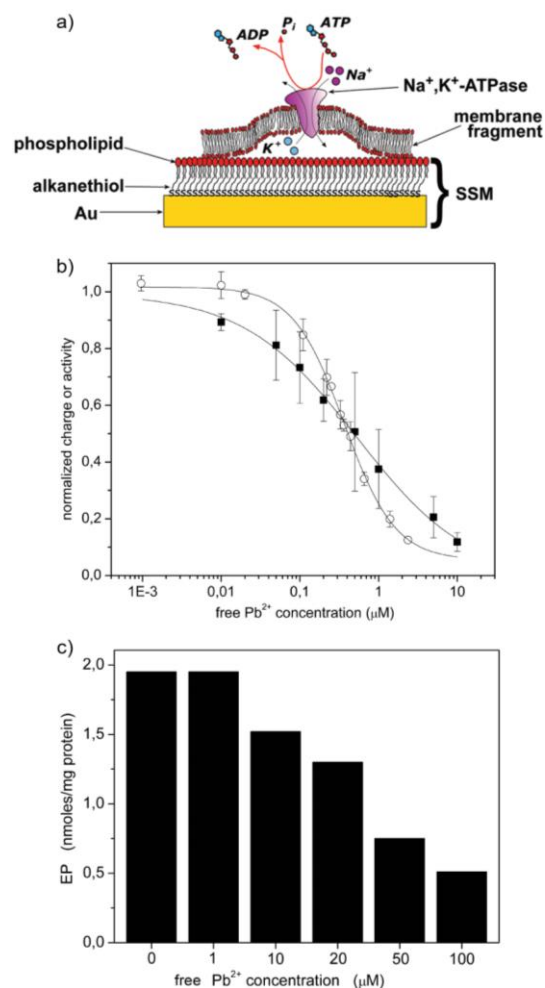


Figure 3. (a) Schematic representation of membrane containing Na^+ , K^+ -ATPase fragments deposited on SSM for ATP activation. (b) ATPase activity in presence of Na^+ and K^+ species (empty circles) and measure of the charge after adding 100 μM ATP + 80 mM Na^+ + 50 mM K^+ (filled squares) by varying the Pb^{2+} concentration. (c) Phosphorylation capability of the ATPase in absence of K^+ cations by varying Pb^{2+} concentration. Reprinted with permission from ref. [33]. Copyright 2009 American Chemical Society.

1.3 Recycling – substitution of Pb

As described above, one of the strategies to prevent the Pb segregation from the PSCs, is by carrying out encapsulation process. However, after finishing the lifetime of the photovoltaic device, some recycling protocols must be followed attending the international electronic waste disposal regulations.[38] In the case of commercial solar technologies such as CdTe and CIS, devices requires mechanical fragmentation, then the metals are removed from the modules through chemical treatments and lastly, some processes such

as mechanical separation, precipitation or electrodeposition are conducted.[38] In this context, the reuse of hazardous materials is the real interest since the disposal of the material waste is expensive. Therefore, the development of potential alternatives to recycling toxic metals such as Pb, which can be effectively applied for expired devices, could solve the waste issues and also be economically rentable.[39] Binek and co-workers[10] have established an interesting approach to remove each component deposited on PSCs based devices, which is ecofriendly and low-cost process. This is based on the layer-by-layer removal of the metal contacts, hole transporting material (HTM), perovskite absorber, and electron transporting material (ETM), simplifying the recycling process. Furthermore, the collected lead precursor (in this case PbI_2) and the expensive conducting glass (fluorine-doped tin oxide, FTO) can be reused, providing a step in the future commercialization of PSCs-based solar technologies.

To perform the recycle process, a PSC device based on MAPbI_3 was synthesized by a conventional method through the use of PbI_2 + MAI in dimethylformamide (DMF) in order to prepare bulk films on a planar structure (FTO/compact- TiO_2 /MAPbI₃/Spiro-OMeTAD/Au). As seen in Figure 4, the Au contact on top of the device is removed by adhesive tape (Step I), and then, Spiro-OMeTAD is dissolved in a suitable solvent as chlorobenzene (Step II). Later, LHP layer is immersed in double distilled water, transforming the light harvesting layer into PbI_2 and MAI (Step III). This organic salt is dissolved into the water, exposing a low concentration of PbI_2 ($\sim 4 \mu\text{g/mL}$) according to the US Environmental Protection Agency (EPA).[10] Subsequently, PbI_2 is removed from the FTO/ TiO_2 substrate by immersing the material into DMF (Step IV). By extending the exposition time into DMF, TiO_2 compact layer is also detached, leaving clean the FTO conducting glass (Step V).

Another promising alternative to avoid the contamination of Pb by using LHPs devices is based on the substitution of the metal with a less toxic ones as the case of Sn, Ge, Sr, among others.[14, 16, 41-43] Under this case, the photophysical properties of the materials are changed, with the purpose to improve the light harvesting, carrier transport and finally, the photoconversion efficiency of the perovskite based devices. In nanocrystals, the incorporation of new metals replacing Pb introduces new energy levels to enhance the optical features of the materials. Yao and co-workers[44] have substituted Pb by Sr into CsPbI_3 nanocrystals, in order to improve the electrical properties of the materials for the fabrication of light-emitting diodes (LEDs). The main factor to satisfy the radiative carrier recombination is through increasing the luminiscence of the perovskite. This property is dictated by the photoluminescence quantum yield, which is defined as the ratio between the number of absorbed photons and the emitted ones.[45] Thus, the PLQY of the Sr-modified nanocrystals is higher than unmodified ones by increasing the Sr content, improving the stability in long-term

(Figure 5). High stability means that the Sr-perovskite is less prone to suffer degradation and thereby provide toxicity in a short period of time.

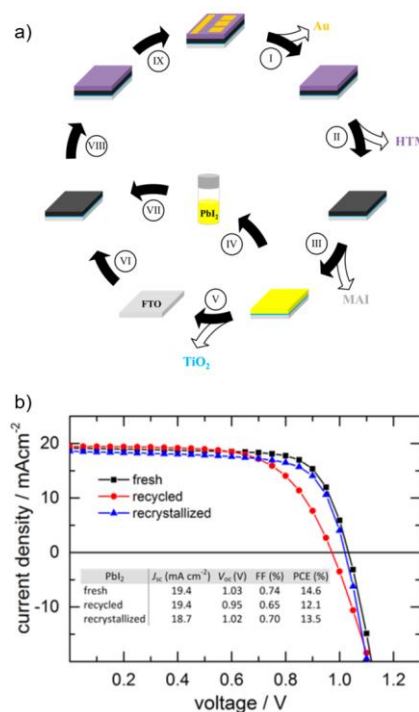


Figure 4. (a) Recycling protocol for perovskite based photovoltaic devices: (I) removal of Au contact by using adhesive tape, (II) Removal of HTM by immersion in chlorobenzene, (III) Transformation of the perovskite into MAI and PbI_2 and extraction of the organic salt through water. (IV) removal of PbI_2 and (V) TiO_2 compact (C- TiO_2) layer using DMF. (VI) Deposition of a new C- TiO_2 layer, (VII) deposition and formation of a MAPbI_3 film, (VIII) deposition of a HTM layer and (IX) evaporation of Au cathode on the device surface. (b) J-V performance of perovskite-based devices fabricated from fresh, reused, and recrystallized PbI_2 . Reprinted with permission from ref. [10]. Copyright 2016 Americal Chemical Society.

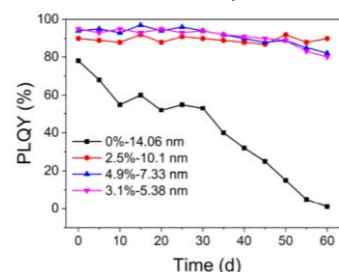


Figure 5. PLQY stability of the pristine and Sr-modified CsPbI_3 nanocrystals by varying the Sr content used for Pb substitution. Reprinted with permission from ref. [44]. Copyright 2019 Americal Chemical Society.

In this case, the amount of lead is not only decreased in the perovskites to give more visibility and attractiveness in perovskite-based technologies, but also be competitive in comparison with the Pb-counterparts. Accordingly, Sr-based devices shows a higher performance in LEDs than unmodified one, attributed to the maximization of radiative recombination, provided by the suppression of structural defects into the perovskite. Hence, the replacement of Sr not

only decrease the toxicity of the perovskite itself, but also promotes the preparation of less defective material with high photoelectronic features and potential use in renewable energy sources such as photovoltaics/optoelectronics.

Smaller metal cations such as Cu^{2+} (0.72 Å vs. 1.19 Å from Pb^{2+}) has been also added into perovskite nanocrystals such as CsPbBrI_2 , in order to promote the crystal lattice contraction and thereby, stabilize the cubic phase of the material.[24] In this case, the Cu^{2+} introduction increase the tolerance factor of the lattice, avoiding the octahedral tilting, which is the main factor for perovskite phase transformation. Here, a maximum PLQY of 94.8% was achieved, with a high stability for 15 days at 25 °C and high relative humidity of 85%. Interestingly, Cu^{2+} has been also added to replace totally Pb into the perovskite lattice, generating a lead-free semiconductor. Aamir and co-workers[46] have revealed that this modified perovskite can be useful for detecting water in DMF. By carrying out some optical measurements such as photoluminescence, water increase the emission features of the material. This improvement is associated to electron donor from water molecules, increasing the density of carriers to perform electron transitions. In the way to replace lead, different perovskite structures such as ASnI_3 ($\text{A}=\text{Cs}^+$, FA^+), $\text{Cs}_2\text{AgBi}(\text{ClBr})_6$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ have been considered as promising materials due to their high stability into the solar devices for more than 2000 h of testing, in fact under air conditions.[47-49] However, the PCEs are still lower compared with their Pb-counterparts (a maximum of 10% has been achieved for CsSnI_3). This fact is associated to the (i) lower cation stability, as the case of Sn^{2+} that prefers to present a stable oxidized Sn^{4+} species, and (ii) different perovskite structures than 3D Pb-materials (2D, double perovskites).[49] Therefore, low mobility and deficient carrier transport capabilities dictate the low photovoltaic performances of the devices. However, these materials show similar optical properties than 3D APbX_3 structures, which could be taken advantage if some devices components are compatible to couple with the light-absorber. Without doubts, lead-free perovskites will have higher PCE values in the future, which will conduct to motive the fabrication of attractive and highly efficient perovskite-based technologies.

3 Concluding remarks

It is unavoidable consider that Pb from perovskites-based materials is a toxic metal that can produce health issues to the living organism. When perovskites are used in solar technologies as solar cells, Pb can be segregated from the deteriorated devices to the environment, being accumulated by plants, food and finally human organisms. Although the concentration of Pb determined in the perovskite materials is low compared with important agencies such as EPA, its accumulation and subsequent metabolism can cause deficiencies on the enzymatic activity for the cell energy production and mainly, the reproduction of red cells of erythrocytes,

which are responsables for the body oxygenation. Under this situation, alternatives such as the recycling of Pb by collecting the lead precursor, or its partial/total substitution in perovskites are not only potential to ensure the mitigation of Pb intoxication to the ambient, but also to provide more visibility, improving the optical and electronic properties of the perovskites that can consider solar energy technologies commercially more rentable than conventional ones.

This contribution gives a detailed understanding about high risk of Pb contamination, and the importance to generate diverse protocols to extract, collect, reuse or avoid the use of Pb, in order to make possible the lowering of the amount of Pb during devices fabrication or/and obtaining absorber layer materials less toxic, ecofriendly and high performance. Furthermore, it is important to consider novel and promising lead-free materials, which depict potential optical properties similar to their Pb-analogous. Undoubtedly, this intrinsic characteristic will be taken advantage to fabricate highly efficient photovoltaic and optoelectronic devices in the near future, if some device components are studied to be compatible with the perovskite. Lastly, we conclude that Pb shows a high risk in the living organisms, specifically humans, if some security restrictions during its manipulation are not considered.

Biographies



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Website: <https://scholar.google.com/citations?user=tcadMvYAAAAJ&hl=es>

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