Lead-free halide perovskites, beyond solar cells and LEDs

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Abstract

In the last decade, halide perovskites have seen tremendous advancements, primarily in the field of solar cells and light-emitting diodes (LEDs). However, their remarkable optical and electronic properties are not only amenable for their use in solar cells and LEDs; as they can also be used for several other applications. While most research has focused on lead-based perovskites, their lead-free counterparts offer several potential advantages. Some of these advantages include reduced toxicity, improved stability, and a more diverse chemistry. Herein, we review some of the ‘other’ most notable applications of lead-free perovskites, including their use as photodetectors, photocatalysts, memristors, field-effect transistors, among others. We conclude by highlighting some of the pressing challenges and promising research avenues in the field.

1. Introduction

In the last decade, lead-halide perovskites (LHPs) have seen tremendous advancements, primarily in the field of solar cells [1] and light-emitting diodes (LEDs) [2]. For instance, perovskite solar cell efficiency has increased from 3.81\% [3] to 25.5\% [4] in little more than a decade. Among other factors, the excellent performance of LHP is attributed to their high optical absorption coefficient (in the order of 105 cm\(^{-1}\)), balanced electron and hole mobilities, long life of photogenerated carriers (up to 1 \(\mu\)s), diffusion lengths down to 1 \(\mu\)m, low trap densities of around 10\(^{15}\)–10\(^{16}\) cm\(^{-3}\), small exciton binding energies, and Urbach energies as small as 12.6 meV [5–10]. However, these notable optical and electronic properties are not only amenable for their use in solar cells and LEDs, instead, they have also been used in several other applications, such as lasers, phosphors, photodetectors, photocatalysts, memristors and field-effect transistors (FET), to name a few [11–14].

Not all is roses though, the presence of lead instils these materials with significant instability and toxicity. While strides have been made to address the stability issues of LHP, toxicity is still a significant concern, particularly when considering that lead in these materials is highly bioavailable [15–17]. To address this problem, recent research has focused on the search for lead-free perovskite and perovskite-like materials [18, 19]. Different directions have been taken to diminish the toxicity of LHP. The first direction was to homovalently replace lead with elements such as Sn\(^{2+}\) [20, 21], Ge\(^{2+}\) [22, 23], and Cu\(^{2+}\) [24, 25], which was followed by heterovalent substitution of lead, with elements such as Bi\(^{3+}\) or Sb\(^{3+}\). The heterovalent replacement can be subsequently divided into two subcategories based on the ways to maintain the charge neutrality: ion-splitting and ordered vacancy [26, 27]. The ion-splitting subcategory can be further divided into mixed anion and mixed cation compounds with formula A\(_2\)B(I)B(III)X\(_6\), which are commonly called double perovskites [28, 29].

Another approach involves the creation of lower dimensional perovskites, which resulted in more diverse materials and properties [30–32]. In fact, dimensional reduction has increased the chemical diversity of perovskite-like materials more than any other approach, as it allows for the incorporation of an almost

\(\text{cm}^{-1}\)
infinite number of A and B cations. Beyond their potential application in solar cells and LEDs, dimensional reduction has also enhanced the properties and increased the potential applications of halide perovskites (HPs) [12, 33, 34]. Finally, a combination of some of these approaches, dimensional reduction and heterovalent substitution, have recently resulted in yet another alternative: layered double perovskites [27], which widens even further the possible materials and applications.

All these combined approaches have resulted in an enormous amount of new materials, many of which have applications beyond solar cells and LEDs. In this regard, herein we review the most recent advances in lead-free HPs, focusing on some of their less studied applications, such as photodetectors, photocatalysts, and memristors (see figure 1). The emphasis is then placed on some applications that have just begun to be studied but are quite promising, such as batteries, lasers, etc. It is important to note that for practical reasons, in this review, we limited our research to three-dimensional (3D) and two-dimensional (2D) HPs, albeit some other one-dimensional (1D) and zero-dimensional ('0D') metal halides have also shown similar properties and applications [29, 35–38]. We conclude by providing a perspective of future research and the main challenges faced by lead-free HPs for applications beyond solar cells and LEDs.

2. FETs

FETs are electronic devices composed of three-terminals: source, drain, and gate. The concept of FETs was extended to thin-film FETs. They consist of a semiconductor film, a gate insulator layer, and three electrodes: two source/drain electrodes separated by a distance, and one gate electrode separated from the semiconductor by the insulator layer (see figure 2(a)) [39]. In a transistor, the voltage is applied to the gate (\(V_{GS}\)) and drain (\(V_{DS}\)) electrodes while the source is grounded (\(V_S = 0\)). When a positive \(V_{GS}\) is applied,
negative charges are induced and electrons are injected; conversely, when a negative $V_{GS}$ is applied, holes are injected. Thus, an appropriate $V_{GS}$ is applied and a conduction channel between the source and drain is formed by the induced charges at the insulator–semiconductor (perovskite) interface. When a second appropriate $V_{DS}$ is applied, the accumulated charges become mobile from the source to drain.

FET devices have different configurations depending on the contact and gate locations in the device, such as bottom contact/bottom gate (BC/BG), top contact/bottom gate (TC/BG), top contact/top gate (TC/TG) and bottom contact/top gate (BC/TG). An example of typical current–voltage ($I_{DS}$ vs $V_{DS}$ at various fixed biases $V_{GS}$) and transfer curves for a thin film FET are shown in figure 2(b). Such curves help to visualize and extract other characteristic parameters such as field-effect charge mobility ($\mu_e$ or $\mu_h$), current ON/OFF ratio ($I_{ON}/I_{OFF}$), the threshold voltage ($V_{th}$), and subthreshold swing. Details of the analytical expressions and extracting procedure parameters can be found in the works of Torsi et al [40] and Guo et al [41].

FETs are a key component in electronic circuits, silicon and organic FETs have been used in many applications such as sensors, devices for medical diagnosis, integrated circuits, telecommunication systems, etc [42–44]. HP are characterized by their high carrier mobilities. Their easy processability makes them suitable as active channel materials for thin film FET devices. Notably, a lead-free hybrid perovskite was the first perovskite material to be incorporated in a FET. In the seminal work by Mitzi et al [45], the 2D perovskite (PEA)$_2$SnI$_4$ (PEA = phenylethylammonium) was employed as the active material in a transistor that was fabricated by a solution-based low temperature process. This first perovskite FET showed decent hole mobilities ($\mu_h$) of 0.62 cm$^2$/V s and an $I_{ON}/I_{OFF}$ current ratio $>10^4$.

Following the first reports on perovskite photovoltaics, others have incorporated (PEA)$_2$SnI$_4$ into FETs. For example, Adachi et al have tested different device architectures, processing methods, varied dielectric materials, and electrodes while retaining (PEA)$_2$SnI$_4$ as the active channel material [46–49]. These studies have allowed the improvement of characteristic parameters (see table S1 available online at stacks.iop.org/JPENERGY/3/032014/mmedia)). In a recent work, using exfoliated large crystals of (PEA)$_2$SnI$_4$ (figure 2(c)), Adachi et al [50] also reported a large hole mobility ($\mu_h$), above 40 cm$^2$/V s, for p-channel devices, with a voltage threshold of $-26.8$ V and an electron mobility of $\mu_e = 35.5$ cm$^2$/V s for an n-channel device. Unfortunately, despite these good results, the fabrication yield was low (<1%), and only very few devices...
showed current transport properties, with only one of the fabricated n-channel devices working. Similarly, the related \((\text{PEA})_2\text{CsSn}_3\text{I}_7\) has been used as the active material in FETs with decent performance (see table S1) and improved stability [51].

Apart from \((\text{PEA})_2\text{SnI}_4\), few other lead-free perovskite materials have been used in FETs, most notably, tin-based and 2D perovskites that incorporate \(\pi\)-conjugated oligothiophene ligands [52]. Although the performance is not as good as that of single-crystal based devices, these materials showed improved stability and more reproducible fabrication (figure 2(d)).

3. Photodetectors

Photodetectors are devices that turn light into an electrical signal. Their applications range from communications systems and optical connections to biomedical imaging and environmental monitoring [53–55]. They can be classified into three different types depending on the mechanisms through which they work: photoconductors, photodiodes, and phototransistors [56].

Photoconductors are the most straightforward devices, as they consist of a semiconductor placed between two ohmic contacts. A voltage difference is then applied between the contacts to force an electric current to flow through the semiconductor. When light interacts with the semiconductor, it creates electron–hole pairs that differ from the equilibrium state. This raises the conductivity of the device and can be observed as an increase in the electric current. These devices have several drawbacks, as they need to have a constant voltage input, and the lifetime of the charge carriers must be long enough for them to reach the contacts. Photodiodes, on the other hand, usually consist of a p–i–n, p–n, or Schottky junction. Current is created by the charge imbalance between the p-type and the n-type site. This is very similar to the working mechanism of solar cells. However, solar cells aim to generate power, while photodiodes consume power for their operation. Lastly, phototransistors have three electrodes: source electrode, drain electrode, and gate electrode, with a thin dielectric film placed between the semiconductor channel and the gate electrode to allow the charge transport of the transistor to be tuned depending on the gate bias, which allows for a better control of the photoelectric response.

Generally speaking, materials suitable for photodetectors require a good light absorption, long charge carrier lifetimes, and large charge carrier mobilities. Several perovskites, lead-containing and lead-free, meet these criteria and have thus been studied for implementation in this field. The efficiency and performance of photodetectors is evaluated through several parameters: responsivity \((R, \text{A W}^{-1})\), noise-equivalent power \((\text{W (Hz}^{1/2})^{-1})\), specific detectivity \((D^*, \text{Jones})\), gain \((G)\), linear dynamic range \((\text{dB})\), and response speed [57]. See equations S1–S3 in SI for a description on how these parameters are calculated.

Photodetectors are commonly made from silicon, germanium, and indium gallium arsenide [58]. Alternatively, others based on ZnO, SnO\(_2\), TiO\(_2\), GaN, PbS, and graphene have also been reported [55, 59–62]. However, these are expensive and generally have limited detectivity \((<5 \times 10^{13} \text{ Jones})\) [63].

The recent advent of perovskite solar cells has motivated many research groups to develop photodetectors based on lead perovskites such as CsPbBr\(_3\), CsPbI\(_3\), MAPbI\(_3\) (MA = methylammonium) and other halide mixtures, (C\(_2\)H\(_4\)NH\(_3\))\(_2\)(CH\(_3\)NH\(_3\))PbI\(_4\) and (C\(_2\)H\(_4\)NH\(_3\))\(_2\)PbBr\(_4\), which have been incorporated in several devices [57]. MAPbI\(_3\) has also been incorporated into devices in conjunction with other photodetecting materials such as graphene [64], PbS [65], GaN [66], or MoS\(_2\) [67]. Some of these devices have excellent properties, with responsivities up to \(8 \times 10^8 \text{ A W}^{-1}\) and response times of few microseconds. However, as the toxicity of lead is a great concern, other perovskites have been studied and implemented in photodetectors, with operating ranges spanning from the deep ultraviolet to the near-infrared.

3.1. Lead-free HPs photodetectors

Several tin perovskites have been used in photodetectors. However, since Sn\(^{4+}\) is prone to oxidation, significant efforts have been made to passivate these materials and find ways to stabilize them.

Like MAPbI\(_3\), its tin analogue, MASnI\(_3\), has also shown promise in several fields, including photodetectors. Waleed et al [68] fabricated a photodetector based on MASnI\(_3\) nanowire arrays (figures 3(a) and (b)), using porous alumina templates and a vapour-phase chemical reaction method. The material decays in a time that is orders of magnitude slower than that of conventional MASnI\(_3\) thin films. When comparing both devices, the light current is also \(\sim 500\) times slower than that of the thin film counterpart. The response times for this device are slow but could be improved by reducing the nanowires’ length, therefore decreasing the carrier transit time.

Another tin-based device with a broad response (350–1000 nm) and improved stability was described by Cao et al [69] by adding SnF\(_2\) and ascorbic acid to the reaction mixture to form CsSnI\(_3\) via a spin coating method. The ascorbic acid promotes crystal growth and prevents or diminishes tin oxidation, while SnF\(_2\) is...
used to create a Sn$^{2+}$-rich environment without creating changes in the lattice constants or creating unwanted phases.

Dimensional reduction has been a common approach to improve specific properties of perovskites. These are usually synthesized by inserting a large organic cation in the A position to form layers of octahedra separated by organic spacers. Qian et al [70] reported a flexible photoconductor based on the 2D HP (PEA)$_2$SnI$_4$. (PEA)$_2$SnI$_4$ was deposited onto flexible electrodes over PET substrates using a spin coating method, coupled with 20–40 mol% of SnF$_2$ to prevent oxidation. These devices are flexible and can withstand over 1500 bending cycles, which can be useful for several applications, such as light simulated synaptic devices.

The structure of the material is critical for device performance. Yang et al [71] reported the synthesis of CsSnX$_3$ (X = Cl, Br, I) nanowires by a chemical vapour deposition method using mica as a growth substrate. They fabricated a photodetection device using CsSnI$_3$ NW, with Ti and Au electrodes, using polymethyl acrylate as a protecting layer to insulate the unstable perovskite from water and oxygen. Liu et al [72] also fabricated a device with an outstanding performance by creating a FASnI$_3$/PEDOT:PSS (FA = formamidinium, PEDOT:PSS = poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) vertical heterojunction photodetector (figure 3(c)). The heterojunction creates a photogating effect that significantly increases the responsivity over a range from 300 nm to 1000 nm, and which is dependent on the thickness of the PEDOT:PSS layer.

Bismuth HPs with large organic spacers have also been implemented successfully in photodetectors, such as the 1D TMHDBiBr$_5$ (TMHDB = N,N,N,N-tetramethyl-1,6-hexanediandiammonium) [73]. This device has a wide photodetection range in frequencies below 600 nm. In addition to these, other bismuth low dimensional perovskite-like materials such as Cs$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$I$_6$, and MA$_3$Bi$_2$I$_9$ have been reported for photodetector applications and have been implemented in several devices [74–78]. These types of materials represent another promising alternative in the quest for cheap and efficient perovskite photodetectors.

Several antimony-based HPs have been implanted in photodetectors using different approaches. Yang et al developed a single-crystal photodetector with (MA)$_3$Sb$_2$I$_9$ with a fast response in the UV–Visible range up to 600 nm [79]. At nanoscale, Zheng et al [80] reported a photodetector based on Cs$_3$Sb$_2$Br$_9$ nanoflakes with comparable responsivity to the (MA)$_3$Sb$_2$I$_9$ single crystal device, while Pradhran et al [81] synthesized Cs$_3$Sb$_2$Cl$_6$ nanowires (figure 3(d)) and managed to increase the responsivity a thousandfold when compared to previous reports of these type of materials. Cs$_3$CuSb$_2$Cl$_9$ is a promising double-layered perovskite [82], and was implemented into a photodetector by Jayasankar et al with decent responsivity and detectivity [83]. However, these structures are incredibly versatile, and more research is required to fully explore their potential.

Silver can be incorporated into a perovskite structure accompanied by a trivalent cation, giving rise to 3D HP structures with the general formula A$_3$AgB$^{III}$X$_6$, where A is a large monovalent cation, B$^{III}$ is a trivalent
cation and X is a halide. Cs$_2$AgBiBr$_6$ is a very promising material that has been implemented in several applications. For example, it has been incorporated in photodetectors, either as a standalone photoactive layer [84], or with GaN (figure 3(e)) [85] or SnO$_2$ [86] heterojunctions. A photodetector using Cs$_2$AgInCl$_6$ has also been reported [87] with a response range in the UV part of the electromagnetic spectrum.

### 3.2. X-ray photodetectors

X-ray detection is extremely useful in various fields, including medical diagnosis, astronomy, high energy physics, non-invasive and non-destructive imaging [88–90]. The most common x-ray detectors measure this radiation indirectly, for example using scintillating phosphors that convert x-ray photons into visible photons, which are then absorbed by a common photodetector [91]. However, it is possible to convert x-ray photons directly into an electrical signal, which gives better spectral resolution and results in a simpler device. Semiconductors such as silicon, germanium, α-Se, and CdZnTe/CdTe have been used for direct x-ray detection. In the realm of perovskites, x-ray detectors based on MAPbI$_3$ thin films and MAPbBr$_3$ single crystals have been reported, achieving excellent sensitivity that can even outperform commercial photodetectors [92–95]. LHPs have also been used as scintillators, absorbing ionizing radiation and emitting photons in other parts of the spectrum [96].

Lead-free HP x-ray detectors have recently been reported, with the first work published in 2017 by Pan et al using Cs$_2$AgBiBr$_6$ (figures 4(a) and (b)) [97]. In that work, single crystals of Cs$_2$AgBiBr$_6$ were synthesized and treated through thermal annealing and surface passivation to reduce Ag$^+$/Bi$^{3+}$ disorder in the crystal structure. The resulting detectors have sensitivity comparable to those made from MAPbBr$_3$. The photophysical pathways were described in a subsequent publication [98], with the sensitivity increased even further at liquid nitrogen temperatures. Later, BiOBr was added into Cs$_2$AgBiBr$_6$ polycrystalline wafers as a heteroepitaxial passivation layer, which suppressed ionic migration, achieving a signal drifting one order of magnitude lower than any previously reported study, moreover, they showed excellent sensitivity. The wafers can also be scaled up, showing promise for commercial use. Li et al also reported a device with Cs$_2$AgBiBr$_6$ as the active layer [99], embedding the HP in organic polymers to form stable composite films. Polymers with hydroxyl groups were the most efficient dispersing the perovskite, and they were able to synthesize uniform films with sensitivities in the same range as those reported by Pan et al.

Dimensional reduction can also be useful for x-ray photodetectors. Xu et al fabricated a photodetector based on the 2D multi-layered double perovskite (BA)$_2$CsAgBiBr$_7$ (BA = butylammonium) (figure 4(c))
[100], where the perovskite structure was layered between organic spacers. The device showed sensitivity comparable to lead perovskite-based x-ray detectors, thus demonstrating that 2D HPs are an attractive alternative for these types of devices. Another approach was described by Zhuang et al., they used the 2D monometallic perovskite (NH$_4$I)$_2$Bi$_4$I$_6$ [101], which provides anisotropic x-ray detection with excellent sensitivity, and hence can be useful for medical applications.

Double HPs have also been used as x-ray scintillators, such as the one reported by Hu et al. based on Cs$_2$NaLnCl$_6$ (Ln = Tb$^{3+}$ or Eu$^{3+}$), which achieves a light yield higher than commercially available scintillators and LHP devices [102]. Recently, Yang Yang et al. developed a scintillator for real-time x-ray imaging [103] based on the double perovskite Cs$_2$AgInCl$_6$ doped with both Na$^+$ and Bi$^{3+}$. While on one side sodium doping partially breaks the parity forbidden transition between the valence band (VB) and conduction band (CB), with Cs$_2$Ag$_{0.6}$Na$_{0.4}$InCl$_6$ single crystals exhibiting a near white-light emission and a maximum photoluminescence quantum yield (PLQY) of 43%. On the other side, bismuth doping increased the x-ray absorption efficiency. The most efficient material in this Na$^+$ and Bi$^{3+}$ family has the chemical formula Cs$_2$Ag$_{0.6}$Na$_{0.4}$In$_{0.85}$Bi$_{0.15}$Cl$_6$. The proposed operation mechanism is depicted in figure 4(d). According to it, first x-rays (from the x-ray source and from Compton scattering) are absorbed by the heavy elements generating photoelectrons and a cascade of secondary electrons. The resulting high energy electrons are thermalized on ultrafast timescales and are then captured into luminescent centres. Once there, the high PLQY of the material ensures a very efficient radiative emission through the recombination of electron–hole pairs in the form of self-trapped excitons. Hence, using Cs$_2$Ag$_{0.6}$Na$_{0.4}$In$_{0.85}$Bi$_{0.15}$Cl$_6$, the authors were able to acquire images of a finger bending in real-time with a shallow radiation dose (figure 4(e)). These results are extremely encouraging for lead-free HP scintillators, which are significantly less toxic and allow x-ray imaging with extremely low radiation doses.

4. Memristors

Chua et al. theorized the concept of memristors (a portmanteau of memory and resistor) as a new two-terminal circuit element that is characterized by a relationship between the magnetic flux ($\phi$) and charge ($q$) [104]. Later, the concept was generalized to a class of nonlinear devices and systems called memristive systems, and it was shown that many systems and physical devices possess properties of memristive systems. These devices can switch between two resistances upon the application of an appropriate voltage or current signal. Thus, memristor devices are characterized by a pinched hysteresis loop and the ability to switch and store the resistive state (non-volatile condition) (figure 5(a)) [105–107].

Owing to their excellent optoelectronic properties, it was expected that HPs would emerge as a new class of memristive materials. Yoo et al. reported the first LHP memristor device using the MAPb$_{1-x}$Cl$_x$ perovskite between Au and fluorine-doped tin oxide (FTO) electrodes [108]. The device presented bipolar resistive switching (RS), endurability (figure 5(b)), low operating voltages, and non-volatile properties with a retention time of $\approx 10^4$ s, thus widely demonstrating HPs’ potential application as memristive systems [109].

To date, the most common and accepted operating mechanisms for HP memristors is the formation and rupture of conductive filaments (CFs), which are caused by the migration of halide ions and vacancies or by the migration of active metal ions. An example of the formation and rupture of Ag filaments is depicted in figure 5(c) [110]. Another type of mechanism proposed is an interface-type caused by the modification of the Schottky barrier [111]. The excellent properties and characteristics of HPs, like long carrier diffusion lengths, high charge carrier mobilities, their easy processing and low cost, have resulted in many HP memristors with high charge carrier mobilities, their easy processing and low cost, have resulted in many HP memristors with high charge carrier mobilities, their easy processing and low cost, have resulted in many HP memristors with

4.1. Memory device parameters and characteristics

Voltage–current ($V$–$I$) sweeps are the easiest way to identify the switching behaviour of a memristor. Thus, choosing the adequate input bias source (voltage or current) is essential. Once the voltage source is determined, a compliance current (CC) to control the maximum current is necessary. In some switching materials, a process called electroforming or forming is necessary to activate the RS behaviour. Electroforming refers to the process of applying a bias voltage to create metallic structures and implies electron transfer via ions. In the case of RS, applying high electrical stress at the initial stage leads to the formation of metallic CFs [125]. The forming process is not disabled for some of the memristor’s applications as non-volatile memories.
RS has different resistance states: as-fabricated, as-electroformed, high resistance state (HRS), and low resistance state (LRS). Some performance parameters for memristors are extracted from $V-I$ sweeps: $V_{\text{SET}}$, $V_{\text{RESET}}$, ON/OFF current ratio $= I_{\text{LRS}}/I_{\text{HRS}}$, whereas other basic parameters, like power consumption, switching time, charge transport mechanism, endurance, and retention time are analysed and estimated through different experimental methods.

The fabrication process and material selection of memristor devices impacts the device performance. From choosing the bottom electrode (BE), selecting the appropriate method to deposit the RS material, and the top electrode (TE). Usually, SiO$_2$/Si is used as a substrate due to low its superficial roughness; then, the substrate is covered by a metal film on the BE; this can be done through electron beam evaporation or sputtering techniques and using shadow masks or photolithography to pattern the electrode in the case of crossbar arrays; for the TE the same methods for BE are used [126].

The crucial step in device fabrication is the deposition of RS material. The typical methods are atomic layer deposition and sputtering. However, HPs have made the deposition of RS on thin films accessible and easier fabrication processes thanks to their solution-processability. Most commonly, spin-coating of the target perovskite on the electrode substrates is the most common process used to fabricate thin-film memristors devices based on HP. Also, conveniently for HP-based devices, materials such as indium tin oxide (ITO) and FTO can be used as BE.

An important characteristic and advantage of memristors is the capability to be scaled down (from micro to nanoscale) and thus be implemented into different applications; some of the mentioned features of memristive systems are improved in small-sized devices [127, 128]. Hwang and Lee [129] reported nanoscale memory devices’ fabrication depositing a MAPbI$_3$ layer on patterned Si wafers with 250 nm via-holes formed by lithography and etching process. The RS HP-based layer was formed by sequential vapour deposition that produced uniform films and good memory cell devices’ performance as good endurance and high retention time.

A useful reference on the fabrication and methodologies used to study RS devices is that of Lanza et al [130]. Research on memristive devices has attracted considerable attention, so much that today these devices...
have assorted applications as non-volatile random-access memories [131–133], logic arrays [134–136], neural networks [137–139], among others [140]. In such devices, metal oxides, chalcogenides, graphene, polymers, organic compounds, and perovskites are commonly used as the semiconducting layers.

4.2. Resistive random-access memories (ReRAMs)

ReRAM devices are one of the most promising applications of lead-free HPs. Some of the ReRAMs potential applications are data storage and programmable logic gates [141]. The key performance requirements for ReRAMs are high ON/OFF ratios, low operating voltages, and large endurance [142, 143].

Sun and Wen reported the potential for lead-free HP to be applied on ReRAMs [122]. They fabricated flexible memory devices with the structure Al/MASnCl3/PVA/ITO/PET (PVA = polyvinyl alcohol). These devices exhibit non-volatile characteristics, and surprisingly, after reaching LRS, the state remains during subsequent voltage scanning or even after turning off the power for 3 h or longer. This kind of response is characteristic of non-volatile write-once-read-many-times memory devices. The data retention was estimated at $2.34 \times 10^5$ s, which is the longest consecutive span reported for a lead-free perovskite device. Also, these devices show conditional switching capability due to an external voltage (a rectangular pulse, 80 ms) that exceeds its threshold switching voltage $V_{SET} (>1.5 \text{ V})$; thus, the devices are converted from the HRS to LRS. The resistive state can be read after another external voltage (+0.2 V) is applied. In this way, they were able to design a memory logic device, with the transient current responding to the applied voltage pulse. The logic states are defined as '1', when the output current is >0.01 mA, and otherwise as '0'. All results were reproducible and stable, allowing the development and implementation of an information display function and memory logic gates. The second by applying one or two +2 V signals, where then they obtained ‘OR’ and ‘AND’ gates, as shown in figure 5(d). Besides, the endurance and flexibility were tested; it was found that after 2000 bending cycles the LRS becomes a volatile state, so the performance of the devices evolves into that of a static random-access memory.

Another promising lead-free perovskite with suitable memory properties was reported by Han et al [123], who fabricated a CsSnI$_3$-based RS memory device using two different TEs: Ag (electrochemically active) and Au (inert). Using such electrodes, they demonstrated the possibility to design memory devices for a specific purpose, as they present distinct switching behaviour depending on the TE material (figure 5(e)).

On one side, the Ag device shows filamentary and bipolar RS behaviour produced by metallic conducting filaments (CFs). They found that the presence of Sn$^{2+}$ vacancies also affect the RS behaviour, and although CF remains as the dominant factor, it was concluded that the Ag devices present electrochemical metallization. The operating voltages were below 0.15 V with a $V_{forming}$ of 0.36 V, which is among the lowest for lead-free perovskite memristors (see table S3), very comparable with operating voltages reported for lead HP memory devices. On the other hand, the Au device has an RS interface type that is indicated by a gradual current change under $I$–$V$ sweeps, so the RS performance is caused by Sn$^{2+}$ vacancies and is attributable to valence change mechanism. In these Au devices, the endurance decreases to 120 cycles, which is significantly lower to than the 600 cycles of Ag devices, and a retention failure occurs. Consequently, the Pt BE was replaced by ITO, resulting in an improvement of the retention time (up to $10^4$ s) and endurance (150 cycles), besides the fact that the device now showed filamentary and bipolar RS behaviour.

Lead-free memristor devices’ stability is an issue that should be further investigated, mainly thinking in practical applications. In this regard, recently Cheng et al [144] took advantage of the high stability at ambient conditions of the lead-free double perovskite Cs$_2$AgBiBr$_6$ to present a memristor based on it [145]. The fabricated Au/Cs$_2$AgBiBr$_6$/ITO memristor retain the RS performance even after its exposure to very harsh environments including high humidity (from 10 to 80%), high temperatures (up to 453 K), burning for 10 s with an alcohol flame, and $^{60}$Co $\gamma$-ray irradiation. Through x-ray diffraction, it was confirmed that the crystal structure remains almost intact after being exposed to the previously mentioned harsh conditions and even after air exposure for 100 days. The remarkable stability was attributed to a strong Ag–Br bond and the good crystallinity of Cs$_2$AgBiBr$_6$. Further, they showed decent performance that suggests Cs$_2$AgBiBr$_6$ is a promising material for ReRAMs.

4.3. Neuromorphic computing

The memory switching properties of HP have attracted widespread interest in other research fields. Neuromorphic computing is a relatively novel concept that aims to use hardware to closely mimic neuro-biological architectures to implement a model of neural systems [146]. Today, the concept comprises computing systems that can run bio-inspired computing models to implement neural and deep-learning networks. Neuromorphic computing offers several advantages over the conventional von Neumann digital approach, where the control processing and memory units operate separately [147–149]. On the other hand, due to similarities between non-volatile RS properties and the memristor structure (two-terminals device) with the function and structure of biological synapsis, memristor-based devices, are an excellent approach to
emulate neuromorphic systems [128, 150]. Naturally, considering the disadvantages of lead perovskites, the study of properties, characteristics, and applicability of lead-free perovskite materials has been extended to neuromorphic properties, showing great potential.

Recently, a MA$_3$Sb$_2$Br$_9$-based device was reported to be applied on this frontier of computing applications [124]. In addition to good switching characteristics (ON/OFF current ratio $\sim 10^5$, endurance of 300 cycles, and retention time $\sim 10^4$ s) obtained without the need for a forming voltage, artificial synaptic characteristics were observed on it (figure 5(f)). The Ag/PMMA/MA$_3$Sb$_2$Br$_9$/ITO device revealed a very interesting feature, that the appearance of CF does not require a forming process. The initial LRS is induced by the presence of metallic Sb (corroborated by x-ray spectroscopy), and the formation/rupture of CF by the migration of bromide vacancies. Thus, the RS mechanism is explained by the valence change of Sb in MA$_3$Sb$_2$Br$_9$. Also, multilevel storage was examined by varying the CC, and three levels of LRS were found. While investigating possible synapsis behaviour, postsynaptic current (PSC) was observed, and changes in synaptic weight $\Delta G = (I_{final} - I_{initial})/I_{initial}$ were calculated using the currents recorded before and after the spikes-pair application. Results show an excitatory PSC and an inhibitory PSC. The former when the partially formed CF is maintained and the latter when the partially ruptured CF is retained in MA$_3$Sb$_2$Br$_9$. Also, long-term potentiation, long-term depression, and spike-timing-dependent plasticity were observed. The calculated energy consumption was as low as 117.9 fJ $\mu$m$^{-2}$. This value is very comparable to those found in Pb-based perovskites used as neuromorphic materials (MAPbI$_3$ = 47 fJ $\mu$m$^{-2}$ [151], CsPbBr$_3$ = 153 fJ $\mu$m$^{-2}$, MAPbBr$_3$ = 345 fJ $\mu$m$^{-2}$, FAPbBr$_3$ = 23 fJ $\mu$m$^{-2}$ [152], (PEA)$_2$PbBr$_4$ = 400 fJ $\mu$m$^{-2}$ [153]), proving that lead-free-based memristors devices are promising for neuromorphic computing applications.

In summary, the performance of lead-free perovskite memristors has made significant progress. However, it is still necessary to further improve the technology to reach characteristic parameters and stabilities comparable with the most successful materials used in memristors.

5. Photocatalysis

Photocatalysis is another area of opportunity for HP. Ideal photocatalytic materials should have strong and broad spectral absorption, efficient charge separation, low exciton binding energy, long carrier lifetimes, long operational stability, and adequate redox capacity for target reactions. Notably, HPs excel in many of these characteristics, and thus, photocatalysis it is an almost natural application niche for HP [154]. Indeed, HPs can be utilized as efficient photocatalysts for numerous electrochemical reactions like hydrogen evolution reaction (HER), CO$_2$ reduction reaction (CRR), organic transformations, and degradation of organic pollutants. Generally, three separate processes carry out general reactions in photocatalytic materials:

(a) Absorption of photons to generate electrons and holes pairs.
(b) Separation of charges and their migration to reaction sites on the surface of the photocatalyst.
(c) Chemical oxidation and reduction at the surface mediated, respectively, by the photogenerated holes and electrons [155].

Additionally, for these processes to occur, a suitable combination of the electronic band structure of a semiconductor and the reaction redox potential is needed [156]. Figure 6(a) shows the relative position of the CB and the VB of the HP involved, respectively, in the reduction and oxidation half-reactions. In a typical HP, the relative position of its CB is usually negative enough for H$_2$ generation, CO$_2$ reduction, and hydroxyl radical generation. The latter is involved in the dye’s degradation because the required potential is above the VB maxima of HPs [157, 158].

The first report of HP-based photocatalysis was published in 2017; therein, Park et al described the use of MAPbI$_3$ as a photocatalyst for H$_2$ evolution, albeit with a low rate (6.94 $\mu$mol g$^{-1}$ h$^{-1}$) compared to traditional photocatalysts [159, 160]. From there on, other LHPs have shown the ability to photocatalyze different reactions with varying degrees of competence [161, 162]. Perhaps more notably, CsPbBr$_3$ and related nanocrystals (NCs) have been employed in a wide range of photocatalytic reactions [163, 164]. However, due to the instability of lead-based perovskites in water, all of these experiments have been made in non-aqueous media, which is not ideal, and it is thus interesting to explore the use of lead-free perovskites, which might provide improved stability and tuneable redox properties.

5.1. Hydrogen evolution reaction (HER)

Artificial photosynthesis has been and remains as the archetypical target for the conversion and storage of solar energy decades. The decomposition of water, using acids like HI to produce value-added chemicals like
hydrogen, is also a very attractive possibility for reducing the use of high temperatures and energy consumption in catalysis [169].

Zhao et al were the first to use a lead-free double perovskite Cs$_2$AgBiBr$_6$ to produce H$_2$ in saturated aqueous solutions of HBr and H$_3$PO$_4$. Since Cs$_2$AgBiBr$_6$ has a low photocatalytic activity (6.1 $\mu$mol g$^{-1}$ per 10 h), the effect of adding Pt, and reduced graphene oxide (RGO) as co-catalysts, was investigated. The use of Pt showed a slight improvement, generating 9.5 $\mu$mol g$^{-1}$. But interestingly, when using RGO, the production of H$_2$ increased about 50 times and reached 489 $\mu$mol g$^{-1}$. This yield was obtained with the optimal Cs$_2$AgBiBr$_6$/2.5% RGO sample (figure 6(b)), presenting an apparent quantum efficiency of 0.16% and good stability for 12 cycles of 10 h each. The proposed mechanism suggests that the presence of RGO favours the separation of the photogenerated electron–hole pairs. Then, the electrons can be transferred rapidly to the conducting RGO suppressing charge recombination, which in turn enhanced H$_2$ production (see table S4.1) [170].

5.2. CO$_2$ reduction reaction (CRR)

Inspired by a natural process which is at the very basis of life as we know it, artificial photosynthesis is a very promising approach to decrease CO$_2$ concentration in the atmosphere. It aims to achieve the ecological conversion of CO$_2$ into chemical fuels (such as methane, methanol, and hydrogen) using solar energy and heterogeneous photocatalysts. One of the biggest challenges in this field is the thermodynamic barrier of CO$_2$ formation and its slow reaction rate [171]. In cases where perovskite halides have been applied as catalysts for CO$_2$ photo-reduction, it has been found that their CB position should be above the redox potential of CO$_2$ [172].

The first report of CRR by a lead-free perovskite was made by Kuang et al, who showed CO$_2$ reduction over Cs$_2$AgBiBr$_6$ NCs synthesized by the hot-injection method. The photocatalytic process showed the evolution of CO and CH$_4$ under simulated solar light irradiation, with no H$_2$ side product detected (figure 6(c)) [166]. Cs$_2$AgBiBr$_6$ NCs have shown remarkable stability to moisture and low polarity solvents. The proposed mechanism suggests the use of nanostructures to improve photocatalytic performance. However, the protecting organic layer on the NCs surface acts as a barrier that blocks the transport of photogenerated carrier transfer process. Reproduced from [168] with permission of The Royal Society of Chemistry.

Figure 6. (a) Scheme of reduction and oxidation half-reactions of different reactions (HER, CRR, organic transformations, and the degradation of organic pollutants) photocatalyzed by HP. Reprinted with permission from [165]. Copyright (2019) American Chemical Society. (b) Schematic mechanism of H$_2$ evolution by CABB/RGO under visible light irradiation. Reprinted from [164], Copyright (2020), with permission from Elsevier. (c) Schematic diagram of the photoreduction of CO$_2$ on the surface of Cs$_x$AgBiBr$_6$. NCs. [166] John Wiley & Sons. (d) Photoexcitation scheme of the MASn$_2$I$_6$/TiO$_2$ (1:9) heterostructure composite and the subsequent photogenerated carrier transfer process. Reproduced from [168] with permission of The Royal Society of Chemistry.
stabilized by Bi^{4+} and oxygen ions, both materials showed better photocatalytic activities compared to MA$_3$Bi$_2$I$_9$, where the holes are stabilized by Bi$^{4+}$, radical cations $\cdot$CH$_2$NH$_3^+$ and oxygen anions which favour the transfer of holes to the water (oxidation channel). Among the factors that affect the catalytic activity for Bi-based perovskites is the introduction of defects to increase the adsorption of CO$_2$ and the trapping of excited electrons [176, 177].

Geyer et al have shown that replacing unsaturated oleic acid with saturated octanoic acid is indispensable to reach the temperature needed to synthesize Cs$_5$Sb$_2$Br$_9$ NCs without CsBr impurities [178]. Once Cs$_5$Sb$_2$Br$_9$ NCs were purified to remove surface ligands, they showed a tenfold increase in the activity of the photocatalytic CO$_2$ reduction compared to the NCs of CsPbBr$_3$, achieving a turnover rate of 510 $\mu$mol CO g$^{-1}$ cat after 4 h. The decrease in catalytic activity with time was mainly attributed to the formation of a surface Sb oxide that reduces the absorption of visible light. Although a decrease in the activity of Cs$_5$Sb$_2$Br$_9$ NCs was observed after 9 h of reaction, the NCs were still five to ten times more active compared to its Pb counterparts.

5.3. Organic transformations

In addition to the photoreduction of CO$_2$ and the division of water for the generation of solar fuels, new research using HPs as photocatalysis has focused on the transformation of organic reagents into value-added chemicals, ideally under mild conditions (ambient temperature and pressure). While the field is still on its infancy, there are exciting results which make HPs a promising alternative to traditional photocatalysts [179]. While there is a significant number of lead-based photocatalysts for organic transformations, so far, to the best of our knowledge, only a few cases have been reported using lead-free perovskites as photocatalysts in organic transformations [167, 180–182].

Tüysüz et al reported the in-situ preparation of Cs$_3$Bi$_2$Br$_9$ and its simultaneous application as a photocatalyst for epoxide alcoholysis under visible light irradiation. The photocatalyst presented high activity (1333 mmol h$^{-1}$ g$_{cat}$ $^{-1}$) and selectivity (>86%) to produce 2-isopropoxy-2-phenyl ethanol from styrene oxide and isopropanol. It also showed good stability and recyclability [167]. In contrast, the lead-based perovskite CsPbBr$_3$ showed a conversion rate of only 1% [183]. The authors have proposed a mechanism where the photogenerated holes and superoxide anions (O$_2^{-}$) produced from the reduction of O$_2$ by the photogenerated electrons react with the alcohol to form its radicals or anions, which serve as nucleophiles for the opening of the ring. On the other hand, Bi-based Lewis acid sites on the photocatalyst activate the basic oxygen atom in the epoxide ring [184]. Finally, the subsequent attack of the activated epoxide by alcohol radicals or anions is carried out through a traditional nucleophilic substitution [185]. In a subsequent paper, Tüysüz et al proposed the use of confined ordered mesoporous SBA-15 silica supported on Cs$_3$Bi$_2$Br$_9$ nanoparticles (2–5 nm), which provides a large number of catalytically active centres to activate C(sp$^3$)–H bonds of hydrocarbons under visible light irradiation in air. Cs$_3$Bi$_2$Br$_9$/SBA-15 photocatalyst, with a loading of 10 wt% presents an astonishing conversion rate of 12 600 mmol g$_{cat}$ $^{-1}$ h$^{-1}$ and a selectivity of 90% towards benzaldehyde (benzyl alcohol was the main by-product), as shown in figure 6(d). A decrease in activity was observed due to the aggregation of Cs$_3$Bi$_2$Br$_9$ nanoparticles, which in turn reduced the number of active sites available, thus favouring the recombination of charges (see table S4.3) [182].

On the other hand, Soo et al synthesized the 2D perovskite (HDA)$_2$SnI$_4$, where the hexadecyl ammonium cations (HDA) improve the perovskite’s hydrophobicity and stability, so even in humid air conditions it can be used in the decarboxylation and dehydrogenation of acids. Hence, the decarboxylation of 5-methyl-indoline-2-carboxylic acid gave indoline with a yield of 30 (units) while the dehydrogenation of 2-methylindoline led to indole with a yield of 47%. Both yields are low when compared to lead-based conditions it can be used in the decarboxylation and dehydrogenation of acids. Hence, the decarboxylation ammonium cations (HDA) improve the perovskite’s hydrophobicity and stability, so even in humid air.

5.4. Degradation of organic pollutants

Environmental pollution and the increasing energy demand of modern civilization are intimately linked. Mechanisms for minimizing the first while boosting the second are among the most pressing challenges faced by contemporary science and society. Once more, HP can be used for the degradation of organic pollutants and environmental bioremediation. Based on the knowledge of different types of inorganic semiconductors, an attempt has been made to decrease the electron–hole pairs’ recombination to favour photocatalytic activity. The photodegradation reactions are greatly dependent on the oxidation ability of metal halide perovskites (MHPs) to produce reactive oxygen species (e.g. H$_2$O$_2$, *O$_2^{-}$, and *CO$_2^{-}$). In 2017, Xu et al first reported the use of the all-inorganic CsPbX$_3$ (X = Br, Cl, and I) quantum dots (QDs) series for the photocatalytic degradation of methyl orange under visible-light irradiation [186].

Zeng et al studied the behaviour of MASnI$_3$/TiO$_2$ (1:9) as photocatalysts, and found them able to completely degrade rhodamine B (Rhb) (97%) in 40 min, which exemplified an heterojunction with better
photocatalytic activity than their individual MASnI$_3$ and TiO$_2$ constituents. This was rationalized as the consequence of the improved absorption of light, a favourable energy band’s alignment, and to the contact interface, which allowed for the transfer and separation of photogenerated carriers between MASnI$_3$ and TiO$_2$ (figure 5(e)). Furthermore, this heterojunction prevents the oxidation and hydrolisys of MASnI$_3$. The excess of MASnI$_3$ is seen to boost the number of recombination centres and limits the separation of charge carriers. The species responsible for the degradation of RhB is the radical $\cdot$O$_2^-$, produced by the photogenerated electrons that reduce molecular oxygen [168]. The MASnI$_3$/TiO$_2$ heterojunction shows a similar degradation performance when compared to other types of lead-free perovskites (see table S4.4). The main difference being that it is 5, 4.5, and 3 times faster than MA$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$I$_9$, and Cs$_2$AgBiBr$_6$, respectively [187–189]. Later, Navas et al used CsSnBr$_3$ for the photodegradation of the crystal violet dye, finding a maximum degradation of 73.1%. The best performance corresponded with the largest amount of perovskite photocatalyst. Since the degradation of the crystal violet dye was affected by the amount of the perovskite photocatalyst, it suggests that the adsorption process is the limiting step. The proposed mechanisms involves various steps: (a) crystal violet molecules are adsorbed to the CsSnBr$_3$ surface; (b) photons from the irradiation source are then absorbed by CsSnBr$_3$, and electrons go from the VB to the CB producing electron–hole pairs; (c) the electrons in the CB produce oxidant species, such as superoxide anion radicals ($\cdot$O$_2^-$); (d) the holes in the VB produce active species, such as ‘OH; and (e) oxidizing species oxidize the dye molecules [190].

The only reported case where a double perovskite is used for the degradation of a dye was presented by Xu et al [174]. There, Cs$_2$AgBiBr$_6$ almost totally degraded RhB (∼98%) in 120 min, showing zero-order kinetics with a linear dependence on irradiation time. This perovskite has high chemical stability, and photocatalytic oxidation of ethanol as solvent was not observed. When Cs$_2$AgBiBr$_6$ was compared with CdS (model inorganic photocatalyst), the perovskite showed higher density of surface catalytic sites (Ag or Bi) than CdS, where the activation of dye molecules or O$_2$ wasfavoured and therefore accelerated the reaction [191]. Notably, the photocatalytic degradation of the dye was blocked after adding 2,2′,6,6′-tetramethylpiperidine-1-oxyl (free radical scavenger) to the solution [192], proving that this photocatalytic process is based on free radicals [189].

6. Other applications

As seen throughout this review, lead-free perovskite halides have developed a wide range of applications, well beyond solar cells and LEDs. There are other emerging fields in which lead-free HPs have shown promise and thus offer areas of opportunity, which need further exploration. In what follows, we summarize what we think represents the most innovative and unconventional research avenues in lead-free perovskite applications, which at this time include but are not limited, to their use as batteries, lasers, and sensors.

6.1. Batteries and capacitors

A very dynamic research area is that of energy storage, where the quest for new materials is constantly investigated for their use as anodes, cathodes, or solid electrolytes in alkali ion batteries [193]. HPs have recently developed devices such as batteries and supercapacitors [194]. Mainly, they have been used in these devices for their ion diffusion inside the HP, although this property is undesirable in solar cells because it causes hysteresis and instability [195]. In general, batteries aim to have a high energy density, low self-discharge, low memory effect, high open-circuit voltage, and high durability [196]. On the other hand, capacitors should have high power density, long cycle life, and a faster charge/discharge rate than batteries. The goal is to use more abundant elements and develop batteries and capacitors that have high energy storage capacity that are highly stable across a large number of charge/discharge cycles [197, 198].

In 2014, Jaffe and Karunadasa first reported the use of the lead-free perovskites (EDBE)CuCl$_4$ (EDBE = 2,2′-(ethylenedioxido)bis(ethylammonium)) as a cathode in a lithium-ion battery. It reached 26 mA h g$^{-1}$ at a current density of 28 mA g$^{-1}$ for more than 200 cycles [199]. After this, the effect of molecular dimensionality on battery performance has been studied [200, 201]. A remarkable case was the use of the 3D perovskite A$_2$CuBr$_4$ ($A = \text{CH}_3\text{NH}_3$/Cs, 2D/3D) as an anode. It displayed a better reversible capacity of 420 mA h$^{-1}$ g$^{-1}$ for up to 1400 cycles, compared to the 2D ($\text{CH}_3\text{NH}_3$)$_2$CuBr$_4$ perovskite, which had a reversible capacity of 630 mA h$^{-1}$ g$^{-1}$ for just 140 cycles, although the energy capacity was somewhat reduced (see table S5) [202]. On the other hand, there is an interesting proposal for using CsSnCl$_3$ as a solid-state electrolyte [203].

Currently, the only capacitor made of a lead-free HP is that of a double-layer electrochemical capacitor using 0D ($\text{CH}_3\text{NH}_3$)$_3$Bi$_2$I$_9$. Exhibiting a maximum areal capacitance of 5.5 mF cm$^{-2}$ and the device retained 84.8% of its initial maximum capacitance even after 10 000 charge/discharge cycles. Because it is a 0D
Figure 7. (a) Normalized emission at low pump fluence and high pump fluence (solid lines, \( \approx 70 \mu J cm^{-2} \)) for CsSnI\(_3\) with different molar concentrations of SnF\(_2\) treatment. (b) Optical image of a butterfly scale from the white part of the wing. Inset is a photograph of the butterfly and SEM image showing lamellae (vertical structures) in the scale. Simulated electric field distribution at resonant cavity mode (950 nm) with embedded CsSnI\(_3\) and comparison of the PL, ASE, and single mode lasing of CsSnI\(_3\) (20% SnF\(_2\)). [207] John Wiley & Sons. (c) Response of MASnI\(_3\) sensor to a variety of gases. Reprinted from [208], Copyright (2020), with permission from Elsevier.

perovskite, the active layer provides an extensive access surface to the electrolyte, presenting a low resistance to charge transport, favouring its performance [204].

6.2. Lasers

The use of HP in lasers was first described by Kondo et al [205], who reported biexciton lasing in the layered perovskite system \([\text{C}_6\text{H}_{13}\text{NH}_3]_2\text{PbI}_4\). After this, research and reports of lead perovskite thin films and nano/micro-structures as optical gain medium have increased. In 2014, Deschler et al [206] demonstrated that it is possible to construct an optical vertical-cavity using a thin film of the tri-HP MAPbI\(_3-x\)Cl\(_x\) between a dielectric mirror, a spaced layer polymethylmethacrylate (PMMA) and a gold mirror. Results evidenced that at high fluences, amplified spontaneous emission (ASE) occurs from this thin film perovskite, and the great potential offered by perovskites for this particular optoelectronic application was shown. Despite the active research in this field, lead-free perovskites have been relatively unexplored. Xing et al [207] showed that the inorganic lead-free perovskite CsSnI\(_3\) has optical gain properties in the near-infrared. The authors found evidence that the orthorhombic phase shows a better crystallization with the addition of SnF\(_2\) at different concentrations (5%, 10%, 20% mol). They also found that the emission peak was centred at \( \approx 950 \) nm and that the treated samples did not show significant peak shifting (figure 7(a)). However, in the perovskite thin films doped with SnF\(_2\), they observed that when photoexcitation fluence increases to \( \approx 70 \mu J cm^{-2} \), a transition from spontaneous emission to ASE takes place (figure 7(a)). In the optimal concentration (20%), the lasing threshold or threshold fluence is 6 ± 1 \( \mu J cm^{-2} \). This value is very low and comparable with the lead perovskite lasing threshold. In a butterfly wing, a cheap and natural photonic crystal is found [207]. The laser line has a FWHM of \( \approx 1.9 \) nm, and a calculated Q-factor \( \geq 500 \). Higher trap concentrations were determined, and importantly, they demonstrated that the coherent light emission in these perovskites was originated from the free-electron–hole bimolecular recombination. Finally, the authors showed the easy tunability characteristics of CsSnBr\(_{3-x}\)I\(_x\) (\( x = 3, 2, 1, 0 \)) perovskites: the ASE peak was tuned from 700 nm to 950 nm and the ASE threshold determined (see table S6). The described work represents a good approach...
that proves the optical gain properties of lead-free Sn-based HP and presents the possibility to continue research on lead-free HP materials as laser sources.

6.3. Sensors
Several lead perovskite sensors have been reported for various gases, including NH₃, pyridine, HCl, NO₂, SO₂, humidity, O₃, and O₂ [209–211]. These devices work either by chemiresistivity or colorimetry and can be sensitive enough to detect gases in concentrations of parts per million (ppm) or even parts per billion (ppb). However, they may not be useful for long term use due to their instability. In 2019, Weng et al reported a thin film humidity sensor based on Cs₂AgBiBr₆ [212], which has fast response and recovery times attributed to the reversible physisorption of water molecules on the thin film’s surface. This device has a linear response in relative humidity ranging from 15% to 78%. Further, this double perovskite shows remarkable stability and reliability.

Hien et al studied the sensitivity of MASnI₃ thin films as sensors for a variety of gases [208] with and without external illumination. MASnI₃ films were most sensitive towards NO₂ (figure 7(c)), with a detection limit of 25 ppb. The device exhibited an increase in resistance in the presence of reduced gases (H₂S and NH₃). On the other side it decreased its resistance when exposed to oxidized gases (NO₂), which is similar to the behaviour of p-type semiconducting metal oxides, suggesting that the change in the device’s resistance results from chemical reactions of the gas and oxygen.

6.4. Others
Based on their excellent optoelectronic properties, lead-free perovskite halides have also shown great potential in other types of devices and possible applications. Some of those emerging areas that are beginning to be studied include transparent conductors [213], scintillators [214], spintronics [215, 216], piezoelectrics [217], ferroelectrics [218], down-conversion [219], second-harmonic generation (SHG) [220], phosphors [13]. Below we describe the efforts on these areas.

6.5. Scintillators
Scintillators are materials that absorb radiation (usually high frequencies) and emit light in another part of the spectrum, normally of lower wavelength. Scintillators are used extensively in x-ray imaging applications. Materials such as NaI/Tl, CdWO₄ and Bi₄Ge₃O₁₂ have been traditionally used as scintillators, but they are difficult to manufacture, are costly and have a low conversion efficiency. Lead perovskites such as CsPbBr₃ have been reported as efficient scintillators, with high conversion and good stability [221].

Recently a scintillator based on the 2D hybrid perovskite (Cs₆H₂[NH₃]₃SnBr₄) was reported [214], which is easily synthesized and has excellent quantum yield. Further, the authors suggest that this perovskite can be embedded in a composite matrix to fabricate a cost-effective, flexible composite film for x-ray imaging. Double perovskites with lanthanide ions, specifically Cs₂NaTbCl₆ and Cs₂NaEuCl₆, have also been studied for implementation as scintillators in radiation detection and medical imaging. This new type of lanthanide double perovskites is extremely promising due to their phospholuminescent properties [102].

6.6. Phosphors and down conversion
Down-conversion is a phenomenon in which a crystal absorbs a photon and re-emits two photons of lower energy. Materials with this property have potential applications as phosphors in LEDs, and down-converted displays [222]. LHP nanoparticles and QDs have been implemented in this type of device, but progress in lead-free HPs is scarce. CsSnBr₃ and CsSnI₃ NCs were reported to have down-conversion properties, emitting light at 683 and 938 nm, respectively [219], demonstrating the capabilities of lead-free HPs in this area. Further, NCs based on C₅H₁₅Br₃/BiOBr nanocomposites emit white light and show a remarkable improvement in PLQY [223], most likely due to the suppression of surface defects of the HP QDs embedded in the BiOBr matrix.

To obtain white light, LED’s usually employ coatings of phosphorescent materials that absorb light in the range of the LED and emit it in other parts of the spectrum. There are dozens of lead-free perovskites reported as potential phosphors in light-emitting applications, with a wide range of wavelengths and narrow and broadband emission. Sodium-doped Cs₂AgInCl₆ has been shown to emit white light [224], while Cs₂NaBiCl₆ doped with Mn²⁺ has an orange-red colour when excited with UV light [13] and Cs₂Bi₃Br₉ QDs have blue photoluminescence and excellent stability [225]. To describe all those reported is well outside the scope of this review, but Luo et al published a comprehensive review focusing specifically on lead-free HPs used as phosphors [226].
6.7. SHG

SHG, is a nonlinear phenomenon where non-centrosymmetric materials are required, and can be useful for several different application such as lasers and microscopy. Although most HPs crystallize in centrosymmetric space groups, mixed cations or chiral cation can break the materials’ centrosymmetry [227].

In the first work on SHG of lead-free perovskites, Kanatzidis et al prepared different Germanium AGel3 (A = Cs, CH3NH3, CH(NH2)2, and CH3C(NH2)2) perovskites and incorporated polar organic cations to orient within the perovskite, and thus increase the SHG response. The second-order nonlinear susceptibility, $\chi^{(2)}$, presented values of 125.3 $\pm$ 10.5, 161.0 $\pm$ 14.5, 143.0 $\pm$ 13.5, and 57.2 $\pm$ 5.5 pm V$^{-1}$, for CsGeI3, CH3NH3GeI3, CH(NH2)2GeI3, and CH3C(NH2)2GeI3, respectively. Theoretical calculations attribute the second-order nonlinear susceptibility to the high density of states in the hybridized Ge and I orbitals’ VB [228]. On the other hand, a series of [NH3(CH2)2]3Br(Cl-IBr)6 single crystals (x = 0, 0.135, 0.255, 0.385, 0.847, and 1), exhibiting a non-centrosymmetric space group R3c, were investigated. Structural distortion caused by mixed cations was related to SHG generation. Mixed halide bismuthate crystals generate a stronger SHG signal with increasing Br [229].

Recently, the incorporation of a chiral amine has been studied to synthesize an isomorphous family of compounds [(R)-1-(4F)PEA]4[E2X10] ((R)-1-(4F)PEA = (R)-1-(4-fluoro)phenylethylammonium; E = Sb, Bi; X = Cl, Br, I), having a monoclinic space group (P21). Although only the compounds with iodide did not show an SHG (probably due to inhomogeneity within these crystals), the other materials showed a polarization-dependent rototonic anisotropy of the compounds expected for P21 space group materials. Higher SH intensities were shown for thick [(R)-1-(4F)PEA]4[Sb2Cl10] (700 $\pm$ 50 µm) compared to a thin one, this due to the quadratic dependence of SH intensity on crystal length [220].

6.8. Spintronics and spin–orbitronics

Electrons in solids possess the charge, spin, and orbital degrees of freedom. Spintronics explores the control of charges by magnetic fields by adding the spin degree of freedom to conventional charge-based electronics or to completely replace charge with spin functionalities [230, 231]. Lead-free HPs are currently being investigated for spintronic applications [232]. This requires examining model systems at the fundamental level. For example, semiconducting Cs4CuSb2Cl12, a spin-1/2 Heisenberg antiferromagnetic chain, was found to present an emergent collective behaviour of its spins that realizes a gapless quantum spin liquid (the spins remain like a ‘liquid’ of disordered spins at very low temperatures) and whose elementary excitation is a type of fractional fermionic quasiparticle called a spinon [215]. As spintronics aims to magnetically manipulate charges, a natural step forward requires investigating the effect of incorporating magnetic elements. Recent advances in this direction involved alloying 3d transition metals (TMs) like Mn$^{2+}$ [233] and Fe$^{3+}$ [216] in semiconducting lead-free HPs. In the first case, it was clearly demonstrated how it is possible through alloying to modulate both the electronic and the magnetic properties of the Cs4Mn1–xCuSb2Cl12 (x = 0–1) family [233]. In the second example, the iron-alloyed double perovskite Cs2Ag(Bi:Fe)Br6, a strong temperature-dependent magnetic response at temperatures below 30 K was observed. This behaviour was tentatively attributed to a weak ferromagnetic or antiferromagnetic response from localized regions in the matrix. Through core level spectroscopies with the soft x-rays tuned at the Mn or Fe L2,3 edges, it was found for both cases that the TM cations were at the centre of a six-coordinated cluster, which is typical for perovskite structures. We think that other TMs (not only from the third period) can be incorporated in lead-free HPs and hence we think this offers a unique opportunity for expansion in the field. Clearly more studies are needed to investigate the magnetism at the atomic, spin and orbital levels in these and other families of magnetic lead-free HPs, and we think that electronic spectroscopies and spectro-microscopies using circularly polarized x-rays, and thus sensitive to spin-up and spin-down bands, could help to deepen our current understanding of this fascinating topic.

On the other hand, in lead-free HPs we often find heavy elements like Sn, Sb and Bi, where the spin and the orbital angular momentum are coupled. The spin–orbit coupling (SOC) is well documented to significantly split the CB in LHPs [234] as well as to induce other subtle effects [232] and the Rashba splitting in the VB [235], and given that the spin–orbit parameter for the valence shells of Sn, Sb and Bi is comparable to that of Pb [236], it would be reasonable to assume that similar effects will be observed in their corresponding perovskites. The Rashba splitting of the VB, as observed by angle resolved photoemission is indeed a spin splitting of the band and arises when orbitals with SOC are subject to symmetry-breaking electric fields. It causes a splitting of a doubly spin-degenerate band into two bands shifted with respect to each other in k space. By substituting Pb$^{2+}$ by Sn$^{2+}$, Sb$^{3+}$ or Bi$^{3+}$, it is in principle possible to modulate the Rashba splitting and thus it is possible in principle to engineer the material accordingly. Since Rashba coupling is sensitive to external electric fields, they can be used to manipulate spins. Other remarkably interesting proposals aiming to exploit the large SOC and the resulting Rashba splitting in these novel materials in what is called in the literature as spin–orbitronics [232]. As we can sense, we are at the earliest
stages of a blossoming field where more fundamental research is needed to elucidate the role of spin splitting and possible spin polarization in existing and future applications.

6.9. Piezoelectricity
Piezoelectricity is the ability of a material to exhibit spontaneous polarization when subjected to a mechanical stress. The material will also show the inverse effect by undergoing mechanical deformation after the application of an electric field. The origin of the piezoelectric effect is related to an asymmetry in the unit cell and the resultant generation of electric dipoles is due to the mechanical distortion. Thus, in an unit cell, we may visualize each pair of positive and negative ions as an electric dipole, and the spontaneous polarization (dipole moment per unit volume) as due to an assembly of these dipoles, which point in the same direction. If the value of the spontaneous polarization (Ps) depends on the temperature, this is called the pyroelectric effect. Pyroelectric crystals show a Ps in a certain temperature range. If the magnitude and direction of Ps can be reversed by an external electric field, then such crystals are known as ferroelectrics.
Several inorganic piezoelectric materials (e.g. BaTiO$_3$, NaNbO$_3$, ZnSnO$_3$ among others) are routinely used across various industries including medical, automotive, electronics, sounds, etcetera. Among these materials, PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) ceramics dominate the market due to its superior piezoelectric response. However, the toxicity inherent to lead content is a key factor which threatens its hegemony. This recognition detonated a quest for creating novel materials with improved eco-friendliness and excellent piezoelectricity [237]. These efforts had permeated chronologically into the realms of lead and lead-free HPs. For example, first by combining piezoelectric formamidinium LHP nanoparticles (FAPbBr$_3$ NPs) with piezoelectric polymer poly(vinylidene fluoride) (PVDF) a high performance piezoelectric nanogenerator was constructed [238], and recently, by incorporating formamidinium tin iodide, FASnI$_3$, also in a PVDF matrix similarly resulted in high-performance large-area flexible piezoelectric nanogenerators [217]. Scientifically, given the vast number of possible combinations which can be generated by using the already known organic blocks found in these family of perovskites, this is a very promising area of opportunity for lead-free HPs. Another important aspect that reinforces the scientific drive comes after considering that the market of piezoelectric actuators is estimated to be nearly US$7 billion and presents a growth rate of 13% per annum [237]. So perhaps in the near future, lead-free HPs could offer few interesting candidates to dethrone PZT in targeted/specific piezoelectric applications.

6.10. Ferroelectricity
When it comes to ferroelectrics, a few 2D [218] and one 3D [239] lead-free HP system have been prepared, although relatively few, these compounds clearly exemplify the promising potential of lead-free HPs for applications exploiting pyro- and ferroelectricity. Obtaining 3D ABX$_3$ organic–inorganic HPs ferroelectric semiconductors is challenging. The 3D OIHP ferroelectric semiconductors are highly desirable for the development of high-performance optoelectronic devices because high structural dimensionality is in favour of excellent optoelectronic properties and device performances. To the best of our knowledge, the very first and up to now only lead-free 3D ABX$_3$ OIHP ferroelectric semiconductor is MPSnBr$_3$ where MP is methylphosphonium ([CH$_3$PH$_3$]$^{+}$). This molecular semiconducting ferroelectric shows clear above-room-temperature ferroelectricity and a direct bandgap of 2.62 eV, making it a good prospect for possible optoelectronic applications. This pioneer work also opened the possibility of preparing other 3D lead-free OIHP ferroelectrics like for instance MPSnI$_3$ [239]. As for 2D lead-free HP, there have been some reports of halobismuthates and haloantimonates that present ferroelectric properties. They have the general formula R$_m$M$_2$X$_{3b+1}$I$_x$ (where R denotes a monopositive cation, M stands for Sb$^{5+}$ or Bi$^{5+}$ and X = Cl, Br, I). They present a variety of the anionic structures, some of which are 2D [218]. Similarly, layered double perovskites have shown room-temperature ferroelectricity. The first such report was that of (3-CPA)$_2$AgBiBr$_7$ (3-CPA = 3-chloropropylammonium), in this case, the asymmetric organic ligand sways the formation of a polar structure [240]. Also, (i-PA)$_2$CsAgBiBr$_7$ (i-PA = isopentylammonium) and (PA)$_4$AgBiBr$_7$ (PA = propylammonium) has shown spontaneous polarization due to the collective effects of an order–disorder transition of the organic cations and the Cs displacement [241, 242]. Both of these materials have decent performance metrics, albeit further improvement must be made to come closer to the state-of-the-art materials. Such improvements could come from the incorporation of chiral ligands that further enhance polarization.

7. Conclusions and outlook
As illustrated in this review, the search for materials to replace lead perovskites in solar cells and LEDs has generated a plethora of new materials and properties. Lead-free perovskites offer excellent platform to replace lead, not only because of the possibility of reducing its toxicity, but because they offer an immense
number of new materials and consequently, new or improved properties. Thus, beyond merely replacing lead, these new materials can dramatically expand the possible applications of HPs. Herein, we have highlighted some of the most notable and developed technologies for lead-free HPs; however, the potential is tremendous in several directions. Generally speaking, we envision three lines of research in the area.

First, the devices and applications discussed herein are, at best, in their infancy. As such, the community will surely devote significant efforts to improve them in the short and medium-term. The improvements shall come from different fronts, such as new materials’ development, device design, and interphase engineering. Hopefully, these improvements will allow the current technologies to catch-up with their lead-analogs and commercial devices or state-of-the-art materials, at least for some applications.

Second, there are still many applications that lead-based perovskites can perform, but lead-free perovskites have not. Thus, a natural step will be to find suitable lead-free materials that can potentially replace lead-based perovskites. Few such examples are the detection of gamma photons [243, 244], alpha particle detection [245, 246], photon up-conversion [247], intelligent photoelectric devices [248], down-conversion displays [222], third-harmonic generation [227, 249], among others [250, 251].

Third, beyond the applications highlighted here, the ever-expanding chemical space of lead-free HPs and properties will surely stimulate their use in applications well-beyond those described in this review. Further, the lessons learned while developing new materials, synthesis and characterization techniques, and devices for lead-free perovskites, will surely be useful for many other materials, particularly to other metal-halides and lower-dimensional (0D and 1D) perovskite-like materials. In conclusion, it will be fascinating to witness in what new directions the field will evolve and how these technologies will mature. Besides, it will be fantastic to see when and how these materials reach some commercial stage, as they surely will... sooner or later.

Data availability statement

No new data were created or analysed in this study.

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