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ABSTRACT

The need for moving electricity generation to a sustainable model requires the development of low cost ubiquitous photovoltaics (PVs) to harvest the planet's primary energy source, the Sun. Building upon the successes of Si-based and CdTe-based PV technologies, PVs with lower-embodied energy and requiring lower carbon dioxide equivalent to produce will be required to meet long-term sustainability goals. In particular, thin-film technologies, such as high-efficiency metal halide perovskite (MHP) PV modules, provide avenues to reduced embodied energy, lower energy payback times, and enabling energy-dense tandems [H. M. Wikoff *et al.*, Joule **6**(7), 1710–1725 (2022) and V. Fthenakis, Renewable Sustainable Energy Rev. **13**(9), 2746–2750 (2009)]. The ability to improve efficiency and lower energy payback time of next generation thin-film PV modules is a critical foundation for green H_2 and electrification more broadly. In this regard, Pb-based MHP-PVs have separated themselves as a result of the high-efficiencies that can be realized across a range of electronic gaps. Questions regarding Pb-based MHP-PVs that are often asked, as the challenges of efficiency and reliability are met, revolve around the "problem" of the Pb content. Specifically, "does Pb toxicity preclude MHP-PV modules from being deployed at the TW scale?" To provide this sense of scale, in 2021, the United States burned 10.5 quads of coal, with 90% of that used for electricity generation. Given the energy content of coal of 29 MJ/kg and a residual lead content in that coal of 30 mg/kg, electricity generation from coal resulted in more lead emitted into the atmosphere than what would be required to produce over 2 TW of MHP-PV name plate capacity (assuming a 20% module efficiency and an ~700 nm active layer). This amounts to more PV power than has been deployed across all PV technologies and geographies to date. This only includes US coal consumption; the rest of the world would be much larger. This example illustrates the scale of the material usage relative to the energy production. Imagine a power-generation technology that offsets these Pb emissions from coal and essentially sequesters this Pb content between two sheets of impermeable glass. Why should we let Pb's history of misuse prevent it from being included in next generation PV modules that can enable a sustainable energy future?

FRAMEWORK

In considering the question of Pb in metal halide perovskite (MHP)-based photovoltaics (PVs), we can lean on the existing literature evaluating lifecycle and environmental impact of other technologies, including incumbent PVs. Indeed, despite a number of analyses and very well done review articles examining this and topics associated with sustainability at the TW scale,[3–5] the perceptions around the suitability of Pb for use in PV technologies at the TW scale persist. In part, this is due to louder but less informed voices. The hope here is to highlight these previous analyses and show that Pb-based MHP-PVs can play a significant role in meeting our climate goals. To do this, we first consider why MHP-PVs based on Pb are dominant. Second, we consider the impact of Pb across the three phases of a technology's life cycle: (1) production, (2) deployment, and (3) end of life. At each of these steps, we can ask whether the use of Pb undercuts our goals for MHP-PV technologies to enable clean sustainable energy. Third, we consider the negative externalities that undercut human health, or damage the environment with toxic waste, both for the technology alone and when considered relative to the alternatives.

Pb-HALIDE SEMICONDUCTORS

Certainly, there are compelling reasons to examine a range of hybrid metal halide perovskite semiconductors beyond the prototypical Pb systems for all types of optoelectronics, catalysis, and other applications. However, it is the role of Pb in defining the electron structure that makes these materials compelling for PVs in many regards. Specifically, the high spin–orbit coupling results in a band structure well-suited to PV applications. Remarkably, the band structure of Pb-based MHP semiconductors is not significantly impacted by the readily formed defects and this so called "defect tolerance" is a key feature of modern, high-performance MHP-based PV absorbers. This has been shown both by performing an array of computational studies and by performing experimental demonstrations.[6–9] This has made well controlled electronic doping across a broad range of carrier densities like what can be achieved in Si or III–V semiconductors a challenge, but this is arguably not a critical feature for MHP-PVs.[10] The pure Sn-based compounds have also indicated some promise in PV applications.[11] Sn-based MHP absorbers particularly shine as alloys with Pb to engineer the bandgap of resulting absorbers to enable all-perovskite tandems.[12–16] Unfortunately, in contrast to Pb systems, the Sn-MHPs do have readily formed defects. The change in the band structure as Sn is substituted for Pb in the MHP lattice is shown in Fig. 1 and indicates the change in the energy of vacancy defects as a function of composition. Sn vacancies, in particular, efficiently generate free carriers, and the subsequent impact of the free carrier density results in a significant recombination detrimental to PV devices. This free carrier generation is a challenge even when Sn is alloyed with Pb. High quality absorbers, even a defect tolerant one, will still have low defect levels. The challenge of engineering reliable and ultimately bankable devices, while not simple for Pb-based systems, becomes increasingly difficult in PbSn alloys and pure Sn materials. Thus, the properties of Pb-enabled materials have facilitated the high efficiencies and a myriad of process variations capable of producing efficient MHP-PVs. The importance of high efficiency, while only one axis of performance, is critical to addressing the balance of system cost. The amenability of Pb-based MHP-PVs to high volume manufacturing, both as single-junction modules or via their integration into high-efficiency tandems with other established PV absorbers, is a clear advantage. While there may be options to enable all the marvelous physical properties that are observed in the Pb system with other metals and structural motifs, such materials have yet to be identified.

MATERIALS AVAILABILITY AND MANUFACTURING

While Pb is clearly toxic, the supposition for the questions around Pb is that its use in MHP-PVs at the multi-TW scale would present a significant hazard for the environment and risk to human health. Perhaps more importantly, considerations around material extraction to enable electrification, while certainly beneficial in the long run, do create near-term impacts if securing the materials for these technologies requires new or expanded mining resources. Examining these concerns, we find several interesting facts. First, Pb production worldwide is considerable, in excess of 10×10^6 metric tons per year. For context in November 2022, the US produced 18 000 metric tons of lead according to the USGS.[17] If this Pb production was committed to manufacturing MHP-PV modules (operating at 20% power conversion efficiency), this would represent between 2.5 and 5 TW of name plate production capacity, as a function of active layer thickness, here, between 700 and 1400 nm.[6,18] This demonstrates several key points. First, it is a clear indication that the Pb supply chain does not represent a limitation for MHP-PV production, i.e., an expansion of the supply chain for Pb would not be required. While Sn is similar, Bi, Ag, Ge, and other metals

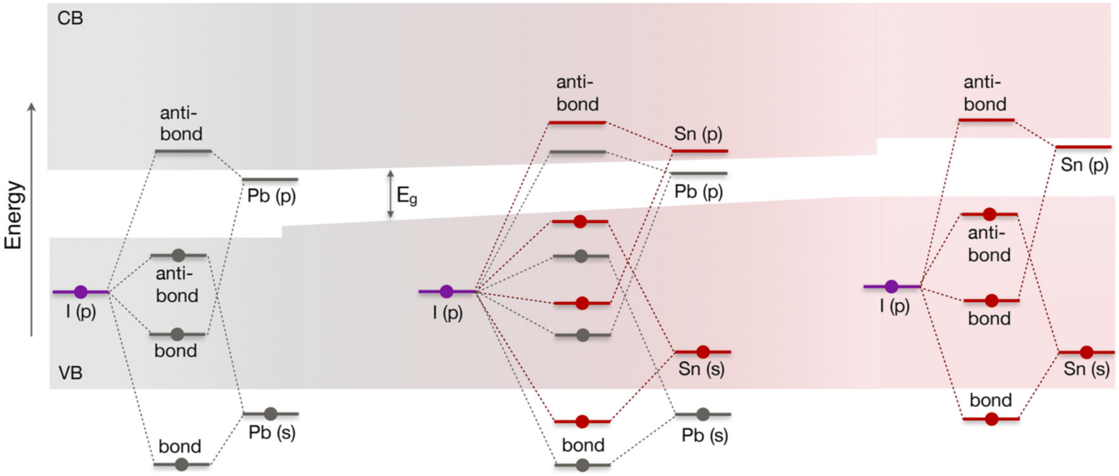

FIG. 1. Defect levels and bandgaps across Sn–Pb compositions. Reproduced with permission from Goyal *et al.*, Chem. Mater. **30**(11), 3920–3928 (2018). Copyright 2018 American Chemical Society.

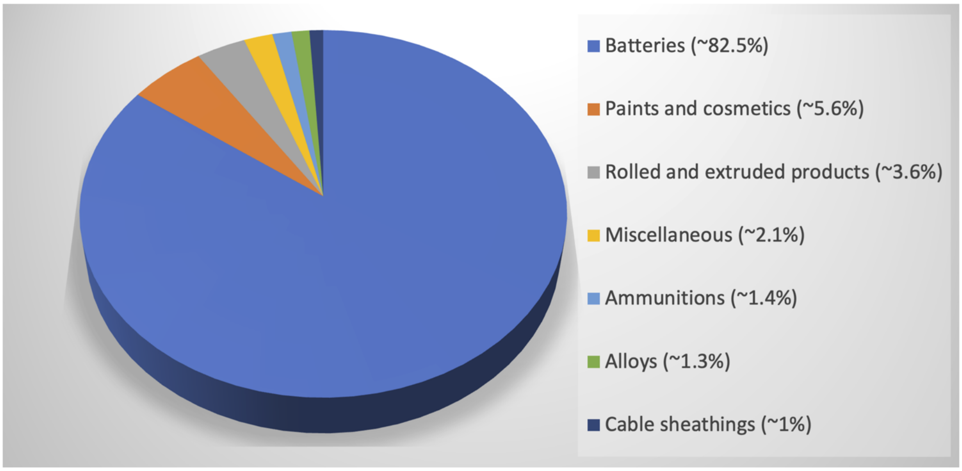

FIG. 2. Breakdown of worldwide Pb use. Adapted from A. Mallick and I. Visoly-Fisher, Mater. Adv. **2**(19), 6125–6135 (2021). Copyright 2021 Author(s), licensed under a Creative Commons Attribution 3.0 Unported License.

would likely require additional mining resources.[19,20] Second and perhaps more striking is the fact that the amount of Pb in our built environment would not be significantly altered or impacted by the addition of MHP-PVs at the multi-TW scale. These data also suggest the extent that Pb should be minimized, and there are other sources along with associated applications other than MHP-PVs that should be prioritized for Pb remediation/replacement. It is also noteworthy that the removal of uncontrolled Pb in the built environment, including improvements to the global recycling supply chain for Pb–acid batteries, could be a raw material resource for significant levels of energy production. In the review by Mallick and Visoly-Fisher, the data in Fig. 2 that indicate that Pb is used in paint and cosmetics might be a good starting point for prioritizing Pb removal.[3]

Of course, the extraction of resources is only one of the production considerations. The manufacture of those materials into efficient MHP-PVs also requires additional energy and material inputs, including process heat and solvents. The extent to which these processes can also undercut the goal for PV technologies or technologies targeting climate change more generally is a serious consideration. However, careful analysis reveals that MHP-based PVs compare favorably to other PV technologies. The human health impacts due to Pb-based MHP-PVs are, indeed, similar to CdTe and other thin-film PV production, which simultaneously have been shown to be better suited to the task of impacting CO_2 targets.[1,2,21] The potential for MHP-PVs to meet or exceed these impacts as a result of improved efficiency over CdTe, copper indium gallium selenide (CIGS), or other thin films, while predicated on demonstrating the durability of MHP-PVs produced by high volume manufacturing approaches, is the source of excitement for this class of materials. Here again, there are opportunities for improvement to the environmental impacts, but most are not linked to Pb rather than some of the other process materials such as solvents or the bottom cell production.[22,23]

DEPLOYMENT AND USE

The most common but likely least consequential concerns for Pb-based MHP modules is the impact when the panels are operational in the field. CdTe, as the only thin film PV technology deployed at the multi-GW scale, is again instructive and where the technology faced similar perceived risks. Examples of risks when MHP-PVs are fielded are associated with a myriad of conditions the modules will face. Breakage (e.g., hail) and fire hazards (e.g., wildfires and building fires) are two key examples. In the case of module breakage where the package is compromised, the extent that the Pb-based MHP active layer can be exposed to the environment is an important consideration. This is particularly true in the context of applications such as agrivoltaics (where PVs are collocated with crop production).

Simply put, lead halide salts that comprise Pb-based MHP-PVs are not readily water soluble and, thus, cannot be washed away by rain falling on a cracked panel (cracks also represent a very small cross section for leaching). Among the pure iodine-based MHP photoabsorbers, the most commonly considered for PV commercialization,[24] PbI_2 has a solubility constant of $K_{sp} = 9.8 \times 10^{-9}$.[25] Such a level is, at best, sparingly soluble and falls in the ppb range. PbI_2 is also the conjugate base of a strong acid (HI), and thus, increasing acidity (decreasing pH) will have little effect on water solubility, with respect to acid rain exposure. Acid rain is commonly comprised of SO_x, and the ion-exchanged salts have a similar solubility [e.g., K_{sp} $(PbSO_4) = 2.8 \times 10^{-8}$].

Furthermore, Pb^{2+} undergoes rapid hydrolysis when exposed to water to $Pb(OH)_2$ ($K_{sp} = 1.43 \times 10^{-20}$), rendering the Pb content water insoluble.[26] $Pb(OH)_2$ and the subsequent dehydrated PbO are soluble in acids, but, as presented above, acid rain would simply revert the oxide species back to sulfate in pH equilibrium, thus never forming a water soluble species.

While these solubility considerations point to the relatively low risk to MHP-PV goals, there are also relatively simple technologies to bind Pb in panels that break. Via chelating complexes, these technologies have been demonstrated with little or no impact to PV performance.[18,27–30] These simple sequestration approaches indicate that there are excellent opportunities to further de-risk issues associated with Pb leakage, which, as we have noted, are modest relative to the benefits in the more global context. Local considerations are important; thus, strategies to mitigate any local impact, however minor, while maintaining low cost and performance are key. In the case of fire, there are additional concerns of putting the Pb into the atmosphere.[31] These considerations mirror the issues around leaded-gasoline, which is still used in aviation fuel (e.g., 100LL). As such, initial studies indicate that, for glass–glass packaged PVs, the Pb emissions from burning panels, while undesirable, are again minimal. This when combined with the risk of fire from PV power plants indicates that this consideration is not a particularly strong or rational argument for the need for Pb-free MHP-PVs. This perspective is informed by the considered analysis of multiple researchers evaluating the materials.[32]

BEYOND END OF LIFE FOR MHP MODULES

The last portion of any product's lifecycle for most systems is decommissioning; disposal; and, as we look forward, recycling, refurbishing, and/or remanufacturing. Related to this, generally, the impact of externalities, as discussed, become more acute after the PV systems no longer provide an adequate energy return on investment (EROI). The issues around disposal and negative externalities generally impact less affluent populations disproportionately. In the context of energy justice considerations, the performance of Pb-based MHP-PVs need not only span efficiency and reliability metrics associated with EROI but also integrate issues of sustainability in ways that really supersede less useful metrics, such as the levelized cost of electricity (LCOE). The role of toxicity to enable performance related to module robustness has been demonstrated in the case of CdTe PVs, and a similar approach should be applied to Pb-based MHP-PVs. Although there are some toxicity concerns, most of the issues more directly relate to perception issues deriving from lead's history of misuse and misapplication (e.g., cosmetics and paints). Furthermore, the need to address toxicity can drive sustainability and circularity.[33] For CdTe, the Cd toxicity and related considerations have driven a high level of recycling. Given the primary use of Pb is in lead–acid batteries, this supply chain includes near-unity Pb recycling/remanufacture in the US and Europe. Thus, establishing a closed loop for the TW scale MHP-PVs can leverage this infrastructure to enhance the degree to which PV technologies can be deployed in an equitable fashion and to ensure that their externalities, while minor compared to other energy generators, do not generate additional injustices. Paradoxically, the level of Pb toxicity creates *the* critical driver that can help ensure that the photovoltaic technologies based on them really do meet the targets for technical performance and the goals that we aspire to with respect to equity and inclusion.

ENABLING ENERGY EQUITY AND MHP's PROPOSED ROLE THEREIN

This brings us back to the consideration of what our goals are for PV technologies, in general, and MHP-PVs, in particular. The immediate considerations are driven by EROI and carbon dioxide equivalent (CO_2e) for PVs and the need to deploy significant CO_2-free or negative generation technologies to support, for example, H_2 at-scale and similar energy storage technologies. The key features of the materials that Pb enables at a basic level are also consistent with forward-looking low capital cost (CapEx) additive manufacturing approaches. The potential reduction in CapEx provides avenues for smaller, less centralized production of MHP-PV technologies, i.e., the democratization of energy.[34] This, in turn, can provide opportunities for communities where the technologies are deployed to benefit from jobs across the various parts of the supply chain for the technology—from manufacture, installation, and remanufacture. Lower energy process and production techniques that simultaneously reduce waste and improve logistics offer pathways that can further reduce the CO_2e associated with device manufacturing that fundamentally underpins the economics and cost. The requirements imposed by the toxicity can also provide a forcing function to ensure that MHP-PV technologies are developed from the start to be circular and sustainable with models that mirror those for Pb–acid batteries. Enforcing circularity minimizes uncosted externalities of technologies that are all too commonly distributed across society unjustly and can exacerbate inequality. Similarly, the challenge for PV researchers is to efficiently and sustainably displace CO_2-producing energy technologies along with their externalities, which, as we have shown, are considerable. Thus, while the breadth of metals can and should be examined for use in metal-halide perovskite materials, it is irresponsible to argue for Pb-free MHP materials at the expense of enabling Pb-based MHP-PVs to be deployed successfully at scale. Indeed, if past is prolog, the toxicity of Pb in MHP-modules, coupled to dropping prices, can provide the template for what it means to develop and field a high-performance, sustainable, and equitable energy generation technology at the TW scale.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Joseph J. Berry: Conceptualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Michael D. Irwin**: Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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