Fire Safety of Lead Halide Perovskite Photovoltaics

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On the Fire Safety of Lead Halide Perovskite Photovoltaics

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In the past 5 years, metal halide perovskites have become the prodigy of photovoltaic technology.[1-3] A tremendous surge of research in the topic has led to a current perovskite solar cell lab scale power conversion efficiency of up to 23.7%, which is on par with more established (and commercialized) competitors such as multi-crystalline Si, CIGS and CdTe, and no too far off from single crystalline Si (=26.6%).[4] Remarkable improvements have been made in terms of environmental and thermal stability as well.[5-9] Arguably the remaining Achilles heel of the technology is that the desirable properties of these perovskites for application in photovoltaics so far have only been achieved with lead (Pb), (and to a lesser extent tin (Sn)) as the metallic cation. Consequently, the associated toxicological hazard in case of unintentional liberation of heavy metal containing chemicals into the environment raises concerns in view of the large-scale applicability of perovskite photovoltaics, even regardless of their exemption from RoHS regulations.[10-13] Evidently, accidental leaching of Pb components into the environment can be prevented by the use of appropriate encapsulation. With this in mind, the most likely cause of Pb liberation into the environment then still lies in the large number of occurrences of fires in residential and commercial buildings worldwide. The fact that almost 4 out of every 10 recorded fires worldwide are structure fires, accounting for over 500 000 annually in the US alone, strongly underpins this notion.[14] In case of significant fire, roof-mounted perovskite PV modules are inevitably exposed to high temperatures. To appraise the involved risk, we present in this Viewpoint the results of fire simulations on Si-perovskite tandem mini-modules, fabricated according to industry standards, together with a rough numerical estimation of the heavy metal concentrations downwind of a typical structure fire.

Even considering the tremendous feat of progress in perovskite PV in only a few years' time, solely perovskite-based modules are not yet at a level that would render them commercially competitive as a standalone technology. As Si/perovskite tandem solar cells of up to 28% have already been reported (which trump the best single c-Si cell), the more likely market introduction of perovskite PV is as an add-on absorber to existing technologies such as Si, CdTe or CIGS.[4, 15-18] Hence, we selected the Si/perovskite tandem module as currently the most promising candidate to be subjected to a fire safety assessment. Figure 1a depicts one of the modules, which are built according to industry standards, but small enough for convenient testing in a laboratory environment. These mini-modules consist of three 1" x 1" cells connected in series and sandwiched between polymer laminate and glass sheets on each side. The used fire simulation setup is shown in Figure 1b, which constitutes a tube furnace in which

the module is placed. A typical experiment entails annealing a module at 760°C under constant supply of fresh air. This temperature is most representative of what is reported for structure fires,[19-25] and follows a standard protocol for Fire Tests of Roof Deck Constructions.[26-27] After cooling down, a chemical analysis is performed on the post mortem module itself and a number of samples mounted downstream in the colder zone of the furnace intended to catch airborne species released from the module. More details can be found in the Methods section.

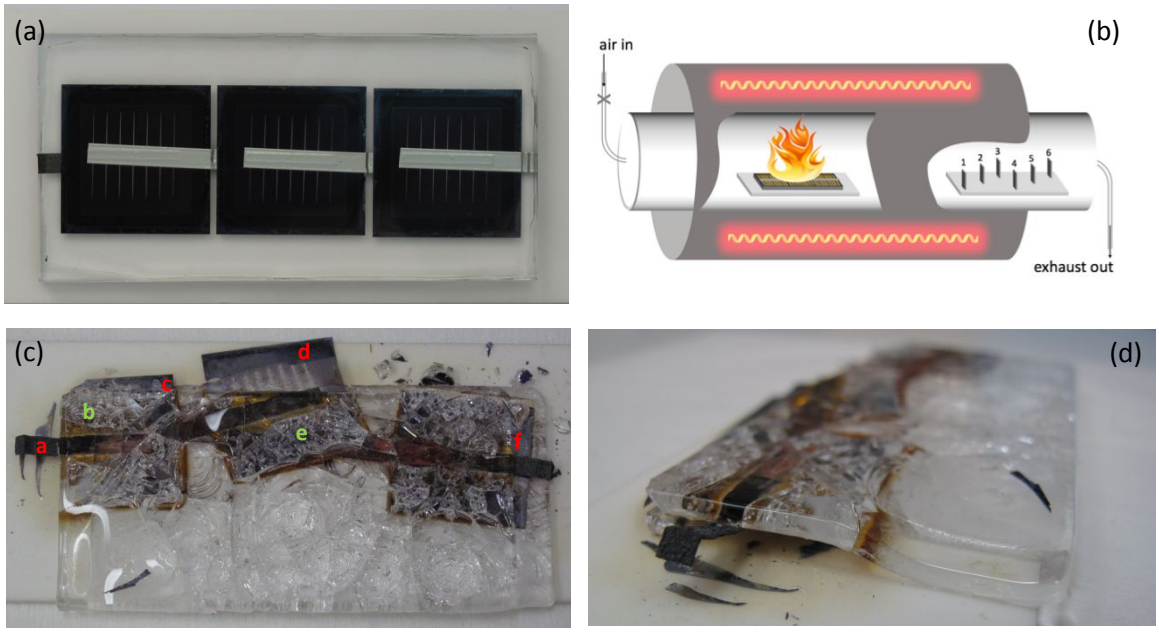

Figure 1. (a) Glass-glass encapsulated Si/perovskite mini-module. (b) Schematic of the experimental setup for the fire treatment. The mini-module is placed in the hot zone of the tube furnace, complemented by vertically oriented samples mounted downstream to capture the fumes. (c) Mini-module from panel (a) after the fire treatment. The colored letters indicate arbitrarily chosen positions where Pb was found (red) or where no Pb was found (green). (d) Side-view of (c).

Figure 1c and d display a module that was subjected to the procedure described above. Obviously, upon exposure to fire-like temperatures, the cover glass has been softening, allowing the individual solar cells to drift away from their original position, thus leaving some areas uncovered (and, therefore, exposed to the environment). To investigate whether or not Pb species still remain on the module, XPS Pb4f core level spectra were acquired at positions as indicated by the letters in Figure 1c (red = Pb; green = no Pb; full spectra can be found in Figure S1 in Supplementary Information). While the glass-covered regions (b and e) are void of any significant Pb traces, the exposed cell areas (c, d, and f) still contain discernable amounts of Pb. Pb is also found on the electrode ribbon (position a), which will be discussed later on.

As initial XPS measurements performed on the perovskite residue were affected by charging effects, the fire simulation experiment was repeated using separate unencapsulated perovskite films (on an inert gold substrate to avoid charging) as reference, allowing for an accurate

assessment of oxidation states. First, to roughly estimate the amount of Pb species left on an exposed sample, a depth profile was made on pristine as well as burnt Au/perovskite reference samples. From a 450 nm fully exposed absorber film, we found that even after the 760°C treatment, the sample still retained ~10 nm of Pb-containing material (see Figure S2).

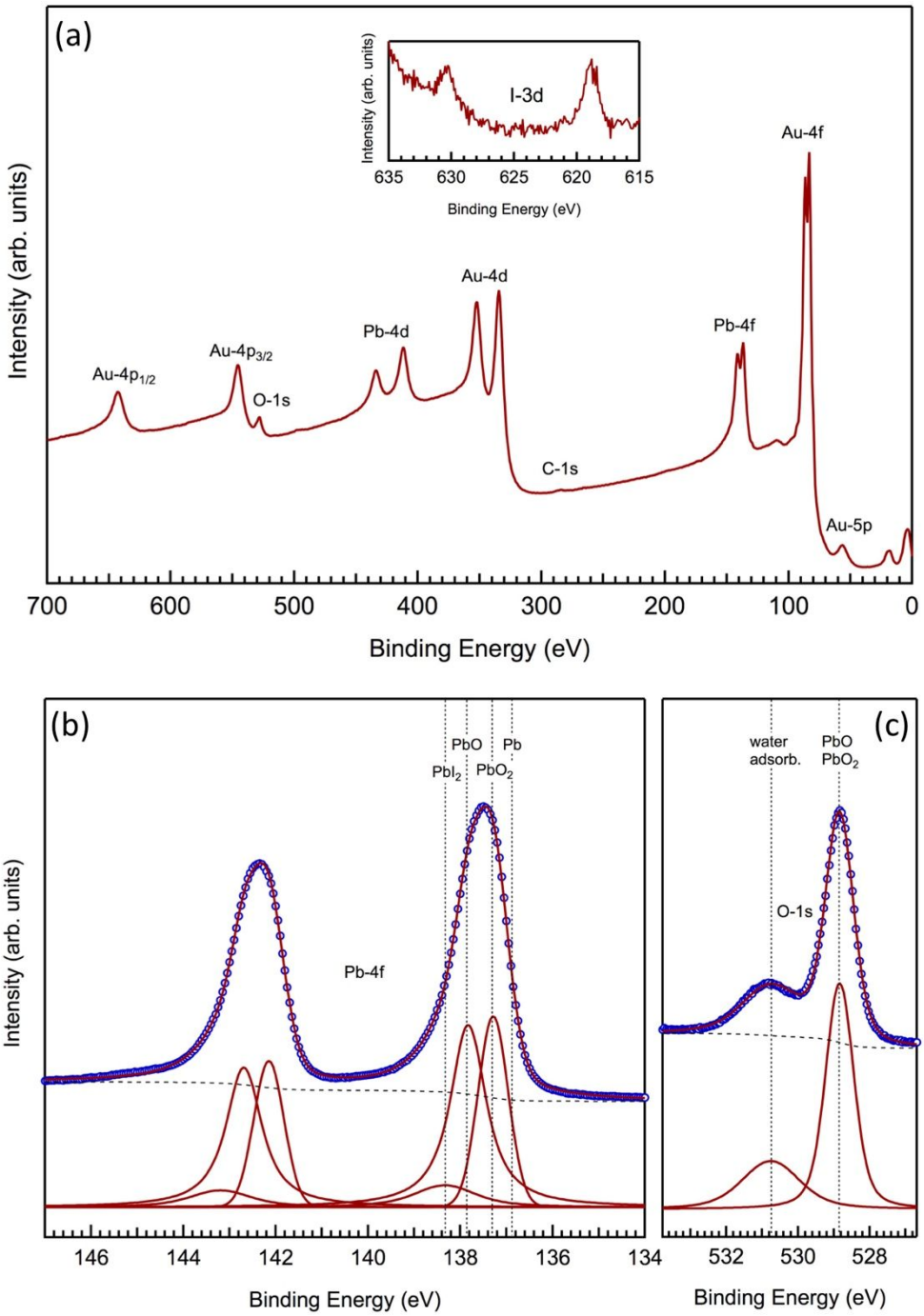

Figure 2. (a) XPS survey scan of a burnt Au/Perovskite reference sample. Corresponding high-resolution Pb4f (b) and O1s (c) core level spectra (open symbols) and their decomposition into different chemical species (solid lines) using a general least-squares fitting procedure.[28]

The survey spectrum for this residue is provided in Figure 2a. Besides Au-related peaks originating from the support, several other salient features are observed. Strong intensities from

lead-derived core levels are detected (Pb4f, Pb4d), together with weaker contributions arising from oxygen (O1s) , carbon (C1s) and iodine (I3d, see inset), the latter pointing to the presence of PbI_2. Given that Au does not oxidize at elevated temperatures, the detection of O1s implies that (an) oxide(s) of Pb has/have formed during the fire simulation. This is confirmed by a high-resolution recording of the Pb4f region, as shown in Figure 2b. The observed composite doublet can only be fitted with three separate doublets with the 7/2 components at 137.3 eV, 137.8 eV and 138.3 eV, of which the first two can be assigned to PbO_2 and PbO (respectively) and the third, smaller component to PbI_2. The formation of lead oxide is also confirmed by a corresponding contribution to the O1s spectrum (Figure 2c). Supported by the fact that temperatures well exceeding typical operating temperatures degrade lead halide perovskites into PbI_2 and more volatile organic components,[29-31] we also infer from our observations here that in fire conditions the organic moiety leaves the perovskite first, thereby forming PbI_2. Subsequently, the PbI_2 is oxidized into PbO and PbO_2. PbI_2 itself evaporates much more readily than the oxides, so we conclude that a part of the freshly formed PbI_2 evaporates directly (and oxidizes subsequently), while the remainder is oxidized on the perovskite residue. The evaporation of freshly formed PbI_2 and its oxidation are in fact expected to be competing processes, considering the heat of formation (170 kJ/mole) and vaporization (104 kJ/mole) of PbI_2, compared to the heat of formation of PbO (219 kJ/mole) and PbO_2 (274 kJ/mole).[32-33]

In an effort to gauge whether Pb species have escaped the burning mini-module, we now focus on the analysis of airborne deposits that may be present downstream of the mini-module. Here, six Si substrates have been positioned at regular distances outside of the heated zone thus reflecting a decreasing temperature profile with increasing distance to the furnace (see Figure 1b). Figure 3 shows images of the sample configuration before (a) and after (b) the fire simulation. The latter contains soot resulting from the burnt organic components of the module, with the exception of sample number 1 residing close to the hot zone of the furnace where bigger aggregates could not be formed yet. This is congruent with the corresponding XPS survey scans (see Figure S3), which show an increased carbon signal and a reduced Si and O signal for the soot-covered samples. Sodium and indium signals were also found, from the glass and transparent electrode of the module, respectively. The Pb4f region for each of the samples can be found in Figure 3c. Clearly, sample number 1 contains a discernable Pb signal, which

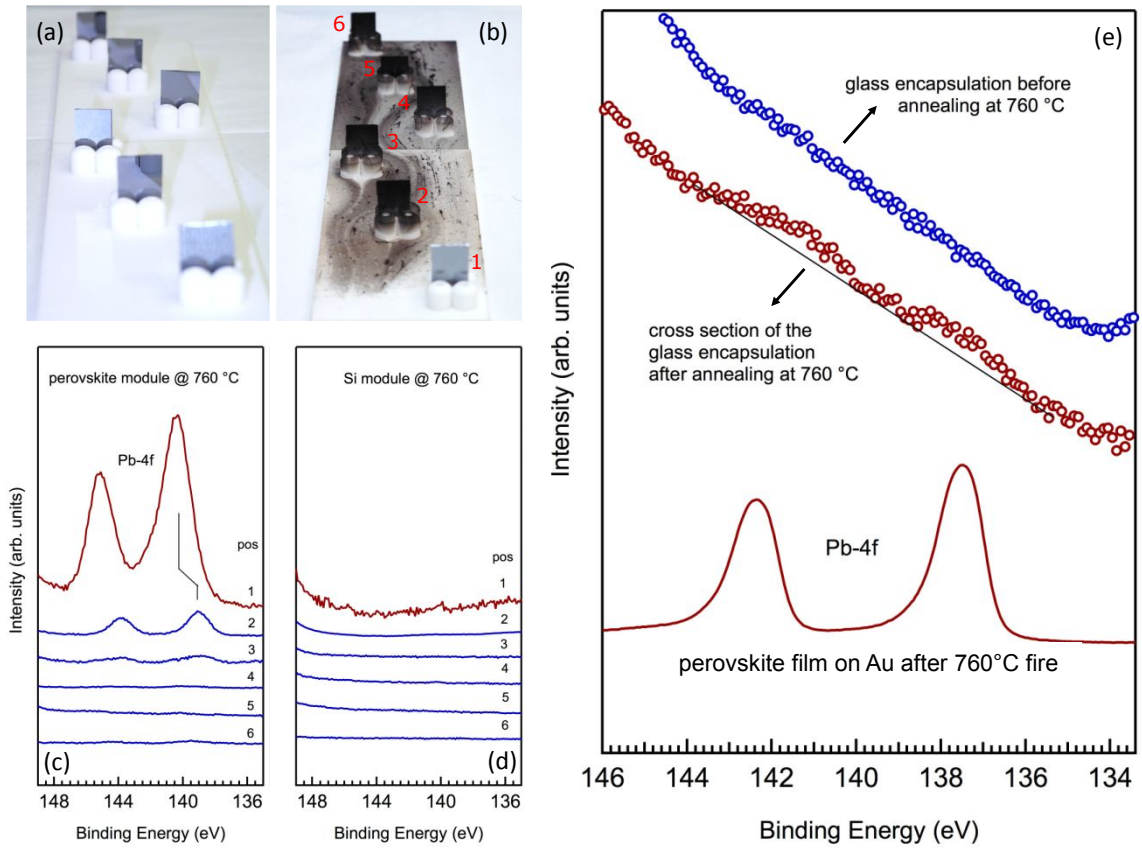

Figure 3. Downstream collection of airborne deposits on Si substrates before (a) and after (b) fire treatment of a Si/perovskite tandem minimodule. Pb4f core level spectra of samples downstream of an encapsulated Si/perovskite minimodule (c) and an encapsulated Si minimodule (d), all treated at 760°C. (e) presents the Pb4f core level region before and after the 760°C fire treatment for a cross section of the glass encapsulation of a Si/perovskite mini-module (top) using the Pb4f results measured on a burnt perovskite film (Figure 2b) as a reference (bottom).

vanishes with increasing distance from the furnace thereby pointing to the depletion of a reservoir of Pb-related species in the gas phase, at colder surfaces downstream outside the furnace. The peak shift to higher binding energy observed for the Pb4f doublet at sample position 1 (Figure 3c) is a consequence of charging during photoemission, due to the (poorly conducting) SiO_2 that has formed on the hottest sample (see Figure S4). To critically test whether the Pb detected downstream originates from the perovskite material but not from the metallic electrode ribbons used to interconnect individual cells in the mini-module, the fire experiment was repeated another time with a mini-module based on pure Si solar cells (no perovskite), using the same ribbons as interconnects. The results are presented in Figure 3d where the absence of Pb4f intensity unambiguously proves that the Pb found downstream for the Si/perovkite tandem module originates exclusively from the perovskite.

Having analyzed the burnt perovskite residue and airborne species transported downstream, it is clear that part of the module's Pb content has been contained in the module. By using the results obtained from the non-encapsulated perovskite reference film, it can be speculated that nearly all the Pb in the *exposed* perovskite areas of the destroyed module must have evaporated in the form of PbI_2, with a small remainder being oxidized in place. This leaves the question as to what happened to the perovskite in areas that have remained covered by the encapsulation glass during the whole fire. Unfortunately, in the *post mortem* condition of the mini-module, those areas are rather difficult to access. Instead, we investigated a cross-section of the glass encapsulation on top of the perovskite (see Figure 3e). Remarkably, we encounter around 13 ppm of Pb in this glass, which is very close to an estimate of 16 ppm calculated assuming that all Pb from the original perovskite layer would dissolve into the glass cover mounted above it. This is clear evidence that the glass used to encapsulate the module is a built-in tool for capturing Pb species that are at risk of being liberated into the environment.

Consolidation for this observation is found in the existence of lead glass, which was discovered several centuries ago and is still used today for all kinds of tableware and decorative items.[34] Typically, up to 40% of the crystal glass can be made up of PbO, aptly illustrating the high affinity between PbO and silica.[35] It is therefore no surprise that the oxidized Pb emitted from a heat-damaged perovskite module (*vide supra*) is easily captured and, subsequently, chemically trapped by the adjacent glass encapsulation—once the polymeric lamination resin has burnt away. Since the Pb concentration found in the cross section of the encapsulation glass was sufficiently high to justify complete absorption of the Pb present in the underlying module, we conclude that (i) the Pb found on the downstream samples originates solely from the exposed perovskite areas, and (ii) the remaining degraded perovskite converts into oxides that are entirely absorbed by the encapsulation glass.

As an important consequence of these findings, it is recommended to manufacturers of such modules to increase the melting temperature of the glass (by proper additives) to avoid damages to the encapsulation during fire. This way, the encapsulation will act as powerful chemical trap enabling the absorption and chemical binding of the whole amount of Pb present in the module by forming a diluted lead glass.

If despite all precautions, Pb-containing combustion byproducts are released from a rooftop installation during a fire as consequence of partial failure of the encapsulation, it is of paramount importance to estimate the gravity of such a situation for an objective assessment of the associated public health risks. This concern is particularly appropriate in case of flexible

modules with plastic encapsulation that offers little to no protection against fire.[13] In the following we consider a reference $5kW_{peak}$ residential installation with a module efficiency of 20%. We elaborate first on the immediate dangers involved in exposure to the released Pb fumes in the direct vicinity of the fire. A relevant piece of information available for this discussion is the "Immediately Dangerous to Life or Health" concentration (IDLH) for airborne Pb and its compounds, as issued by the National Institute for Occupational Safety and Health (NIOSH). This concentration is determined to be 100 mg/m^3, and represents the maximum level from which one could escape within 30 minutes without severe (irreversible) health defects.[20] Note that the IDLH threshold of 100 mg/m^3 is based upon oral toxicity data in humans and animals scaled roughly to reflect airborne exposures. In a fire scenario, where the mode of intake is exclusively through inhalation, 15 mg/m^3 is a more accurate figure for airborne Pb and its compounds.[10]

Assuming the emission of PbO and PbO_2 as most likely Pb-related species (as from our findings above) from the burning installation, a threshold value of 15 mg/m^3 translates into a concentration of about 2 ppm or, equivalently, into the homogeneous dilution into a cubic volume of air with edges of just under 10 m which is comparable to the volume of a residential building itself. Considering now that the process of incinerating the PV installation occurs in a timeframe that allows for the formation of a plume of much larger volume (with lead compounds diffusing *away* from the fire due to concentration gradients and the buoyancy of the hot plume), it is legitimate to assume that the realistic toxin concentrations available for inhalation within a burning residential building will typically be much lower than the 15 mg/m^3. This suggests that the likelihood for acute Pb-induced incapacitation at the fire scene is very low while, on the other hand, longer-term effects are more likely and can occur in a broad range of severity—keeping in mind the revoked minimum safe threshold issued by WHO.[36]

To put this statement in an even broader perspective, it also has to be considered that besides Pb-based ones, other types of airborne toxins (e.g., CO) are released in a structure fire, to the extent that most fatalities from fires are in fact a result of their inhalation.[37] In addition, many synthetic materials such as carpeting, furniture, decorative items and insulation are known to produce toxic gases upon burning, such as carbon monoxide, hydrogen cyanide and hydrogen chloride.[19, 37-40] Depending on the degree of confinement and ventilation, the concentration of these and other gases can rise to levels able of incapacitating a victim to the point of suffocation.[38] On the other hand, unless a victim is asleep, trapped or otherwise harmed, escape and survival are usually expected in the course of the first two minutes of a typical fire since toxic threats accumulate near the ceiling of a room at first.[38] It can be concluded that due to the

retrospective nature of fire investigations and the wide variety and diversity of the involved relevant parameters, it has been proven difficult to provide a general quantitative assessment of the toxicity of fire smoke, including heavy metals. It has been advocated, however, that the toxicological significance of heavy metals (including Pb) in early death from a fire accident is subordinate to the immediate effects of carbon monoxide, hydrogen cyanide and pulmonary irritants.[41] This implies that, within the timeframe of the fire, it is much more plausible that victims unable to escape would perish as a consequence of other more acutely aggressive toxicants before a lethal concentration of Pb toxins is reached in the same space. Hence, the residual hazard associated with Pb containing PV installations involved in structure fires would manifest itself on the longer timescale in the form of a certain degree of Pb poisoning, which, however less dramatic than complete loss of life, needs to be avoided as well.

An associated potential threat that cannot be overlooked is the atmospheric dispersion of Pb-bearing toxicants, once released from a PV module. Inadvertent spreading of toxic soot over larger distances could potentially contaminate the nearby surroundings, including unwitting local residents. To arrive at an estimate on the distribution of airborne toxicants in the near vicinity of their source, we performed a simulation using the same model as exploited earlier to analyze the risks from fire accidents with CdTe, GaAs and CIS solar modules.[20] **Error! Reference source not found.**a shows the calculated maximum concentration of PbO_2 in the air downwind of the reference $5kW_{peak}$ residential installation, with the wind direction parallel to the horizontal axis, given the worst-case meteorological conditions (More details can be found in the Methods section). The highest concentration found in the area amounts to 41 $\mu g/m^3$, equivalent to an inhaled ~5 μg of PbO_2, on the center line of the plume (during the assumed 15 minutes of fire). Deviations from the center line result in a quick concentration decrease, while in the direction of the wind it takes almost 2 km for the concentration to drop one order of magnitude. 20 km downwind from the source, the concentration would have lowered to a value of 0.16 $\mu g/m^3$ (equivalent to 19 ng PbO_2 inhalation in 15 minutes). Additional analysis (see Supplementary Information) suggests it may be useful for residents downwind of a perovskite fire to keep their windows closed, particularly on the upper floors of their home. To provide a frame of reference for the reported toxin concentrations, we compare them with European and American air quality standards. The European Commission and the US Environmental Protection Agency prescribe maximum allowable Pb concentrations of 0.5 $\mu g/m^3$ averaged over 12 months, and 0.15 $\mu g/m^3$ averaged over 3 months, respectively.[42-43] The European Commission issues a separate value of 50 $\mu g/m^3$ for a one-day exposure, not to be exceeded more than 35 times per calendar year.[42] Our maximum simulated value of 41 $\mu g/m^3$ (within a

confined timeframe of just 15 minutes, and assuming—higher molecular weight—PbO_2 instead of pure Pb) falls two orders of magnitude below this value. This suggests that, at least based upon the atmospheric dispersion model used for the current study, the associated health hazard from exposure of perovskite PV fumes from a burning 5 kW_{peak} residential installation, on medium (few 100 meters) and long-range distances from the source, would not be alarming. Finally, it has to be kept in mind that despite the existence of maximum tolerances for Pb *concentrations*, the WHO has revoked their once enforced maximum safe *blood lead levels* and *provisional tolerable weekly intake (PTWI)*, and now basically considers exposure unhealthy altogether.[36]

In this Viewpoint, have examined a fire scenario analysis on Si/perovskite miniature PV modules in an effort to assess the associated health hazard as caused by the Pb content of the perovskite. Post mortem chemical analysis of encapsulated modules and exposed samples, together with the corresponding down-stream fumes, yields two important revelations: (1) During a fire, perovskite degrades into PbI_2 (besides carbonaceous species) which in the absence of encapsulation oxidizes in place and partly evaporates into the environment; (2) On areas where glass encapsulation is present, it captures PbO/PbO_2-species from the perovskite, thereby preventing them from being released from the module. Hence, it is advisable for manufacturers of perovskite containing modules to use encapsulation glass with higher melting temperature to avoid damages during the fire and thus fully exploit its Pb capturing capability. A critical appraisal of a worst-case scenario with full evaporation of a typical rooftop installation suggests that the health hazard from Pb for direct victims or those in the near vicinity of the fire would either be overshadowed by the amount of more acutely toxic gases produced in a structure fire, or manifest itself on the longer term in the form of Pb poisoning. Precautionary chelation therapy could be advisable in the latter case. Estimates of the downwind Pb concentrations on medium and longer-range distances from the same incident are determined to be far below official air quality standards, based on a rudimentary atmospheric dispersion model. In coming to a consolidated conclusion on the fire safety of perovskite-based photovoltaic technology, more numerical and experimental proofs are desirable, and in doing so, it is important that the distinction is made between rigid glass-encapsulated modules which, according to our observations, are able to capture the full perovskite Pb content, and their far more vulnerable flexible plastic-sealed counterparts.

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Associated content

The Supporting Information, including Methods section, is available free of charge on the ACS Publications website at DOI:….

XPS survey spectra for the positions on the post mortem Si/perovskite mini-module

Depth profile of a perovskite film on a Au substrate before and after 760°C fire treatment

XPS survey spectra of the downstream samples

Si2p core level region of the downstream samples

Temperature profile of the fire simulations

Simulated PbO2 concentrations downwind of a perovskite module fire.

Experimental methods

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Author contributions

B.C. and H.B.G. conceived, designed and performed the experiments and analyzed the data. A.B. contributed to sample delivery and planning. All authors contributed to the writing of the paper.

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References

(1) Green, M. A.; Ho-Baillie, A. Perovskite Solar Cells: The Birth of a New Era in Photovoltaics. *ACS Energy. Lett.* **2017**, *2*, 822-830.
(2) Correa-Baena, J.-P.; Abate, A.; Saliba, M.; Tress, W.; Jesper Jacobsson, T.; Gratzel, M.; Hagfeldt, A. The Rapid Evolution of Highly Efficient Perovskite Solar Cells. *Energy Environ. Sci.* **2017**, *10*, 710-727.
(3) Petrus, M. L.; Schlipf, J.; Li, C.; Gujar, T. P.; Giesbrecht, N.; Müller-Buschbaum, P.; Thelakkat, M.; Bein, T.; Hüttner, S.; Docampo, P. Perovskite Solar Cells: Capturing the Sun: A Review of the Challenges and Perspectives of Perovskite Solar Cells (Adv. Energy Mater. 16/2017). *Adv. Energy Mater.* **2017**, *7*, n/a-n/a.
(4) Best Research-Cell Efficiencies. https://www.nrel.gov/pv/assets/images/efficiency-chart.png (accessed 25 February 2019).
(5) Leijtens, T.; Bush, K.; Cheacharoen, R.; Beal, R.; Bowring, A.; McGehee, M. D. Towards Enabling Stable Lead Halide Perovskite Solar Cells; Interplay between Structural, Environmental, and Thermal Stability. *J. Mater. Chem. A* **2017**, *5*, 11483-11500.
(6) Saliba, M., et al. Incorporation of Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance. *Science* **2016**, *354*, 206-209.
(7) Lin, Y.; Bai, Y.; Fang, Y.; Chen, Z.; Yang, S.; Zheng, X.; Tang, S.; Liu, Y.; Zhao, J.; Huang, J. Enhanced Thermal Stability in Perovskite Solar Cells by Assembling 2d/3d Stacking Structures. *J. Phys. Chem. Lett.* **2018**, *9*, 654-658.
(8) Park, C.; Ko, H.; Sin, D. H.; Song, K. C.; Cho, K. Organometal Halide Perovskite Solar Cells with Improved Thermal Stability Via Grain Boundary Passivation Using a Molecular Additive. *Adv. Funct. Mater.* **2017**, *27*, 1703546-n/a.
(9) Grancini, G., et al. One-Year Stable Perovskite Solar Cells by 2d/3d Interface Engineering. *Nat. Commun.* **2017**, *8*, 15684.
(10) Babayigit, A.; Ethirajan, A.; Muller, M.; Conings, B. Toxicity of Organometal Halide Perovskite Solar Cells. *Nat. Mater.* **2016**, *15*, 247.
(11) Babayigit, A.; Duy Thanh, D.; Ethirajan, A.; Manca, J.; Muller, M.; Boyen, H.-G.; Conings, B. Assessing the Toxicity of Pb- and Sn-Based Perovskite Solar Cells in Model Organism Danio Rerio. *Scientific Reports* **2016**, *6*, 18721.
(12) Serrano-Lujan, L.; Espinosa, N.; Larsen-Olsen, T. T.; Abad, J.; Urbina, A.; Krebs, F. C. Tin- and Lead-Based Perovskite Solar Cells under Scrutiny: An Environmental Perspective. *Adv. Energy Mater.* **2015**, *5*, 1501119-n/a.
(13) Babayigit, A.; Boyen, H.-G.; Conings, B. Environment Versus Sustainable Energy: The Case of Lead Halide Perovskite-Based Solar Cells. *MRS Energy & Sustainability* **2018**, *5, DOI:10.1557/mre.2017.17*.
(14) Brushlinsky, N. N.; Ahrens, M.; Sokolov, S. V.; Wagner, P. *World Fire Statistics Report No. 22*; 2017.
(15) Duong, T., et al. Rubidium Multication Perovskite with Optimized Bandgap for Perovskite-Silicon Tandem with over 26% Efficiency. *Adv. Energy Mater.* **2017**, *7*, 1700228-n/a.
(16) Lal, N. N.; Dkhissi, Y.; Li, W.; Hou, Q.; Cheng, Y.-B.; Bach, U. Perovskite Tandem Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1602761-n/a.
(17) Lee, J.-W.; Hsieh, Y.-T.; De Marco, N.; Bae, S.-H.; Han, Q.; Yang, Y. Halide Perovskites for Tandem Solar Cells. *J. Phys. Chem. Lett.* **2017**, *8*, 1999-2011.
(18) Horantner, M. T.; Snaith, H. J. Predicting and Optimising the Energy Yield of Perovskite-on-Silicon Tandem Solar Cells under Real World Conditions. *Energy Environ. Sci.* **2017**, *10*, 1983-1993.
(19) Ruokojärvi, P.; Aatamila, M.; Ruuskanen, J. Toxic Chlorinated and Polyaromatic Hydrocarbons in Simulated House Fires. *Chemosphere* **2000**, *41*, 825-828.

(20) Moskowitz, P. D.; Fthenakis, V. M. Toxic Materials Released from Photovoltaic Modules During Fires: Health Risks. *Solar Cells* **1990**, *29*, 63-71.
(21) Ezekoye, O. A.; Lakshminarasimhan, K.; Seers, P.; Nicks, R. Effects of Ppv Attack on Thermal Conditions in a Compartment Downstream of a Fire. *Fire Technology* **2005**, *41*, 193-208.
(22) Ezekoye, O. A.; Lan, C. H.; Nicks, R. In *Positive Pressure Ventilation Attack for Heat Transport in a House Fire*, The 6th ASME-JSME Thermal Engineering Joint Conference, Kohala, Hawaii, USA, Japan Society of Mechanical Engineers: Kohala, Hawaii, USA, 2003.
(23) Kerber, S.; Walton, W. D. *Effect of Positive Pressure Ventilation on a Room Fire*; National Institute of Standards and Technology Internal Report (NISTIR): March 1, 2005.
(24) Crewe, R. J.; Stec, A. A.; Walker, R. G.; Shaw, J. E. A.; Hull, T. R.; Rhodes, J.; Garcia-Sorribes, T. Experimental Results of a Residential House Fire Test on Tenability: Temperature, Smoke, and Gas Analyses. *Journal of Forensic Sciences* **2014**, *59*, 139-154.
(25) Lilley, D. G. In *Temperature Measurements in a Small House Fire*, IECEC 96. Proceedings of the 31st Intersociety Energy Conversion Engineering Conference, 11-16 Aug. 1996; 1996; pp 75-78 vol.1.
(26) Ul1256 Standard: Fire Test of Roof Deck Constructions. Underwriters Laboratories Inc.: Northbrook, IL, 2002.
(27) Fthenakis, V. M.; Fuhrmann, M.; Heiser, J.; Lanzirotti, A.; Fitts, J.; Wang, W. Emissions and Encapsulation of Cadmium in Cdte Pv Modules During Fires. *Progress in Photovoltaics: Research and Applications* **2005**, *13*, 713-723.
(28) Wertheim, G. K.; Dicenzo, S. B. Least-Squares Analysis of Photoemission Data. *J. Electron. Spectrosc. Relat. Phenom.* **1985**, *37*, 57-67.
(29) Conings, B., et al. Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite. *Adv. Energy Mater.* **2015**, *5*, 1500477-n/a.
(30) Niu, G.; Guo, X.; Wang, L. Review of Recent Progress in Chemical Stability of Perovskite Solar Cells. *J. Mater. Chem. A* **2015**, *3*, 8970-8980.
(31) Dualeh, A.; Gao, P.; Seok, S. I.; Nazeeruddin, M. K.; Grätzel, M. Thermal Behavior of Methylammonium Lead-Trihalide Perovskite Photovoltaic Light Harvesters. *Chem. Mater.* **2014**, *26*, 6160-6164.
(32) Chase, M. W. J. Nist-Janaf Themochemical Tables, Fourth Edition. *Journal of Physical and Chemical Reference Data* **1998**, *Monograph 9*, 1-1951.
(33) Lide, D. R., *Crc Handbook of Chemistry and Physics 88th Edition* CRC Press: Boca Raton, FL, 2007.
(34) Davison, S.; Newton, R., *Conservation of Glass*; Butterworth, 1989.
(35) Hurst-Vose, R., *Glass*; Collins: London, 1980.
(36) *Exposure to Lead: A Major Public Health Concern*; World Health Organization: 2010.
(37) Stefanidou, M.; Athanaselis, S.; Spiliopoulou, C. Health Impacts of Fire Smoke Inhalation. *Inhalation Toxicology* **2008**, *20*, 761-766.
(38) Alarie, Y. Toxicity of Fire Smoke. *Crit. Rev. Toxicol.* **2002**, *32*, 259-289.
(39) Kealey, G. P. Effects/Treatment of Toxic Gases. *Journal of Burn Care & Research* **2009**, *30*, 146-147.
(40) Jones, J.; McMullen, M. J.; Dougherty, J. Toxic Smoke Inhalation: Cyanide Poisoning in Fire Victims. *The American Journal of Emergency Medicine* **1987**, *5*, 317-321.
(41) Birky, M. M.; Clarke, F. B. Inhalation of Toxic Products from Fires. *Bulletin of the New York Academy of Medicine* **1981**, *57*, 997-1013.
(42) Directive 2008/50/Ec of the European Parliament and of the Council of 21 May 2008: On Ambient Air Quality and Cleaner Air for Europe. *Official Journal of the European Union* 2008, pp 1-44.

(43) Review of the National Ambient Air Quality Standards for Lead. In *Federal Register*, Environmental Protection Agency: 2016; Vol. 81, p 71906.
(44) Conings, B.; Babayigit, A.; Klug, M. T.; Bai, S.; Gauquelin, N.; Sakai, N.; Wang, J. T.-W.; Verbeeck, J.; Boyen, H.-G.; Snaith, H. J. A Universal Deposition Protocol for Planar Heterojunction Solar Cells with High Efficiency Based on Hybrid Lead Halide Perovskite Families. *Adv. Mater.* **2016**, *28*, 10701-10709.
(45) Beychok, M. R., *Fundamentals of Stack Gas Dispersion (4th Ed.)*; The Author, 2005.
(46) Turner, D. B., *Workbook of Atmospheric Dispersion Estimates: An Introduction to Dispersion Modeling (2nd Ed.)*; CRC Press, 1994.
(47) Seinfeld, J. H., *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change.*; Wiley, 2006.
(48) Hanna, S. *Handbook on Atmospheric Diffusion*; U.S. Department of Energy: 1982.
(49) Pasquill, F.; Smith, F. B., *Atmospheric Diffusion (3rd Edition)*; Ellis Horwood (Wiley), 1983.
(50) Moskowitz, P. D.; L.D., H.; Morris, S. C.; Novak, K. M.; Rowe, M. D. *Photovoltaic Energy Technologies: Health and Environmental Effects Document*; Brookhaven National Laboratory, 1990.