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Direct calorimetric verification of thermodynamic instability of lead halide hybrid perovskites

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Hybrid perovskites, especially methylammonium lead iodide (MAPbI$_3$), exhibit excellent solar power conversion efficiencies. However, their application is plagued by poor chemical and structural stability. Using direct calorimetric measurement of heats of formation, MAPbI$_3$ is shown to be thermodynamically unstable with respect to decomposition to lead iodide and methylammonium iodide, even in the absence of ambient air or light or heat-induced defects, thus limiting its long-term use in devices. The formation enthalpy from binary halide components becomes less favorable in the order MAPbCl$_3$, MAPbBr$_3$, MAPbI$_3$, with only the chloride having a negative heat of formation. Optimizing the geometric match of constituents as measured by the Goldschmidt tolerance factor provides a potentially quantifiable thermodynamic guide for seeking chemical substitutions to enhance stability.

hybrid halide perovskites | thermodynamic instability | solar cells | tolerance factor | enthalpy of formation

Organic–inorganic hybrid materials which adopt the perovskite structure have gained increasing attention due to their excellent solar to electric power conversion efficiencies (PCEs). Methylammonium lead halide (MAPbX$_3$) perovskite leads the race with a PCE of 20%. Although these perovskites were discovered in 1978 by Weber, who described their structural and physical properties (1, 2), their solar cell application was explored only in 2009 by Miyasaka and coworkers. (3). Recently a very impressive PCE of 20% has been claimed for these materials (4). The extraordinary performance of hybrid perovskites has been attributed to their large absorption efficiency, favorable band gap, high charge mobility, and long-range electron hole transport (5–8). The AMX$_3$ perovskite structure provides great flexibility for modifications where, in principle, a range of similar compounds with different energy gaps can be synthesized by variation and/or partial substitution of the organic moiety (A = methylammonium, ethylammonium, formamidinium, or other possible organic cations), the metal (M = Pb, Sn and possible others), or the halide (X = I, Br, Cl). All these factors make organic metal halide perovskites front-runners compared with other conventional solar cell materials (9).

Despite their excellent photovoltaic efficiency, a major hurdle in the progress of commercially viable AMX$_3$ solar cells is that these materials lack stability to external factors like temperature, oxygen, humidity, and solar irradiation (10). They are susceptible to chemical reactions, phase transformations, phase segregation, and other degradation processes under ambient conditions. A review by Zhao and Park (11) describes several aspects of MAPbI$_3$ degradation including photostability, thermal stability, and stability in the presence of ambient air (O$_2$/H$_2$O). In the presence of water, MAPbI$_3$ undergoes reactions to form PbI$_2$ and CH$_3$NH$_3$I, which further undergo degradation to CH$_3$NH$_2$ and HI. Hydrolysis reactions may be involved so it is not clear whether the decomposition to binary halides proceeds directly, catalyzed by water, or whether dissolution–reprecipitation steps or other complex mechanisms are involved. In the presence of O$_2$, deprotonation of MAPbI$_3$ occurs, leading to decomposition forming PbI$_2$, I$_2$, CH$_3$NH$_2$, and H$_2$O. Such degradation has been partially overcome by using moisture-resistant organic/inorganic hole transport media

(12, 13). However, there is continued need for understanding and enhancing the stability of these materials for their applications on the industrial scale. Evaluating their thermodynamic properties is crucial to understanding their stability and persistence. Two recent density functional theory (DFT) calculations (14, 15) suggest that these perovskites may be of limited stability but there have been no direct experimental studies of thermodynamic properties. This article presents experimentally measured formation enthalpies of MAPbX$_3$ perovskites (X = Cl, Br, and I), based on acid solution calorimetry, confirming increasing thermodynamic instability with larger anions and showing that MAPbI$_3$ is intrinsically thermodynamically unstable with respect to decomposition to its binary halide components even in the absence of water, oxygen, heat, or irradiation.

Results and Discussion

Powder X-ray diffraction patterns of all three synthesized compounds are shown in Fig. 1, which confirmed phase-pure products. MAPbI$_3$ adopts a tetragonal structure and MAPbBr$_3$ and MAPbCl$_3$ crystallize in a cubic structure (Table S1), which are the room-temperature structures previously reported for these materials (16). Thermogravimetric analysis (TGA) curves are given in Fig. S1. No mass loss below 250 °C is observed, indicating that the phases are anhydrous. Above 250 °C all three samples exhibit mass loss due to degradation of methylamine and dehalogenation. The measured enthalpies of solution in 5 M HCl of all three MAPbX$_3$ samples and their constituent halides are listed in Table 1. Enthalpies of formation of MAPbX$_3$ were calculated from their corresponding lead halide and methylammonium halide using the thermochemical cycle in Table 2. The formation enthalpy is strongly positive (34.50 ± 1.01 kJ/mol) for MAPbI$_3$, weakly positive

Significance

Organic metal halide perovskites are a promising class of materials for next-generation solar cells. However, they are chemically labile, raising questions of thermodynamic stability and posing a significant challenge for their use. This paper provides direct calorimetric measurements of their heats of formation from binary halide constituents. The positive formation enthalpy of methylammonium lead iodide from MAI and PbI$_2$ (MA = methylammonium) confirms thermodynamic instability, thus limiting long-term persistence even in the absence of air, moisture, heat, or light. The enthalpy of formation of the iodide, bromide, and chloride perovskite becomes less positive with increasing Goldschmidt tolerance factor, suggesting a criterion in the search for more stable hybrid perovskites.

Fig. 1. (*A*) Structure of MAPbI₃ perovskite. Powder X-ray diffraction patterns of (*B*) MAPbI₃, (*C*) MAPbBr₃, (*D*) MAPbCl₃.

(6.69 ± 1.41 kJ/mol) for MAPbBr₃, and weakly negative (−9.03 ± 0.68 kJ/mol) for MAPbCl₃. Although entropy effects may play a role, it is unlikely, especially at ambient temperature, that the TΔS term would be positive enough to render the iodide perovskite stable with respect to its components. The thermodynamic stability of these materials thus decreases in the order MAPbCl₃, MAPbBr₃, MAPbI₃.

To understand the observed results, we examine three factors that might influence the heat of formation of these lead halide perovskites: (*i*) geometric factor or bond length mismatch, (*ii*) Pb–X bond strength, and (*iii*) electronegativity of the halogen. The ideal cubic perovskite structure defines the optimum ratio of bond lengths on the 12-coordinated and 6-coordinated sites, and deviations from this ratio are described by the Goldschmidt tolerance factor (*t*) (17). In hybrid perovskites, a modified version of Goldschmidt's equation is used to calculate *t*, because there is a molecular cation instead of a monatomic one (18). Cheetham and coworkers (19, 20) modified the tolerance factor equation to use an effective radius of the organic cation (Table S2). The details of this calculation for the methylammonium cation are shown in the

SI Text. The calculated tolerance factors are 0.91 (MAPbI₃), 0.93 (MAPbBr₃), and 0.94 (MAPbCl₃). In inorganic oxide perovskites, ideal cubic structures form when the tolerance factor is close to 1. In the current case, tolerance factors are in the range of 0.91–0.94, suggesting deviation from ideal cubic structure, and indeed the I

Table 1. Enthalpies of solution of compounds and constituents and enthalpies of formation of MAPbX₃ from MAX and PbX₂

Compound	ΔH_sol, kJ/mol	ΔH_f, kJ/mol
PbI₂	33.28 ± 0.55(5)	
PbBr₂	18.15 ± 1.37(4)	
PbCl₂	8.14 ± 1.65(4)	
MAI	19.60 ± 0.11(3)	
MABr	14.40 ± 0.24(4)	
MACl	8.96 ± 0.15(4)	
MAPbI₃	18.38 ± 0.85(4)	34.50 ± 1.01
MAPbBr₃	25.86 ± 0.25(4)	6.69 ± 1.41
MAPbCl₃	26.13 ± 0.32(4)	−9.03 ± 1.68

Table 2. Thermochemical cycle used to calculate the formation enthalpy of MAPbX$_3$

Reaction scheme	Enthalpy measurement*
CH$_3$NH$_3$PbX$_{3(s)}$ → PbX$_{2\ (aq)}$ + CH$_3$NH$_3$X$_{(aq)}$	$\Delta H_1 = \Delta Hs(\text{CH}_3\text{NH}_3\text{PbX}_3)$
CH$_3$NH$_3$X$_{(s)}$ → CH$_3$NH$_3$X$_{(aq)}$	$\Delta H_2 = \Delta Hs(\text{CH}_3\text{NH}_3\text{X})$
PbX$_{2(s)}$ → PbX$_{2(aq)}$	$\Delta H_3 = \Delta Hs(\text{PbX}_2)$
PbX$_{2(s)}$+CH$_3$NH$_3$X$_{(s)}$ → CH$_3$NH$_3$PbX$_3$	$\Delta H_4(f, \text{CH}_3\text{NH}_3\text{PbX}_3) = -\Delta H_1 + \Delta H_2 + \Delta H_3$

*All of the ΔHs values can be found in Table 1.

perovskite is tetragonal whereas the Br and Cl perovskites are cubic. The trend in formation enthalpy versus tolerance factor (Fig. 2A) is similar to that for many inorganic perovskites, where the enthalpy of formation becomes more exothermic approximately linearly with increasing tolerance factor (21). Thus, in the MAPbX$_3$ series the energetically least stable perovskite with iodide is indeed the one with the least favorable match of bond lengths or effective radii, the smallest tolerance factor, and the strongest distortion from cubic symmetry.

In the three perovskites studied, X, the halogen, is the only compositional or structural variable. Fig. 2B shows that the enthalpy of formation becomes more negative with increase in bond strength between Pb and halide (22). Another relevant parameter is electronegativity, which decreases in the order Cl$^-$, Br$^-$, I$^-$ (23), and hence energetic stability of MAPbX$_3$ increases with increase in electronegativity of X (Fig. 2B). Thus, all three factors, geometric mismatch, bond strength, and electronegativity (which are of course related, stemming from the same fundamental chemistry), affect energetics as expected from elementary chemical considerations, causing the iodide perovskite to be the least stable with respect to the binary halides. With respect to the elements, both the binary halides (Table S3), and the perovskites are strongly exothermic in enthalpy, becoming less so in the series Cl$^-$, Br$^-$, I$^-$. However, the stability of the perovskite with respect to the binary halides would depend on the difference in enthalpy of formation from elements of the perovskite and its binary

components. This difference is measured directly by our solution calorimetric technique, which does not require knowledge of enthalpy of formation from elements.

The maximum PCE is exhibited by MAPbI$_3$ followed by MAPbBr$_3$ (4). The calorimetric results show that MAPbI$_3$ is energetically metastable and is thermodynamically allowed to decompose to its binary components, even in the absence of humidity, atmospheric oxygen, or light. This result is very significant because it was initially thought that the only major hurdle in the application of MAPbI$_3$ in devices was its sensitivity to moisture and air, leading to disintegration of the perovskite to PbI$_2$ and CH$_3$NH$_3$I or to form a hydrated structure (CH$_3$NH$_3$)4PbI$_6$·2H$_2$O, which exhibits very low PCE (24, 25). Thus, if moisture and oxygen could be excluded by appropriate coating or encapsulation, it was anticipated that the material could be used in solar cells for long periods of time (24). The thermochemical data point to the intrinsic instability of this material; thus its decomposition is thermodynamically inevitable, although the rate of decomposition will be controlled by kinetic factors. Indeed, Kamat and coworkers (25) and Conings et al. (26) have shown that, even in the absence of moisture and air, MAPbI$_3$ disintegrates slowly to PbI$_2$ and CH$_3$NH$_3$I (over 76 d absorbance decays to 50% of its initial value).This suggests that kinetic factors limiting the now-proven thermodynamically favorable decomposition are not strong enough to permit long-term operation of the solar cell unless other means of kinetic inhibition can be found.

Recent DFT calculations also indicate that MAPbI$_3$ is least stable among the three halide perovskites (14, 15). The calculated formation enthalpies are −0.1, −0.25, −0.7 eV (−9.64, −24.12, and −67.54 kJ/mol) for MAPbI$_3$, MAPbBr$_3$, and MAPbCl$_3$, respectively (14). The trend of decreasing stability with heavier halogen is similar to that obtained by our direct calorimetric measurements, although the numerical values of enthalpy of formation are different and are all negative. The authors of ref. 14 suggest that the small negative enthalpy of formation of MAPbI$_3$ supports that it is prone to destabilization under conditions of heating or light soaking. A second recent DFT study (15) shows that the calculated energy change associated with degradation of perovskite to its components is negative for MAPbI$_3$, implying the formation enthalpy is positive (6.7 kJ/mol). This indicates
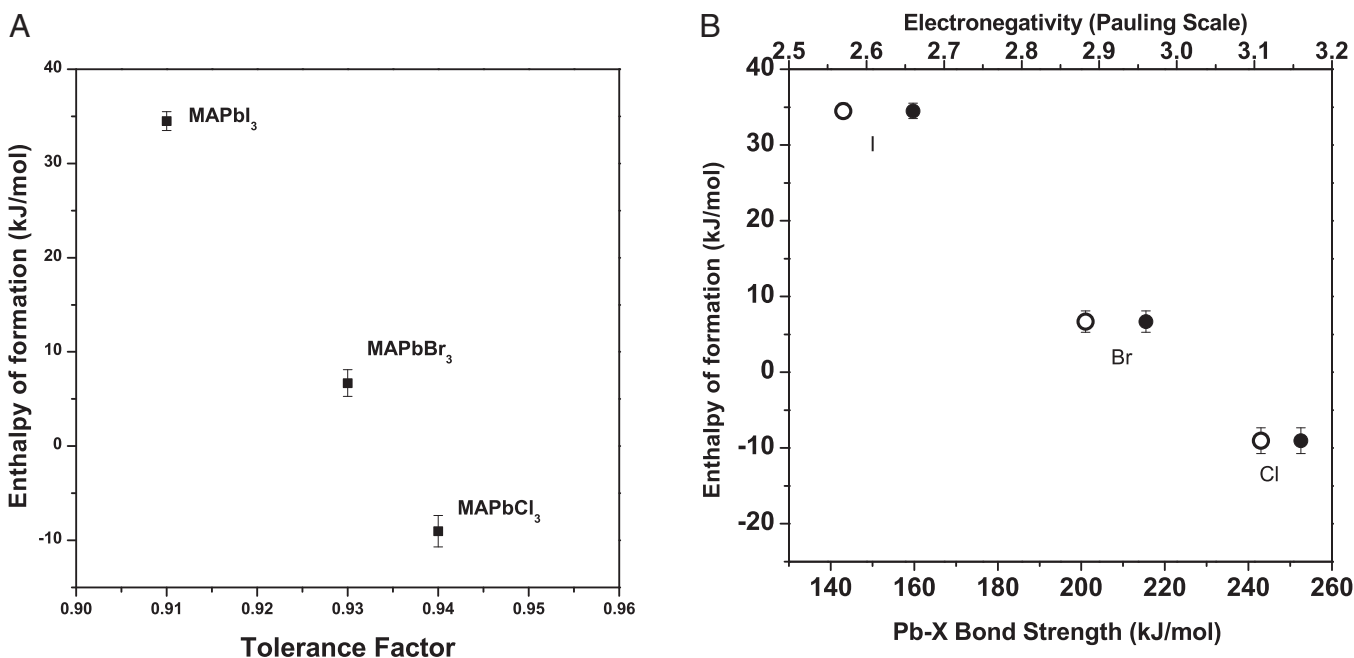

Fig. 2. Enthalpy of formation of MAPbX$_3$ as a function of (A) tolerance factor; (B) lead–halogen bond strength (open circles) and electronegativity (solid circles).

that the decomposition of $MAPbI_3$ to its components is spontaneous and this material is intrinsically unstable, which is in line with the present calorimetric study, although the enthalpy values are somewhat different. Thus, one must conclude that $MAPbI_3$ may not be a viable solar cell material for long-term use, because one must rely on kinetic barriers to its thermodynamically favorable decomposition to prevent its degradation.

Different approaches are currently being explored to improve the stability of hybrid perovskites, which show excellent PCE but whose decomposition is a challenge to the photovoltaic industry (27–29). Chemical approaches to obtain greater thermodynamic stability while not sacrificing too much PCE appear to be fruitful. Recent investigations on elemental substitution at A, B, and X sites have proven that efficiency can be maintained or even enhanced and apparent stability of perovskites can be increased (4). Because $MAPbCl_3$ is clearly thermodynamically stable, and $MAPbBr_3$ may be at the edge of stability (small positive enthalpy of formation could be offset by small positive entropy of formation), substitution of some of the iodide by chloride or bromide may lead to stable materials while retaining reasonable PCE. Fig. 3A shows a calculated plot, based on linear dependence of enthalpy on tolerance factor for such substitutions, to estimate possible stabilization. However, the large size mismatch of the various halide ions may further destabilize the solid solutions through a positive heat of mixing. The prediction of energetic stability in these mixed halide perovskites is not very encouraging, because negative enthalpies of formation are predicted only for materials with large chloride content.

Substituting Pb by other metals like Sn and Ge or replacing $CH_3NH_3^+$ by other organic $[CH(NH_2)_2]^+$/or inorganic (Cs^+) cations may also enhance stability. Plots of tolerance factor as a function of elemental substitution are given in Fig. 3 B and C. If, as for the perovskites studied here, energetic stability with respect to components occurs when the tolerance factor is greater than about 0.92, one can make some predictions of likely thermodynamically stable candidates to investigate for solar cell applications. It can be seen from Fig. 3B that $FASnCl_3$ has the highest tolerance factor and may be energetically stable. However, Sn-based perovskites may be prone to destabilization due to change in the oxidation state of Sn. Another attractive material is $FAPbX_3$, which is already
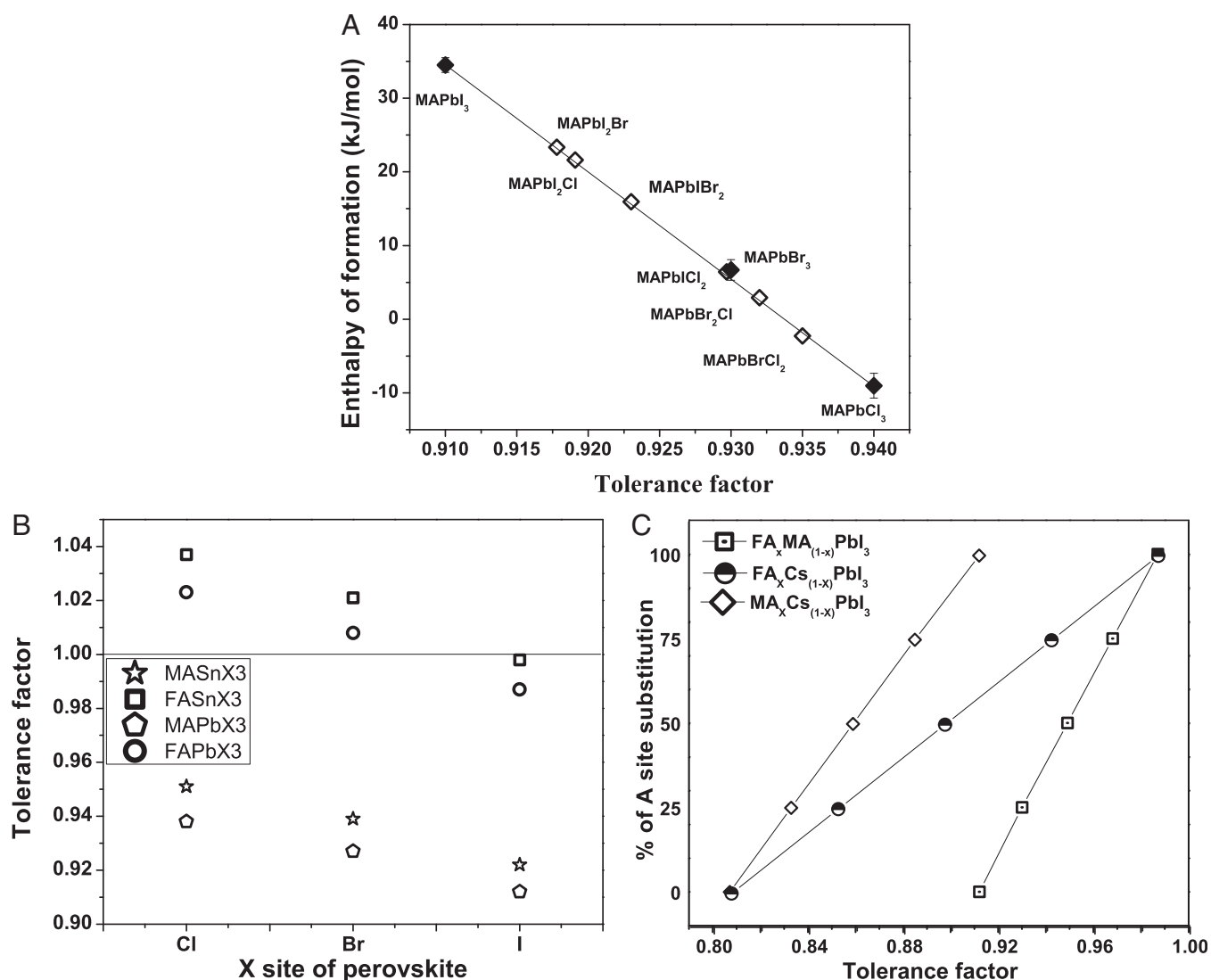

Fig. 3. (A) Linear fit of measured enthalpy of formation vs. tolerance factor of $MAPbX_3$ end members (filled symbols). Calculated values for other possible compositions (open symbols) are plotted vs. their calculated tolerance factors. Plots of tolerance factor as a function of (B) X-site substitution of $MAPbX_3$, $MASnX_3$, $FAPbX_3$, and $FASnX_3$ and (C) A-site substitution of $APbI_3$.

being explored by several groups (27, 28). Partially replacing MA by FA to give $MA_{(1-x)}FA_xPbI_3$, has also shown promising PCE (28) and Fig. 2C shows that such a substitution for x > 0.4 leads to tolerance factors >0.92, suggestive of thermodynamic stability. Partial substitution of MA or FA by Cs (29) on the A site is another alternative route that has shown good PCE values (29). However, in such a substitution the tolerance factor decreases and the thermodynamic stability is uncertain. Efforts are being made by several groups around the globe to arrive at a "magical" composition which gives a stable perovskite with high PCE (30, 31). Thermodynamics must underlie this "magic" and the thermodynamic arguments made here will help guide further exploration. In particular, a starting point for identifying thermodynamically stable hybrid perovskites may be the use of the tolerance factor; hypothetical perovskites with t closer to unity (roughly >0.92) should be favored for exploration.

Conclusion

To understand the thermodynamic stability of methylammonium lead halide perovskites, possible new materials for solar cell applications, we performed room-temperature acid solution calorimetric measurements to determine their heats of formation. The resulting formation enthalpies from methylammonium halide plus lead halide are positive for both iodide and bromide perovskites and slightly negative for the chloride perovskite, indicating that the iodide and bromide are thermodynamically unstable, even in the absence of ambient air, water, light, or heat, thus limiting their long-term use in devices. New hybrid perovskites with Goldschmidt tolerance factor closer to unity should be explored as possible more stable alternatives.

Materials and Methods

Synthesis. $MAPbI_3$ and $MAPbBr_3$ were prepared by crystallization from a concentrated hydrogen halide solution containing lead and methylamine, using the method described by Poglitsch and Weber (16). In a typical synthesis,

1.88 g of lead (II) acetate was dissolved in 40 mL HX solution (48 wt % for HBr and 57 wt % for HI) and warmed (~90 °C) in a water bath. To this, 0.45 g of CH_3NH_2 dissolved in 2 mL of HX was introduced. Crystals were obtained by slow cooling of this solution from ~90 °C to room temperature over 3 h. The product was washed with acetone and dried overnight at 100 °C in a vacuum oven. Crystals were stored in a N_2-filled glovebox for further characterization and calorimetric experiments. $MAPbCl_3$ was prepared by dropcast method using a mixture of $PbCl_2$ and CH_3NH_3Cl on a glass substrate. An equimolar ratio of $PbCl_2$ and CH_3NH_3Cl was dissolved in N, N'- dimethylformamide separately. $PbCl_2$ solution was warmed on a hotplate (~90 °C) to which CH_3NH_3Cl solution was added. The hot solution was dropped onto a glass substrate and subsequently annealed at 100 °C for 10 min, which results in the formation of a white powder. The powder was scraped off the glass substrate and stored in a nitrogen-filled glovebox.

Characterization. Powder X-ray diffraction patterns were recorded using a Bruker-AXS D8 Advance diffractometer operated at 40 kV and 40 mA using Cu-Kα radiation. Data were collected from 10° to 70° 2θ at a step size of 0.02° 2θ with 1 s per step. The Rietveld technique was used for structure refinement of all of the phases using GSAS software. Published crystal structures were used as starting points for the data refinement. DIAMOND software was used to visualize the obtained structure and to evaluate bond distances. Both $MAPbBr_3$ and $MAPbCl_3$ were found to crystallize in a cubic structure and $MAPbI_3$ in a tetragonal structure, which are the room-temperature phases previously reported for these materials (1). Thermal analysis was performed using a Netzsch 449 thermogravimetric/differential scanning calorimetry instrument under Ar atmosphere (25–800 °C, heating rate 10 °C/min, alumina crucible).

Isothermal Acid Solution Calorimetry. A Calorimetry Sciences Corporation (CSC) 4400 isothermal microcalorimeter operated at 25 °C was used for the measurements of enthalpy of dissolution. Five mg of each sample was hand pressed into a pellet and dropped into a 5 N HCl solvent (~25 g) which is equilibrated in the calorimetric sample chamber. Mechanical stirring was used to aid dissolution. The calorimeter was calibrated by dissolving 15-mg pellets of KCl in water with stirring at 25 °C (see the *SI Text* for details).

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