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Solid-state principles applied to organic–inorganic perovskites: new tricks for an old dog†

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Hybrid organic–inorganic materials that adopt perovskite-like architectures show intriguing order–disorder phase transitions and exciting electronic properties. We extend the classical concept of ionic tolerance factors to this important class of materials and predict the existence of several hitherto undiscovered hybrid perovskite phases.

Introduction

Perovskites of general formula ABX_3 have played a central role in the evolution of materials chemistry and condensed matter physics over the last 70 years. The development of perovskite oxides ABO_3 has been particularly significant and they are used in a wide range of applications such as ferroelectrics, high-temperature superconductors, and giant magnetoresistance devices.[1] It is exciting to observe, therefore, that a new class of hybrid organic–inorganic perovskites is now attracting the attention of chemists and physicists, and is making remarkable strides in fields such as multiferroics and thin-film solar cells. The present contribution explores the extent to which learning from the literature on oxide perovskites can be applied towards the discovery of new organic–inorganic analogues.

Hybrid organic–inorganic frameworks, which include the wide family of metal–organic frameworks (MOFs), have evolved over the last 15 years into one of the fastest growing research fields in materials science. The unlimited combinations of metal ions and organic linkers, which give rise to enormous structural and chemical diversity,[2,3] enable the targeted design of materials for many applications. Most of the research on MOFs hitherto has concerned porous systems, which are being explored for applications in gas storage,[4] chemical sensing,[5] biomedicine[6] and catalysis.[7] There is growing interest, however, in dense MOFs, which show potential for applications in many other areas, such as optical devices, batteries and semi-conductors.[8] A subset of these dense hybrid frameworks adopt the perovskite architecture and exhibit a remarkable range of properties. In ABX_3 formates such as $[AmH]M(HCOO)_3$ (A = protonated amine, $[AmH]^+$, $B = M^{2+}$ and $X = HCOO^-$), the divalent metal cation occupies BO_6 octahedra which are linked by formate bridges to form a pseudo-cubic ReO_3-like cavity. The amine cation, which is located in the perovskite cavity (Fig. 1a), is often disordered at ambient temperatures and the systems show an fascinating range of ferroelectric and multiferroic properties on cooling.[9–11] A second class of hybrid perovskites of general composition $[AmH]MX_3$ ($M = Sn^{2+}$, Pb^{2+} and $X = Cl^-$, Br^-, I^-)[12] has attracted a great deal of attention recently. In particular, lead based iodides show impressive performances in solar cell applications and take advantage of straightforward processing methods such as spin-coating, dip-coating and vapour deposition techniques.[13,14] Their electrical power conversion efficiencies, although sensitive to measurement parameters, have increased from 3.8% in 2009 (ref. 15) to over 15% by the end of 2013[13,16,17] leading to a surge of interest in the study of hybrid perovskites.

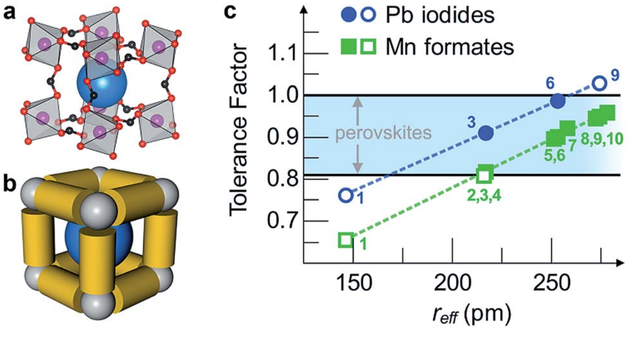

Fig. 1 A strong correlation exists between tolerance factors and underlying crystal structures and all currently known perovskite MOFs exhibit tolerance factors between 0.81 and 1.01. (a) Structure and polyhedral connectivity of $[(CH_3)_2NH_2]Mn(HCOO)_3$ to highlight the perovskite-like architecture. Hydrogen atoms are omitted and atomic radii are chosen for clarity; purple: manganese, red: oxygen, black: carbon and blue: $[(CH_3)_2NH_2]^+$. (b) Schematic of the model that is used for the calculation of the tolerance factors of formates. (c) Tolerance factors of Pb iodides (circles) and Mn formates (squares) plotted *versus* cation size. Open symbols indicate reported compounds with a non-perovskite structure. The light blue area highlights the range where perovskite-like frameworks are expected to form. The uncertainty in the tolerance factors is estimated to be 6%.

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The complex interplay between different types of bonding interactions makes crystal engineering of hybrid perovskites a challenging task, even though some important studies have addressed this issue.[18,19] Inspired by Mitzi's 2001 work,[18] the present study explores the extent to which learnings from inorganic perovskites can be applied quantitatively to their hybrid analogues.

The tolerance factor

In 1926, V. M. Goldschmidt introduced a geometrical parameter α, the so-called tolerance factor, to evaluate ionic size mismatches which the perovskite-structure will tolerate until a different structure-type is formed, see eqn (1):[20]

$$\alpha = (r_A + r_X)\Big/\sqrt{2}(r_B + r_X), \tag{1}$$

with r_i being the radii of ions in the perovskite ABX_3, and i = A, B and X, respectively. Eqn (1) is a semi-empirical relationship that combines the idea of dense ionic packing with early estimates of ionic radii; it continues to be widely used as a guiding principle in the study of oxide perovskites. For values of α in the range 0.9–1.0, mostly cubic perovskites are found, whereas values of 0.80–0.89 predominantly lead to distorted perovskites which can be further classified by using Glazer's concept of octahedral tilting.[21] Below ~0.80, other structures such as the ilmenite-type ($FeTiO_3$) are more stable due to the similar sizes of the cations A and B. Values of α larger than 1 lead to hexagonal structures where layers of face-sharing octahedra are introduced into the structure.

Tolerance factors of hybrid frameworks

The challenge in determining tolerance factors for organic–inorganic compounds lies in estimating the ionic radii of molecular ions. This problem has been addressed in the past and a set of thermochemical radii for molecular anions was proposed by Kapustinskii and Yatsimirskii in the 1940s.[22] In the case of hybrid perovskites we are dealing with molecular cations, where varying bond lengths due to hydrogen–bonding interactions make it difficult to define an ionic radius. Even highly symmetrical cations, such as $[NH_4]^+$ and $[(CH_3)_4N]^+$, exhibit radii which depend significantly on their anionic counterparts,[23] making tolerance factors for hybrid perovskites a challenging problem. In 2001 Mitzi applied eqn (1) to the hybrid lead iodides and obtained a maximum radius for the protonated amines of ~260 pm.[18] In the present work we expand on this initial work and also extend the tolerance factor concept to the formate perovskites. We use crystallographic data from known perovskite-like hybrid frameworks to estimate a consistent set of effective radii for different organic ions. In particular, assuming free rotational freedom around the centre of mass, a rigid sphere model is applicable to organic cations (Fig. 1a) and leads to a consistent set of effective ionic radii, r_{Aeff}. We have used eqn (2) to suggest effective ionic radii for the most common nitrogen based cations, Table 1.

Table 1 Effective radii of molecular cations and anions. Ionic radii of divalent metal ions were used according ref. 21

Cation		Effective radius r_{Aeff} (pm)
1	Ammonium $[NH_4]^+$	146
2	Hydroxylammonium $[H_3NOH]^+$	216
3	Methylammonium $[(CH_3)NH_3]^+$	217
4	Hydrazinium $[H_3N–NH_2]^+$	217
5	Azetidinium $[(CH_2)_3NH_2]^+$	250
6	Formamidinium $[NH_2(CH)NH_2]^+$	253
7	Imidazolium $[C_3N_2H_5]^+$	258
8	Dimethylammonium $[(CH_3)_2NH_2]^+$	272
9	Ethylammonium $[(C_2H_5)NH_3]^+$	274
10	Guanidinium $[C(NH_2)_3]^+$	278
11	Tetramethylammonium $[(CH_3)_4N]^+$	292
Anions		
Iodide, I^-		$r_{\text{xeff}} = 220$
Formate, $HCOO^-$		$r_{\text{xeff}} = 136$ $h_{\text{xeff}} = 447$

$$r_{\text{Aeff}} = r_{\text{mass}} + r_{\text{ion}}, \tag{2}$$

with r_{mass} being the distance between the centre of mass of the molecule and the atom with the largest distance to the centre of mass, excluding hydrogen atoms; r_{ion} is the corresponding ionic radius of this atom.[21] For example, in case of the guanidinium cation we found $r_{\text{mass}} = r(\text{C–N}) = 132$ pm and $r_{\text{ion}} = r(N^{3-}) = 146$ pm; therefore according to eqn (2) $r_{\text{Aeff}} = 278$ pm. This approach gives a set of effective radii that can be used to estimate tolerance factors. For molecular anions such as $HCOO^-$, CN^- and N_3^-, the situation is complicated by the high anisotropy of the anion. We have therefore treated all molecular anions as rigid cylinders, with effective radius r_{xeff} and an effective height h_{xeff}, see Fig. 1b (yellow cylinders). The radius and the height of the cylinder are then evaluated according eqn (2). Eqn (1) is then modified to give eqn (3):

$$\alpha = \left(r_{\text{Aeff}} + r_{\text{Xeff}}\right)\Big/\sqrt{2}\left(r_B + 0.5h_{\text{Xeff}}\right), \tag{3}$$

In Fig. 1c, tolerance factors of the hybrid Pb iodides and Mn formates calculated according to eqn (2) and (3), are plotted as a function of the *A* cation radius. The larger ReO_3 cavity of the formates leads to a horizontal shift of the critical cation sizes for perovskite formation to larger A cation radii, $r_{\text{Aeff}} = 168$–259 pm (lead iodides) and $r_{\text{Aeff}} = 213$–295 pm (manganese formates). The maximum cation size for iodides is in excellent agreement with the previous reported result, r_{Aeff} ~260 pm.[18]

Currently, nearly all reported hybrid frameworks with an ABX_3 perovskite-like structure exhibit tolerance factors between 0.81 and 1.01; in other words, the relative packing density of MOFs plays a crucial role in the formation of hybrid frameworks with the perovskite structure, which include perovskite-like cyanides and structurally flexible ABX_3 azide frameworks.[24–26] Although the complexity of the hybrid systems leads us to expect that more exceptions will be discovered in the future, and clearly the exact boundaries are subject to uncertainty due to inaccuracies relating to r_{eff}, the relationship between hybrid perovskites and their solid-state analogues is remarkably strong. For example, with decreasing size of the cation A, the relative density of the perovskite-formates steadily decreases until around $\alpha = 0.81$, where an unusual chiral structure becomes energetically comparable to the perovskite-type architecture.[27] Both polymorphs have been observed for $[NH_2NH_3]M(HCOO)_3$ (M = Mn, Zn, Co, Mg) and the synthetic procedure appears to determine which phase forms.[28] It will be interesting to see if both polymorphs can be stabilized at room temperature and (reversible) pressure-driven phase transitions occur.

So far, the upper limit of tolerance factors where a pseudo-cubic perovskite-structure is expected to form is well defined. Similar to the perovskite oxides, $[(C_2H_5)NH_3]PbI_3$ ($\alpha = 1.05(4)$) adopts an hexagonal structure with 1D chains of face-sharing PbI_6 octahedra. Such structural motifs are absent in formate based compounds due to the face-sharing connectivity. However, an interesting case where the tolerance factor concept does not seem to apply is found for the guanidinium tin chlorides and bromides. In such compounds, a stereochemically active lone pair leads to heavily distorted perovskite structures. For example, three short Sn–Cl distances (~2.5 Å) are observed in $[(NH_2)_3C]SnCl_3$, whereas the other three Sn–Cl bonds (between 3.2 Å and 3.7 Å) are elongated due to repulsion effects between the tin lone pairs and the halide ions.[29,30] The structure is therefore better described as containing $SnCl_3^-$ anions, rather than the $SnCl_6$ octahedra required by the perovskite structure. As a consequence, use of the tolerance factor concept becomes inappropriate.

Based on the considerations presented above, we can predict the existence of three hitherto unknown perovskite-like compounds: $[H_3NOH]PbI_3$ ($\alpha = 0.90(9)$), $[N_2H_5]PbI_3$ ($\alpha = 0.91(2)$) and $[(CH_2)_3NH_2]PbI_3$ ($\alpha = 0.98(0)$). A fourth compound, $[C_3N_2H_5]PbI_3$ has a tolerance factor close to the borderline ($\alpha = 0.99(7)$) and is likely to exist in a perovskite structure. The preparation of hydroxylammonium and hydrazinium based compounds is particularly exciting (although experimentally challenging) as they exhibit similar tolerance factors to the high-efficient photovoltaic material $[(CH_3)NH_3]PbI_3$ ($\alpha = 0.91(2)$). A further predicted compound, $[NH_2(CH_2)NH_2]Mn(HCOO)_3$, was reported during writing this paper,[31] underlining the utility of our concept.

Conclusion

In conclusion, we have defined a consistent set of effective ionic radii for organic and molecular ions which we then used to estimate tolerance factors for organic–inorganic hybrid perovskites of lead iodides and manganese formates. The methodology is also applicable to related hybrid families, for example cyanides and azides, and the excellent agreement between calculated tolerance factors and experimental structural observations bodes well for future efforts to identify promising amine–metal–anion combinations. So far, the limitations of tolerance factors for hybrid materials are not yet clear, but we expect that this study will encourage further research in this field, taking us one step closer to the ambitious goal of designing materials with distinct physical properties.

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