

Ordered B-site vacancies in an ABX_3 formate perovskite

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Abstract: We report the synthesis and structural characterisation of a series of aliovalently doped metal–formate ABX_3 perovskite frameworks $[C(NH_2)_3]Mn_{1-x}^{2+}(Fe_{2x/3}^{3+}, \square_{x/3})(HCOO)_3$ (\square = B-site vacancy). For sufficiently large x , the vacancies order, lowering the crystal symmetry from orthorhombic $Pnna$ to monoclinic $P2/n$. This system establishes B-site vacancies as a new type of defect in formate perovskites, and one with important chemical, structural, and functional implications. Monte Carlo simulations driven by a nearest-neighbour vacancy repulsion model show checkerboard vacancy order to emerge for $x > 0.6$, in accord with experiment.

Molecular perovskites—coordination polymers with the ABX_3 perovskite stoichiometry and topology—are an important contemporary materials family, as they combine the well-established functionality of the perovskite structure type with the mechanical and compositional flexibility of metal–organic frameworks (MOFs).^{1,2} The organic lead–halide and formate perovskites are probably the best known examples—the former famous for its efficient photovoltaic response, and the latter favoured for its variety of magnetic, dielectric, and ferroelectric behaviour.^{1,3–6}

For conventional inorganic perovskites, the inclusion of vacancies within the ABX_3 structure type has been a crucially important design tool. By way of example, A-site vacancies allow for intercalation chemistry (whether reductive or inert)^{7,8} and negative thermal expansion;^{9,10} vacancies on the X-site can give rise to fast ion conductors,¹¹ and relate the perovskite structure to that of high- T_c superconductors such as $YBa_2Cu_3O_{7-\delta}$.¹² B-site vacancies are much rarer in oxide perovskites, but the discovery of efficient hole transport properties in Cs_2SnI_6 ($\equiv Cs(Sn_{1/2}\square_{1/2})I_3$) has helped refocus attention on this compositional degree of freedom in the halide analogues.¹³ Indeed this family has recently been extended to include the molecular systems A_2PtI_6 (A = organic monocation).¹⁴ The particular motivation for developing B-site vacancy chemistry comes from the prospect for exploiting such vacancies to tune B-site oxidation state, promote low-coordination intercalation, and/or amplify anion–anion interactions.¹⁵

Given the recent discovery that B-site cation substitution is straightforwardly achieved in formate perovskites, we were interested to establish whether this family might support B-site vacancies. An obvious strategy is to employ B^{n+} cations with charges $n > 2$: since the organic A-site cation is nearly always monovalent, charge balance could be achieved by reducing the B-site occupancy to $2/n$. Yet there are relatively few reported examples of formate perovskites containing trivalent B-site cations (and none, of which we are aware, with higher charge states). It is known, for example, that B^{2+} can be substituted for an equimolar mixture of (ordered) B^+/B^{3+} ,^{16–18} but this has the same average charge state and so does

not of course give rise to vacancies. Alternatively, small amounts ($< 15\%$) of Cr^{3+} and other trivalent cations have been included in some dimethylammonium formate perovskites, but in all known cases charge balance is achieved not by incorporating B-site vacancies but by replacement of the A-site cation by neutral formic acid molecules.^{19,20} This resembles the mechanism for charge compensation in oxide perovskites, where aliovalent substitution is usually accompanied by the formation of A-site vacancies. In the formates, higher levels of trivalent substitution $> 15\%$ have so far led to a charge-ordered niccolite structure, rather than A- or B-site deficient perovskites.^{21–25}

It was in this context that we explored aliovalent doping of guanidinium ($C(NH_2)_3^+$) metal–formate perovskites. Guanidinium is noteworthy in the context of hybrid formate perovskites for forming a particularly strong set of six hydrogen bonds with its surrounding formate anions.^{26,27} This contrasts the much weaker cation–framework interactions in dimethylammonium metal formates: the dimethylammonium cation is relatively small and only forms weak hydrogen bonds, resulting in dynamical disorder when encapsulated in either a niccolite or perovskite cage.^{3,27} Guanidinium formates retain orientational order at all accessible temperatures.²⁷ Hence we reasoned that these systems may allow stabilisation of the perovskite topology to larger defect concentrations than is otherwise possible.

We prepared a series of polycrystalline samples of formula $[C(NH_2)_3]Mn_{1-x}^{2+}(Fe_{2x/3}^{3+}, \square_{x/3})(HCOO)_3$ (nominal composition $x_{nom} = 0, 0.05, 0.1, 0.2, \dots, 1.0$) by adapting the method reported in Refs. 26,28. Compositions were determined by atomic absorption spectroscopy (AAS); we found the true values (denoted x) to deviate significantly from the x_{nom} , and so the former is used hereafter. The rapid precipitation methodology we used, together with the absence of any visible colour change, collectively suggest that there was no substantial autoreduction of Fe^{3+} to Fe^{2+} during synthesis.

Using synchrotron powder X-ray diffraction measurements, we explored the phase behaviour of the entire solid solution (see SI for details). We found the endmember $[C(NH_2)_3]Mn(HCOO)_3$ (**1**) to crystallise with orthorhombic $Pnna$ symmetry, as reported in 26. On increasing Fe^{3+} content, this symmetry persists until $x \simeq 0.6$ [Fig. 1(a)]. Beyond this point, the crystal symmetry is lowered from $Pnna$ to the maximal subgroup $P2/n$, as evidenced by the appearance of reflections forbidden in $Pnna$ but allowed in $P2/n$. A non-standard setting of $P2/n$ ($\equiv P2/n11$) is used to allow direct comparison of the unit-cells between the two phases. Group-theoretical analysis gives that the symmetry lowering from $Pnna$ to $P2/n$ must be driven by checkerboard ordering of distinct species at the B-sites. In the case of the Fe-rich endmember $[C(NH_2)_3]Fe_{2/3}(HCOO)_3$ (**2**), for example, this implies that the B-site Fe occupancy alternates between two different values. The relatively narrow peak profiles suggest that whatever drives this symmetry lowering does not lead to any significant strain.

A candidate structural model for **2** could then be derived from

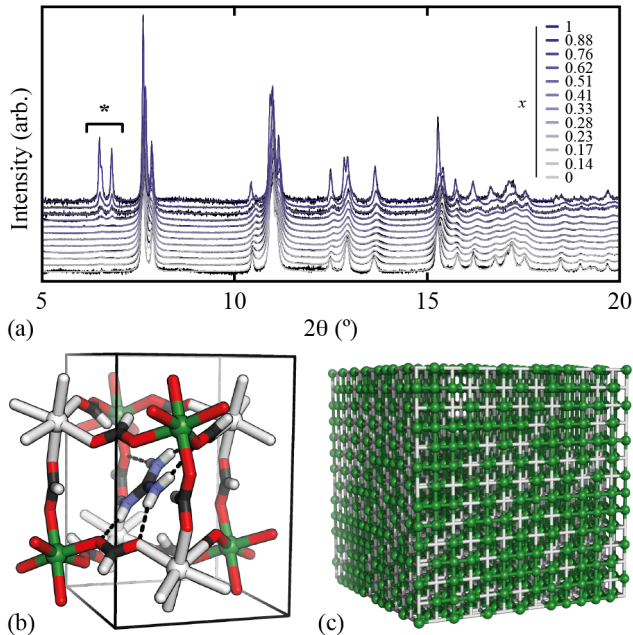


Figure 1. (a) Experimental powder X-ray diffraction patterns (black lines, $\lambda = 0.8248300(1)$ Å) and Pawley refinement fits (coloured lines) as a function of composition x in $[\text{C}(\text{NH}_2)_3]\text{Mn}_{1-x}(\text{Fe}_{2x/3}, \square_{x/3})(\text{HCOO})_3$. The additional peaks marked by an asterisk are characteristic of symmetry lowering from $Pnna$ to $P2_1/n$, which we find to occur for $x \geq 0.6$. (b) Structural model for **2** discussed in the text. C atoms in black, H in white, N in blue, and O in red. Fully- and partially-occupied Fe sites shown as green and white octahedral nodes, respectively. In the non-standard $P2_1/n11$ setting, the b axis is vertical and the c axis is approximately horizontal. (c) Representative Fe occupancy distribution in **2** as determined by MC simulations: green and white sites indicate Fe centres and vacancies, respectively. Our analysis is not sensitive to the presence or otherwise of formate anions (although from charge balance and hydrogen-bonding perspectives we anticipate few X-site vacancies).

that of **1** (Ref. 26) but with two alternating B-site Fe occupancies of 100% and 33% [Fig. 1(b)]. This model gave an excellent match to our experimental diffraction pattern in Rietveld refinements even without any refinement of the atomic coordinates [see SI]. Alternative models, *e.g.* containing A-site vacancies, do not have the correct crystal symmetry and could not account for our data. Hence our measurements suggest that $[\text{C}(\text{NH}_2)_3]\text{Fe}_{2/3}\square_{1/3}(\text{HCOO})_3$ contains a substantial fraction of B-site vacancies. Indeed the total defect concentration of 33% exceeds that of many other defective metal–organic frameworks and coordination polymers,^{29–32} including even the family of Prussian blue analogues, where as many as one in six B-site cations is missing.^{33–35}

Pawley refinements then allowed us to track structural changes throughout the entire solid solution as Mn^{2+} is replaced by a combination of Fe^{3+} and vacancies [Fig. 1(a)]. The dominant effect is a variation of the normalised cell volume, which first decreases by $\sim 2\%$ within the $Pnna$ phase and subsequently increases for $x \geq 0.6$, just as vacancy order emerges and the crystal symmetry lowers to $P2_1/n$ [Fig. 2]. This deviation from Vegard’s-law behaviour suggests strong effective interactions between the B-site substituents, with anti-clustering of Fe dopants indicated by the volume reduction for maximum mixing ($x \sim 0.5$).³⁶ That both endmembers have very similar molar volumes (231.66(2) and 231.88(3) Å³ for $x = 0$ and 1, respectively) means that the effective radius at the vacant B-site is larger than that of Mn^{2+} , since $r(\text{Fe}^{3+}) < r(\text{Mn}^{2+})$. We cannot rule out the possibility that small neutral species, such as H_2O , reside in the vacant B-sites.

Having established the presence of B-site vacancies in

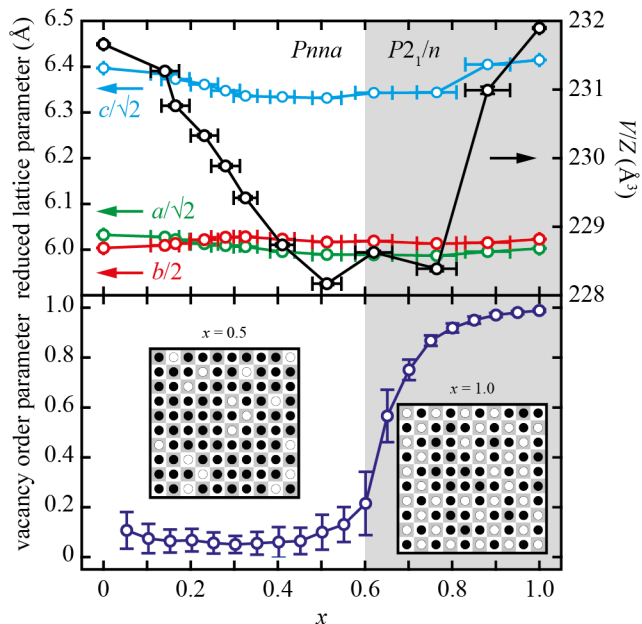


Figure 2. Variation in (top) experimental lattice parameters and reduced cell volume, and (bottom) MC vacancy order parameter with composition x . The transition from disordered $Pnna$ to ordered $P2_1/n$ vacancy arrangements occurs for $x \simeq 0.6$ in both cases. Insets show representative MC simulation sections for $x = 0.5$ and 1.0; occupied (vacant) B-sites as black (white) circles, with underlying lattice sites as alternating white and grey tiles. For low x , both types of lattice site contain vacancies; for $x \gtrsim 0.6$ vacancies are distributed on only one sublattice (here, grey).

$[\text{C}(\text{NH}_2)_3]\text{Mn}_{1-x}(\text{Fe}_{2x/3}, \square_{x/3})(\text{HCOO})_3$, we sought to understand the mechanism of vacancy ordering for $x \geq 0.6$. Since vacancies carry an effective negative charge relative to the average 2+ charge state of the perovskite B-site, we reasoned that short-range vacancy–vacancy repulsions may be the most physical driving force for vacancy order. To test this hypothesis we carried out a series of Monte Carlo (MC) simulations for different B-site vacancy fractions spanning the experimental values of 0–33% ($x = 0$ –1). Our MC configurations represented a $14 \times 14 \times 14$ supercell of the aristotypic perovskite cell. Vacancies of a fixed number were initially distributed randomly throughout these supercells. The configurational energy was determined as a simple sum of the number of nearest-neighbour vacancy–vacancy pairs. We used a combined MC / simulated annealing approach to find a ground state configuration for each vacancy concentration. In seeking to interpret our experiment results in terms of these ground state structures, our assumption is that the actual energy penalty associated with forming vacancy pairs is large with respect to ambient temperature (*i.e.* $\gg 2.5$ kJ mol⁻¹). Our simulations show that long-range vacancy order emerges spontaneously for vacancy concentrations $\gtrsim 20\%$ (*i.e.* $x \gtrsim 0.6$). This order splits the B-sites into two symmetry-inequivalent sites, which alternate throughout the lattice and correspond to cation occupancy fractions of 1 and $(1 - 2x/3)$ [Fig. 2]. So this simple model can account for the emergence and nature of vacancy order observed experimentally.

The additional stabilisation mediated by supramolecular hydrogen-bonding interactions likely explains the retention of the perovskite network even in the absence of a large fraction of B-site cations. Taking into account the guanidinium–formate hydrogen bonds, the network structure of **2** is fully connected in three-dimensions, irrespective of the arrangement of Fe atoms on the vacancy-rich B-site [see Fig. 1(c) for a representation of vacancy distributions in **2**]. These results suggest that guanidinium metal–formates should might reasonably be considered

as supramolecular, rather than covalent, frameworks. We note that guanidinium is known for forming a range of supramolecular frameworks, including perovskite-like systems.^{37,38}

The B-site vacancies we identify have several implications for the structural and functional behaviour of the metal–formate perovskites. First, as the metal centres in $[\text{C}(\text{NH}_2)_3]\text{Mn}_{1-x}^{2+}(\text{Fe}_{2x/3}^{3+}\square_{x/3})(\text{HCOO})_3$ are diluted by vacancies, any properties depending on coupling between neighbouring B-site cations are naturally affected. This is relevant to cooperative magnetic and orbital order, for example, both of which are important features of formate perovskite physics.^{28,39–41} Second, the hybrid perovskite family might now be extended to accommodate a larger variety of trivalent cations, which in principle allows for the synthesis of lanthanide-containing analogues and, in turn, new luminescent materials. Third, we expect that B-site vacancies will allow transport phenomena not usually associated with hybrid perovskites. For example, the intercalation of small cations onto the B-site could accompany reduction of Fe^{3+} to Fe^{2+} . Noting the octahedral coordination of Na^+ by formate in $\text{NaMn}(\text{HCOO})_3$,⁴² one might infer the accessibility of mixed-valent Na^+ -intercalated species such as $[\text{C}(\text{NH}_2)_3]\text{Na}_{1/3}\text{Fe}_{2/3}^{2+/3+}(\text{HCOO})_3$. Likewise the proton conductivity behaviour of other formates⁴³ might be enhanced by exploiting cation vacancies. Fourth, we would expect different mechanical and thermal expansion properties in defective and stoichiometric systems.^{44–47} In this context, we note that the network of guanidinium and formate ions in **2** form a herringbone pattern, which is a motif often associated with anomalous elastic phenomena.^{48–50} And, fifth, the symmetry-lowering effect of vacancy order might be exploited to drive hybrid improper ferroelectricity *via* coupling to other distortions, such as orientational order of the A-site cations.^{51,52}

Our results highlight the intriguing chemistry present at the intersection of MOF and perovskite chemistry. Both types of compounds are able to host substantial number of vacancies, yet with different manifestations. Metal–organic frameworks and coordination polymers show a broad variety of defects,^{53–56} but reports of metal vacancies as a result of mixed valence are rare.⁵⁴ The prototypical example of a defective MOF is UiO-66,^{57,58} where the missing-cluster defects aggregate into compositional nanoregions.^{32,59} In oxide perovskites, mixed-valent solid solutions are ubiquitous, yet the charge compensation is more commonly achieved through vacancies on the A-site, rather than the B-site.^{60,61} Here, we have demonstrated how mixed valence in a metal–organic framework with the perovskite architecture results in partially ordered vacancies on the metal B-site. The homogenous vacancy distribution contrasts with the compositional nanoregions of iso-valent mixed-metal systems.^{62,63} The high concentration of metal vacancies is facilitated by the guanidinium cation and its strong hydrogen bonding interactions with the anionic formate X-site species. Our results have important implications for the functional response of these materials and suggest that strong hydrogen bonding can play a key role in stabilising a particular structure type.

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