

The same and not the same: molecular perovskites and their solid-state analogues

Received 00th January 20xx,
Accepted 00th January 20xx

Gregor Kieslich^a and Andrew L. Goodwin^b

DOI: 10.1039/x0xx00000x

Dedicated to the 70th birthday of Anthony K. Cheetham, FRS

www.rsc.org/

There has been enormous interest in ABX₃ perovskite-type materials where at least one ion, usually A or X, is replaced with a molecular building unit. In this Minireview we highlight the unique properties that arise as a result of these molecular building units, drawing on topical examples of the recent literature. We focus in particular on phenomena related to low energy lattice modes that tie the molecular building-units to the fascinating properties observed in molecular perovskites.

Introduction

The perovskite motif is ubiquitous throughout the most important areas of solid-state chemistry, from high- T_c superconductors¹ to (multi)ferroics.² Indeed it is difficult to find an equally diverse structure-motif that has impacted the evolution of materials chemistry and condensed-matter physics in such a profound manner. In this context, it is perhaps unsurprising that amongst the enormously diverse family of hybrid inorganic-organic frameworks of recent interest^{3–5} it is those with perovskite-like structures that have risen to particular prominence. In this article, we ask the natural question: what are the key similarities and differences between these hybrid perovskites and their inorganic parents?

Before addressing the characteristics of this emerging class, we consider first the perovskite motif itself in more general terms. For us, it is advantageous to describe the perovskite structure as a ReO₃-type lattice, formed by the B cation and the X anion. In this lattice type, [BX₆][−] octahedra share corners in three dimensions generating a framework with cubic (α -Po) topology. The A cation occupies the dodecahedral void of the framework and further charge balances the structure (Figure 1a).

In hybrid inorganic–organic perovskites, the perovskite architecture is essentially maintained, while at least one ion – usually A and/or X – is replaced by a molecular unit. The coordination of the B-cation remains octahedral, subject to distortions as a result of *e.g.* Jahn-Teller activity or disorder. A striking example is the family of lead halide perovskites, including the compounds [CH₃NH₃]PbI₃ and [(NH₂)₂CH]PbI₃,^{6,7} which is the basis of a new paradigm in the area of photovoltaic research.⁸ Another important family includes formate- and

azide-based perovskites,⁹ such as [(CH₃)₂NH₂]Zn(HCOO)₃ and [CH₃NH₃]Mn(N₃)₃. These have been of significant interest for their dynamic behaviour; *e.g.*, remarkable ferroelectric-to-paraelectric phase transitions, glassy phase transitions and multiferroic properties at low temperatures.^{10–12} The long-studied family of Prussian blue analogues (PBAs), A_xM[M'(CN)₆]_y, with A an alkali metal cation and M and M' divalent or trivalent transition-metal cations, can also be viewed as defective perovskites with molecular building-units. The term “*molecular perovskites*” describes all these contemporary systems, serving to highlight the use of molecular components on the A- and/or X-sites. In effect, it is the presence of these molecular building-unit which in turn leads to exceptional material properties.

To begin, we ask simply why is it that perovskites have become so successful? The key is surely the compositional flexibility of the perovskite lattice, as captured by Goldschmidt's geometric concept of ionic Tolerance Factors,¹³ with the Tolerance Factor equal to $(r_A + r_X)/\sqrt{2}(r_B + r_X)$ and r_i being the radii of ions in the perovskite formula ABX₃, and $i = A, B$ and X , respectively. In the 20s, Goldschmidt showed that all perovskites known at the time exhibited a Tolerance Factor between 0.8 and 1. Later on, the tolerance factor concept proved useful not only in predicting the existence of perovskite structures, but also in establishing their propensity to distort. For example, systems with Tolerance Factors close to 1 tend to adopt highly symmetric structures, whilst decreasing the Tolerance Factor by *e.g.* using smaller A-site cations decreases the symmetry due to tilting of the [BX₆][−] octahedra. It was Glazer in the 70s – and later Howard and Stokes in the 90s – who systematically analysed octahedral tilting.^{14,15} The manipulation of these tilts (so-called ‘tilt-engineering’) as a mechanism of controlling macroscopic polarisation and/or magnetisation is an area of intense current interest.¹⁶

Goldschmidt's concept can also be applied to molecular perovskites, suggesting a similarly significant role for packing density on the formation of molecular perovskites.^{17,18}

^a Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, Garching, GER.

^b Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK.

However, additional factors coming from the increased chemical complexity (*e.g.* hydrogen bonding interactions and entropic contributions^{19–23}) gain in importance and factors that govern the formation of molecular perovskites are still being explored. For instance, in the case of significant covalent contributions in the ReO_3 -type framework, *e.g.* in $[\text{CH}_3\text{NH}_3]\text{PbI}_3$, the concept of ionicity becomes less applicable and it can be useful to apply corrections accordingly.²⁴ When looking at molecular perovskites more closely, it is convenient to distinguish between materials with an inorganic ReO_3 -type lattice (I^3O^0) and materials in which molecular building units form the framework (I^0O^3).²⁵ Figure 1b. Glazer tilt systems still hold for I^3O^0 -type perovskites, whilst additional tilts are now accessible in I^0O^3 -type perovskites. For instance, neighbouring octahedra in I^0O^3 molecular perovskites are separated by molecular building-units and are not corner-shared anymore. This allows for the occurrence of ‘forbidden’ tilting modes, *e.g.* as found in some Prussian Blue analogues, azides, formates or dicyanometallates, in which neighbouring octahedra rotate in the same way as each other.^{26–28}

The introduction of molecular linkers on the X-site has an important consequence on the nature of the chemical bonding present in the ReO_3 -type framework. When X is a single ion, *e.g.* I^- or O^{2-} , strong covalent and/or ionic interactions are present, thereby facilitating the formation of an extended electronic band structure (electronic conductivity) or magnetic interactions (magnetism). In the case of X being a molecular linker (I^0O^3), *e.g.* CN^- or HCOO^- , coordination bonds are present, which favour electron localisation and reduce magnetic exchange. So most molecular perovskites are band-gap insulators, and any magnetic exchange interactions are weak; *e.g.* in formate based frameworks magnetic order occurs only below ~ 50 K.²⁹ From a phenomenological viewpoint, it is also important to note that presently only molecular linkers with a single negative charge are known, constraining the oxidation states of all other ions.

So despite the common topology of molecular perovskites and their solid-state analogues, their chemical interactions and, as we will see, the physics and chemistry related to them, can be significantly different. Therefore, we have chosen the title of this manuscript — “*The same and not the same*” — inspired by Hoffmann’s text.³⁰ In the following we focus on the impact of molecular building-units on the links between structure and function in molecular perovskites, drawing on topical examples from recent literature.

Polar order in molecular perovskites

In the study of molecular perovskites, a significant focus has been on cooperative order of molecular dipole orientations in the context of ferroelectrics. Since the discovery of ferroelectricity in Rochelle salt by Valasek,³¹ the phenomenon has remained a property of substantial importance with particular recent emphasis on its coupling to other order parameters, *e.g.* magnetization or strain. Ferroelectricity describes the reversible change of polarization upon the application of an electric field. Prerequisite for the response is

an acentric space-group and a unique axis, which leads to a spontaneous electric polarization in the material. This polarization is the ‘anchor’ on which the electric fields can ‘hook’. This phase transition is related to symmetry-breaking processes, occurring when the material is cooled.

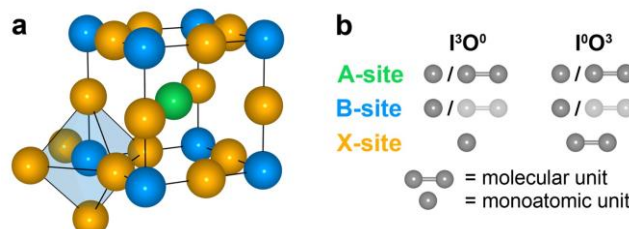


Figure 1. Shown is the perovskite architecture (a) in which $[\text{BX}_6]$ octahedra form a ReO_3 -type framework with the A-site cation located in the dodecahedral void of X-site anions. In (b) the general possibilities for creating a I^3O^0 and I^0O^3 lattice are visualised. Note that yet no perovskite with a molecular B-site unit is known; however, the existence of such chemical complex perovskites should not be excluded.

What symmetry-breaking mechanisms can operate in molecular perovskites? An intuitive example is related to chemical interactions between the positively charged A-cation and the negatively charged ReO_3 -type framework—an interaction inherently absent in solid-state perovskites. For instance, at high temperatures both compounds $[\text{NH}_3\text{NH}_2]\text{Mn}(\text{HCOO})_3$ and $[\text{CH}_3\text{NH}_3]\text{Mn}(\text{HCOO})_3$ crystallise in the centrosymmetric space-group $Pnma$.³² On cooling $[\text{NH}_3\text{NH}_2]\text{Mn}(\text{HCOO})_3$ transforms to a polar structure with space-group symmetry $Pna2_1$, while $[\text{CH}_3\text{NH}_3]\text{Mn}(\text{HCOO})_3$ remains in $Pnma$ at all temperatures. On examining both structures, the origin of this difference in behaviour becomes clear. At high temperatures, the NH_2 -group of $[\text{NH}_3\text{NH}_2]^+$ in $[\text{NH}_3\text{NH}_2]\text{Mn}(\text{HCOO})_3$ is disordered between two positions. When the temperature is lowered, the NH_2 -group locks in, thereby eliminating a mirror plane and forcing the space-group to change to $Pna2_1$. Qualitatively the phase transition can be seen as a balance between enthalpic and entropic contributions.¹⁹ The subtle chemical differences of $[\text{NH}_3\text{NH}_2]^+$ and $[\text{CH}_3\text{NH}_3]^+$ have a rather large consequence in this case, pointing out challenges, as well as the additional freedom the experimentalists possess to design new materials with fascinating (coupled) ordering phenomena. Other polar ordering mechanisms in molecular perovskites involve multipolar order of the A-cation, such as those present in the guanidinium cation. Recently it has been shown that when multipolar order is combined with orbital order, *e.g.* arising due to a Jahn-Teller distortion, net polarization of the material can be enforced in molecular perovskites.³³

The case of $[\text{CH}_3\text{NH}_3]\text{PbI}_3$

After discussing the phenomena of polar order, we now turn our attention to lead halides, in which polar order together with a dynamic lattice seemingly lead to exceptional photovoltaic properties. Amongst molecular perovskites, it is in fact the family of lead halides such as $[\text{CH}_3\text{NH}_3]\text{PbI}_3$ and $[(\text{NH}_2)_2\text{CH}]\text{PbI}_3$ that has attracted the largest research community.³⁴ The

enormous interest in their photovoltaic properties has led to a thorough understanding of these materials within a short amount of time. Yet many open questions remain. For simplicity, we confine our discussion to the ambient-temperature phase of $[\text{CH}_3\text{NH}_3]\text{PbI}_3$, although similar conclusions can be drawn with respect to related compounds. In the crystallographic description of $[\text{CH}_3\text{NH}_3]\text{PbI}_3$, $[\text{CH}_3\text{NH}_3]^+$ is 8-fold disordered due to symmetry requirements enforced by the tetragonal space-group at room temperature. Early permittivity measurements showed that $[\text{CH}_3\text{NH}_3]\text{PbI}_3$ can be described by a polar liquid approach,³⁵ owing to the reorientation of $[\text{CH}_3\text{NH}_3]^+$ within the lead iodide framework. It is now clear that the movement of the dipoles is not independent and local dipolar coupling occurs, leading to (anti)ferroelectric domains.^{36,37} This finding is itself of interest, although the question remains how such motions and coupling phenomena impact the properties. To further discuss these questions, we must turn our attention to the PbI_3 -framework. Evidence for large-amplitude atomic displacements in single crystal diffraction measurements, together with the results of molecular dynamics simulations, reveal a remarkably dynamic PbI_3 framework. Moreover, high-energy-resolution inelastic X-ray scattering has revealed dynamic tilting modes of PbI_6 octahedra, which are coupled to the movement and dynamics of $[\text{CH}_3\text{NH}_3]$.³⁸ This coupling appears to originate from hydrogen-bonding interactions between the A-cation and negatively charged PbI_3^- framework.³⁹ $[\text{CH}_3\text{NH}_3]^+$ is not expected to directly influence the electronic properties, *e.g.* $[\text{CH}_3\text{NH}_3]^+$ has no contributions to the band edges of the material, while coupling might contribute to the dynamics of the PbI_3^- lattice and therewith to a rather dynamic band structure as suggested by *ab initio* molecular dynamic simulations.⁴⁰ Interestingly, indications of coupled motions have been found in both $[\text{CH}_3\text{NH}_3]\text{PbBr}_3$ and CsPbBr_3 ,⁴¹ implying a role of Pb^{2+} lone pairs in the dynamics of the octahedra. However, the origin of the coupling in CsPbBr_3 is likely related to an off-centre displacement of Cs^+ that reflects the intrinsic dipole present in $[\text{CH}_3\text{NH}_3]^+$. It is the dipolar nature of molecular $[\text{CH}_3\text{NH}_3]^+$, and more importantly the dipolar coupling of neighbouring $[\text{CH}_3\text{NH}_3]^+$ molecules, that is implicated in the low-energy lattice modes observed in lead iodide perovskites. The remarkable photovoltaic properties of these systems are surely linked to these phenomena,⁴² but the precise mechanism remains an important open question.⁴³

NTE in Prussian Blue analogues

Arguably the longest-known molecular perovskite is the classic coordination compound Prussian Blue, $\text{K}_x\text{Fe}_{1-y}(\text{CN})_3 \cdot z\text{H}_2\text{O}$.⁴⁴ As in other molecular perovskites, low-energy dynamics are now known to be a recurring feature in the physics of PBAs,⁴⁵ linking PBAs to the aforementioned discussed topics. Although of intense recent interest for a range of applications, from solid electrolytes⁴⁶ to catalysis,⁴⁷ we focus here on the counterintuitive phenomena of negative thermal expansion (NTE) of PBAs. In contrast to A-site molecular perovskites it is the X-site that leads to NTE in PBAs. NTE itself is not only

fascinating from a fundamental viewpoint but also technologically relevant as it can compensate for the more usual positive thermal expansion (PTE). In *invar*, a Fe-Ni alloy, and some perovskite-type materials NTE arises from electronic or magnetic transitions.⁴⁸ In 'classical' NTE systems such as ZrW_2O_8 or ReO_3 ,⁴⁹ NTE is understood in terms of low-energy vibrations of M-O-M' units. Transverse motion of the oxygen atom reduces the M...M' distance, resulting in NTE if this vibration can propagate throughout the crystal at sufficiently low energy cost.⁵⁰ The molecular nature of the CN^- unit in PBAs makes a crucial difference because contraction of M-CN-M' motifs can result from two different types of local vibration: transverse displacement of the whole CN^- ion onto one side of the M...M' axis and CN^- rotation such that C and N atoms move towards opposite sides of the axis.⁵¹ Hence NTE is relatively common amongst PBAs. For instance, $\text{CdPt}(\text{CN})_6$ is even a better NTE material ($\alpha = -10 \text{ MK}^{-1}$) than ZrW_2O_8 ($\alpha = -9.1 \text{ MK}^{-1}$), and is far superior to conventional NTE perovskites such as ReO_3 ($\alpha = -0.7 \text{ MK}^{-1}$).^{49,52} Even more remarkable effects have been reported for defective PBAs such as $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$ ($\alpha = -39.6 \text{ MK}^{-1}$).⁵³ The chemical versatility of this family means thermal expansion can be controlled in interesting ways: $\text{Fe}[\text{Co}(\text{CN})_6]$ has near-zero thermal expansion ($\alpha = -1.5 \text{ MK}^{-1}$),⁵⁴ and $\text{Zn}[\text{Pt}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ switches from PTE to NTE on varying x .⁵² Recent calculations show that the low-energy lattice modes responsible for NTE in PBAs can involve both conventional (Glazer-type) octahedral tilts and 'columnar shifts'. This new form of NTE mode is only possible in molecular perovskites of the I^0O^3 type, and appears to be important also in the phase behaviour of various formate- and azide-based molecular perovskites.^{26,55}

Concluding remarks

At this point we can confidently conclude that the predominance of low-energy lattice modes that originate in molecular building-units is the key to understand the fascinating properties of molecular perovskites. Consequently, phenomena related to (vibrational) entropy^{19,56} which can be oftentimes directly manipulated by the choice of the A-cation are emphasised, as shown above for disorder-order transitions, vibrational mechanisms for electron/hole separation and NTE.

When looking forward, we strongly believe that the perovskite-story is far from finished. On the contrary, we have started a new chapter: low energy lattice modes directly impact the thermal conductivity behaviour, thus making molecular I^3O^0 perovskites attractive for thermoelectrics. Other potentially interesting fields include mechanocalorics, dielectrics and piezoelectrics. At the same time, the additional degrees of freedom in molecular perovskites give access to new ways of manipulating and breaking crystal symmetries, offering the opportunity of engineering polarisation via molecular orientations, shifts and Jahn-Teller distortions. In this context we believe that the community requires a common language – similar to Glazer notation – which then can be the foundation and preface of a new chapter in the story of (molecular) perovskites.

Acknowledgments

The title is inspired by the book “The same and not the same” of Roald Hoffmann, who turns 80 in 2017.

References

- J. G. Bednorz and K. A. Müller, *Zeitschrift für Phys. B Condens. Matter*, 1986, **64**, 189–193.
- M. Fiebig, T. Lottermoser, D. Meier and M. Trassin, *Nat. Rev. Mater.*, 2016, **1**, 16046.
- H. H.-M. Yeung, Y. Wu, S. Henke, A. K. Cheetham, D. O'Hare and R. I. Walton, *Angew. Chemie Int. Ed.*, 2016, **55**, 2012–2016.
- P. Lloveras, E. Stern-Taulats, M. Barrio, J.-L. Tamarit, S. Crossley, W. Li, V. Pomjakushin, A. Planes, L. Mañosa, N. D. Mathur and X. Moya, *Nat. Commun.*, 2015, **6**, 8801.
- M. J. Cliffe, W. Wan, X. Zou, P. a Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert and A. L. Goodwin, *Nat. Commun.*, 2014, **5**, 4176.
- D. Weber, *Z. Naturforsch. B*, 1978, **33**, 1443–1445.
- C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, **52**, 9019–9038.
- M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science (80-.)*, 2012, **338**, 643–647.
- W.-J. Xu, Z.-Y. Du, W.-X. Zhang and X.-M. Chen, *CrystEngComm*, 2016, **18**, 7915–7928.
- T. Besara, P. Jain, N. S. Dalal, P. L. Kuhns, A. P. Reyes, H. W. Kroto and A. K. Cheetham, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 6828–6832.
- P. Jain, V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby, N. S. Dalal, H. W. Kroto and A. K. Cheetham, *J. Am. Chem. Soc.*, 2009, **131**, 13625–13627.
- Z. Wang, K. Hu, S. Gao and H. Kobayashi, *Adv. Mater.*, 2010, **22**, 1526–1533.
- V. M. Goldschmidt, *Naturwissenschaften*, 1926, **14**, 477–485.
- A. M. Glazer, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 3384–3392.
- C. J. Howard and H. T. Stokes, *Acta Crystallogr. Sect. B Struct. Sci.*, 1998, **54**, 782–789.
- M. J. Pitcher, P. Mandal, M. S. Dyer, J. Alaria, P. Borisov, H. Niu, J. B. Claridge and M. J. Rosseinsky, *Science (80-.)*, 2015, **347**, 420–424.
- G. Kieslich, S. Sun and A. K. Cheetham, *Chem. Sci.*, 2014, **5**, 4712–4715.
- G. Kieslich, S. Sun and A. K. Cheetham, *Chem. Sci.*, 2015, **6**, 3430–3433.
- K. T. Butler, A. Walsh, A. K. Cheetham and G. Kieslich, *Chem. Sci.*, 2016, **7**, 6316–6324.
- G. Kieslich, A. C. Forse, S. Sun, K. T. Butler, S. Kumagai, Y. Wu, M. R. Warren, A. Walsh, C. P. Grey and A. K. Cheetham, *Chem. Mater.*, 2016, **28**, 312–317.
- D. B. Mitzi, in *Progress in Inorganic Chemistry, Volume 48*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 1999, pp. 1–121.
- J.-H. Lee, N. C. Bristowe, P. D. Bristowe and A. K. Cheetham, *Chem. Commun.*, 2015, **51**, 6434–6437.
- J. Li and P. Rinke, *Phys. Rev. B*, 2016, **94**, 45201.
- W. Travis, E. N. K. Glover, H. Bronstein, D. O. Scanlon and R. G. Palgrave, *Chem. Sci.*, 2016.
- A. K. Cheetham, C. N. R. Rao and R. K. Feller, *Chem. Commun.*, 2006, 4780.
- H. Boström, J. A. Hill and A. Goodwin, *Phys. Chem. Chem. Phys.*, 2016.
- J. A. Hill, A. L. Thompson and A. L. Goodwin, *J. Am. Chem. Soc.*, 2016, **138**, 5886–5896.
- S. G. Duyker, J. A. Hill, C. J. Howard and A. L. Goodwin, *J. Am. Chem. Soc.*, 2016, **138**, 11121–11123.
- K.-L. Hu, M. Kurmoo, Z. Wang and S. Gao, *Chem. - A Eur. J.*, 2009, **15**, 12050–12064.
- R. Hoffmann, *The same and not the same*, Columbia University Press, 1997.
- J. Valasek, *Phys. Rev.*, 1921, **17**, 475–481.
- S. Chen, R. Shang, B.-W. Wang, Z.-M. Wang and S. Gao, *Angew. Chemie Int. Ed.*, 2015, **54**, 11093–11096.
- N. L. Evans, P. M. M. Thygesen, H. L. B. Boström, E. M. Reynolds, I. E. Collings, A. E. Phillips and A. L. Goodwin, *J. Am. Chem. Soc.*, 2016, **138**, 9393–9396.
- H. J. Snaith, *J. Phys. Chem. Lett.*, 2013, **4**, 3623–3630.
- N. Onoda-Yamamuro, T. Matsuo and H. Suga, *J. Phys. Chem. Solids*, 1992, **53**, 935–939.
- J. M. Frost, K. T. Butler and A. Walsh, *APL Mater.*, 2014, **2**, 81506.
- A. M. A. Leguy, J. M. Frost, A. P. McMahon, V. G. Sakai, W. Kochelmann, C. Law, X. Li, F. Foglia, A. Walsh, B. C. O'Regan, J. Nelson, J. T. Cabral and P. R. F. Barnes, *Nat. Commun.*, 2015, **6**, 7124.
- A. N. Beecher, O. E. Semonin, J. M. Skelton, J. M. Frost, M. W. Terban, H. Zhai, A. Alatas, J. S. Owen, A. Walsh and S. J. L. Billinge, *ACS Energy Lett.*, 2016, **1**, 880–887.
- K. T. Butler, K. Svane, G. Kieslich, A. K. Cheetham and A. Walsh, *Phys. Rev. B*, 2016, **94**, 180103.
- A. L. Montero-Alejo, E. Menéndez-Proupin, D. Hidalgo-Rojas, P. Palacios, P. Wahnón and J. C. Conesa, *J. Phys. Chem. C*, 2016, **120**, 7976–7986.
- O. Yaffe, G. Yinsheng, L. Z. Tan, D. A. Egger, T. Hull, C. C. Stoumpos, F. Zheng, T. F. Heinz, L. Kronik, M. G. Kanatzidis, J. S. Owen, A. M. Rappe and M. A. Pimenta, *arxiv:1604.08107v3*, 2017.
- M. Sendner, P. K. Nayak, D. A. Egger, S. Beck, C. Müller, B. Epding, W. Kowalsky, L. Kronik, H. J. Snaith, A. Pucci and R. Lovrinčić, *Mater. Horiz.*, 2016, **3**, 613–620.
- J. M. Frost and A. Walsh, *Acc. Chem. Res.*, 2016, **49**, 528–535.
- K. R. Dunbar and R. A. Heintz, in *Progress in Inorganic Chemistry, Volume 45*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 1996, pp. 283–391.
- A. L. Goodwin and C. J. Kepert, *Phys. Rev. B*, 2005, **71**, 140301.
- H.-W. Lee, R. Y. Wang, M. Pasta, S. Woo Lee, N. Liu and Y. Cui, *Nat. Commun.*, 2014, **5**, 5280.
- A. Peeters, P. Valvekens, R. Ameloot, G. Sankar, C. E. A. Kirschhock and D. E. De Vos, *ACS Catal.*, 2013, **3**, 597–607.

- 48 M. Van Schilfgaarde, I. a Abrikosov and B. Johansson, *Nature*, 1999, **400**, 1–4.
- 49 K. Takenaka, *Sci. Technol. Adv. Mater.*, 2012, **13**, 13001.
- 50 M. T. Dove and H. Fang, *Reports Prog. Phys.*, 2016, **79**, 66503.
- 51 A. L. Goodwin, *Phys. Rev. B*, 2006, **74**, 134302.
- 52 A. L. Goodwin, K. W. Chapman and C. J. Kepert, *J. Am. Chem. Soc.*, 2005, **127**, 17980–17981.
- 53 S. Adak, L. L. Daemen, M. Hartl, D. Williams, J. Summerhill and H. Nakotte, *J. Solid State Chem.*, 2011, **184**, 2854–2861.
- 54 K. W. Chapman, P. J. Chupas and C. J. Kepert, *J. Am. Chem. Soc.*, 2006, **128**, 7009–7014.
- 55 I. E. Collings, J. A. Hill, A. B. Cairns, R. I. Cooper, A. L. Thompson, J. E. Parker, C. C. Tang and A. L. Goodwin, *Dalt. Trans.*, 2016, **45**, 4169–4178.
- 56 G. Kieslich, S. Kumagai, K. T. Butler, T. Okamura, C. H. Hendon, S. Sun, M. Yamashita, A. Walsh and A. K. Cheetham, *Chem. Commun.*, 2015, **51**, 15538–15541.