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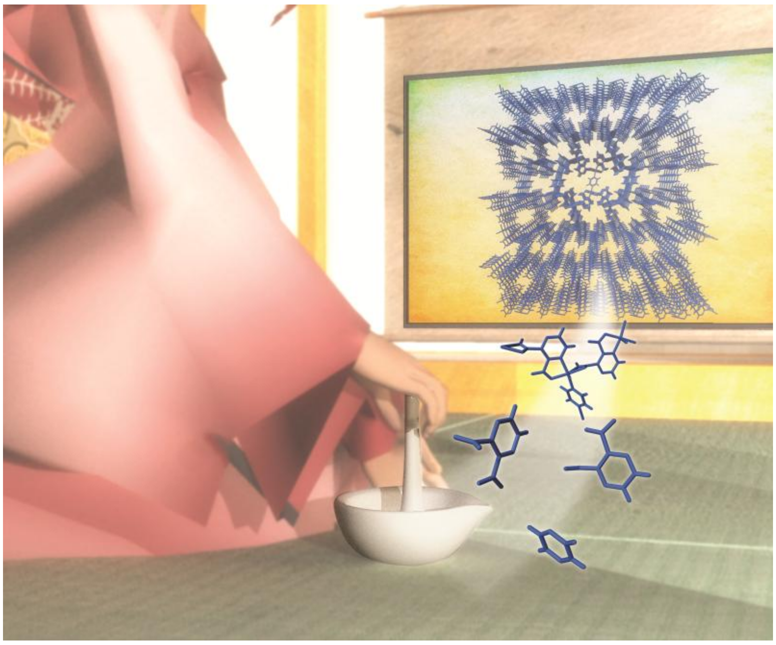

Articles in this issue include:

Communications

Highly oriented surface-growth and covalent dye labeling of mesoporous metal–organic frameworks
Florian M. Hinterholzinger, Stefan Wuttke, Pascal Roy, Thomas Preuße, Andreas Schaate, Peter Behrens, Adelheid Godt and Thomas Bein

Papers

Supramolecular isomers of metal–organic frameworks: the role of a new mixed donor imidazolate-carboxylate tetradentate ligand
Victoria J. Richards, Stephen P. Argent, Adam Kewley, Alexander J. Blake, William Lewis and Neil R. Champness

Hydrogen adsorption in the metal–organic frameworks Fe_2(dobdc) and $Fe_2(O_2)$(dobdc)
Wendy L. Queen, Eric D. Bloch, Craig M. Brown, Matthew R. Hudson, Jarad A. Mason, Leslie J. Murray, Anibal Javier Ramirez-Cuesta, Vanessa K. Peterson and Jeffrey R. Long

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COMMUNICATION

Influence of ligand field stabilization energy on the elastic properties of multiferroic MOFs with the perovskite architecture†‡

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We report the mechanical properties of four isostructural metal–organic frameworks (MOFs) that adopt the ABX_3 perovskite topology: $[(CH_3)_2NH_2]M(HCOO)_3$, where M = divalent Mn, Co, Ni, and Zn. Their Young's moduli were measured *via* single-crystal nanoindentation. We show that the mechanical stability of such isostructural frameworks with octahedral coordination increases with greater ligand field stabilization energy (LFSE).

In the past decade there has been intense growth in the field of hybrid framework materials, which opens up new possibilities for discovering unique properties that may not be found in purely inorganic or organic systems.[1] One major subclass of hybrid materials is the metal–organic frameworks (MOFs), whose extended 3-D structures are constructed from metal ions (or metal ion clusters) bridged by multifunctional organic linkers.[2] Given that the majority of MOFs are indeed nanoporous, they are primarily aimed at potential applications concerned with gas storage, separations, catalysis, drug delivery, *etc.*[3] Very little attention, however, has been devoted to the development of MOFs with ferroic and multiferroic properties, although such materials can be of immense technological importance.[4,5] Single-phase multiferroic materials are believed to be rare, even amongst purely inorganic compounds,[6] though recent findings on rare-earth manganites[7] suggest that they may be more common than hitherto thought.

Earlier candidates of multiferroic MOFs display questionable structural stability under ambient conditions, because they rely on weakly bound guest molecules (especially low boiling point solvents, *e.g.* water, methanol and ethanol)[8] entrapped within their nano-sized cavities to accommodate electrical ordering at low temperatures. Recently, some of us have reported a new class of multiferroic MOF material that adopts the ABX_3 perovskite architecture (Fig. 1): dimethylammonium metal formate or DMMF; $[(CH_3)_2NH_2]M(HCOO)_3$, where M = divalent metal cation.[4] As depicted in Fig. 1, DMMF features MO_6 octahedra linked by formate ion ($HCOO^-$) bridges to form a ReO_3-type cavity, in which the dimethylammonium cation [DMA^+ = $(CH_3)_2NH_2^+$] is located at the centre. Notably, previous studies have revealed that DMA^+ is disordered at room temperature, but cooperative ordering occurs upon cooling (*ca.* 160–190 K).[4,9] Additionally, unlike typical open-framework MOFs, there is no solvent accessible volume (*SAV*) present within DMMF. As such, DMMF is deemed to be structurally more robust, not only because the hybrid framework is essentially dense,[10] but also the nature of its electrical ordering is intrinsic to the parent structure and thereby independent of extra guest molecules. Whilst the multiferroic properties of DMMF have been systematically characterized in the last few years,[4,9,11] their mechanical behaviour has not yet been reported, though basic information about their structural stability when subjected to mechanical stresses is crucially important for practical applications.

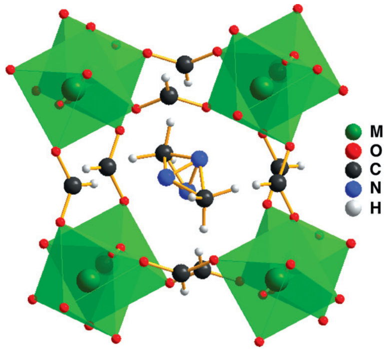

Fig. 1 Crystal structure of DMMF, featuring the ABX_3 perovskite architecture in which A = $(CH_3)_2NH_2^+$, B = M^{2+} transition metal cation, and X = $HCOO^-$. Under ambient conditions, DMA^+ at the centre of the cavity is disordered *viz.* the nitrogen atom can occupy three equivalent positions with same probability; this is the result of disordered hydrogen bonding (N–H···O $\simeq$ 2.9 Å).

In the present work, we have studied the elastic properties of DMMF single crystals by means of nanoindentation. The availability of good quality single crystals (Fig. 2 and Fig. S1†) presented us with the interesting opportunity to compare the Young's moduli (E) of four isostructural DMMF materials that

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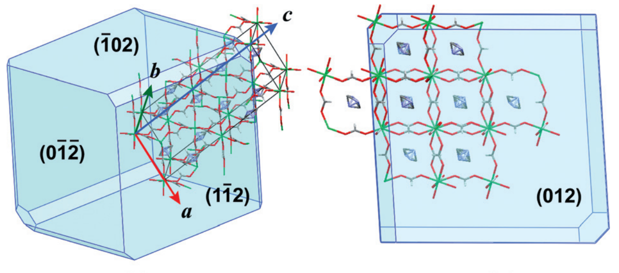
† Electronic supplementary information (ESI) available: Optical micrographs of the pseudo-cubic DMMF single crystals suitable for nanoindentation studies. Additional correlations to solvate volumes and enthalpy of solvation. See DOI: 10.1039/c2dt12300b

‡ DMMF single crystals used in this study were synthesized *via* solvothermal reactions following the methods previously reported.[4] Their X-ray crystallographic files (CIFs) can be obtained from the Cambridge Crystallographic Data Centre CCDC 703288, 246991 to 246993.



(a) (b)

Fig. 2 (a) Typical morphology of the DMMF single crystals, illustrating the predominant crystal facets and orientation of the rhombohedral unit cell ($R\bar{3}c$ space group) in relation to the pseudo-cubic crystal habit. (b) View down the (012) facet, highlighting orientation of the underlying framework structure (*NB.* Stick representation, colour code as in Fig. 1).

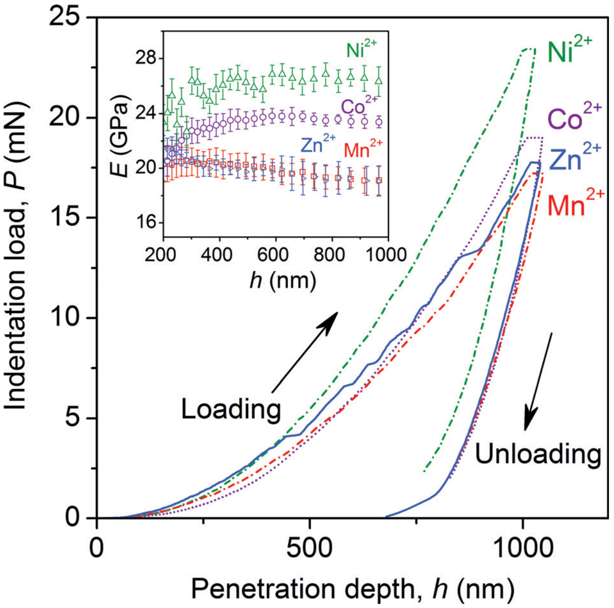


Fig. 3 Nanoindentation load–displacement (P–h) curves showing the typical response of the DMNiF, DMCoF, DMZnF and DMMnF single crystals when indented on the {012}-oriented facets. Note that the Zn compound exhibits "pop-ins" or displacement bursts;[12,13] inspection of the residual indents under the optical microscope indicates that this phenomenon is linked to surface cracking. The inset presents the Young's modulus data of the four isostructural frameworks as a function of surface penetration depths; the moduli appear to be independent of depth beyond the first 300 nm. Here the Poisson's ratio (ν) was taken as 0.3.[14] The error bars denote standard deviations of ten individual indents.

differ only in terms of their transition metal cations, of which M = Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}.

Nanoindentation experiments on the pseudo-cubic single crystals of DMMF (Fig. 2a) were conducted under ambient conditions by employing a three-faced pyramidal (Berkovich) diamond tip. Dynamic-mode (CSM) depth-sensing measurements were carried out on the {012}-oriented crystal facets (Fig. 2b) to a maximum surface penetration depth of 1000 nm, under a constant strain rate of 0.05/s. The raw data collected (P–h curves in Fig. 3) were analysed according to the Oliver and Pharr method[15] to establish the Young's moduli (E) of different compounds. It is noted that such an approach has been previously applied successfully for probing the mechanical behaviour of a range of dense[13,14,16] and nanoporous[17,18] hybrid framework materials.

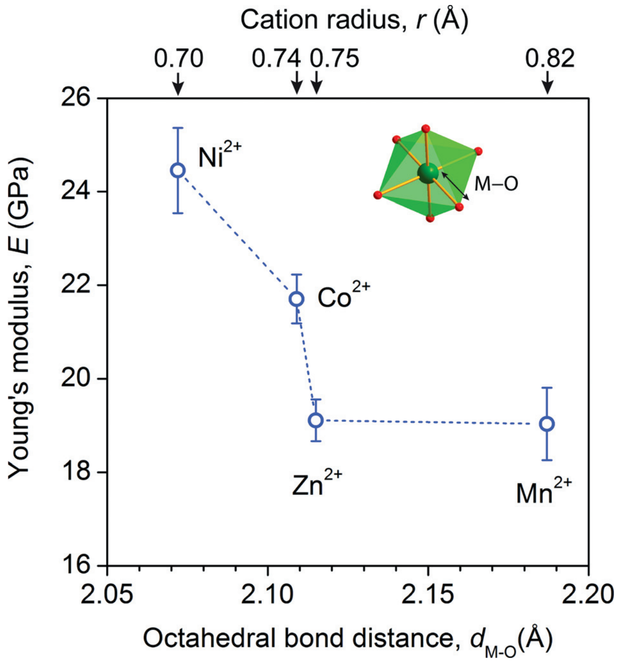


Fig. 4 Young's modulus (E) of the isostructural DMNiF, DMCoF, DMZnF and DMMnF compounds plotted against the transition metal–oxygen bond distances, $d_{\mathrm{M–O}}$ (inset). The experimental E values were averaged from nanoindentation depths of 200–1000 nm (Fig. 3 inset). The cation radii[19] that correspond to coordination number of six appear at the top of the graph. As summarised in Table 1, the crystal field stabilization energy of octahedral fields increases in the order (Mn^{2+}(d^5) = Zn^{2+}(d^{10}) = 0) < Co^{2+}(d^7) < Ni^{2+}(d^8).[20] *NB.* Dashed lines serve as guides to the eye.

It can be seen from Fig. 3 that the representative load–displacement curves are distinct to each of the DMMF framework structures, when probed along the same crystallographic orientation. Given that the four compounds are in fact isostructural, the differential mechanical response evidenced here (with respect to maximum load and elastic strain recovery) must be the direct consequence of incorporating different divalent cations (M^{2+}) into the MO_6 octahedral site. The Young's moduli of the isostructural compounds are presented in the inset of Fig. 3; the framework structure of DMNiF was found to be the stiffest ($E \approx$ 25 GPa), whereas those of DMMnF and DMZnF are considerably more pliant and also relatively similar in magnitude ($E \approx 19$ GPa). In comparison, the stiffness of the DMCoF structure ($E \approx$ 22 GPa) is intermediate between those of its counterparts. Hence in relation to the Young's modulus of the DMMF frameworks encompassing different M^{2+} cations, our nanoindentation measurements reveal that the stiffness of the structure increases in the sequence $Mn^{2+} \approx Zn^{2+} < Co^{2+} < Ni^{2+}$ (see Fig. 4). To put our findings into perspective, the Young's modulus of DMMF (density, $\rho \approx 1.7$–1.9 g cm^{-3}) lies between those of highly porous MOFs containing large accessible porosity (typically $E \lesssim$ 9 GPa, $\rho \approx 0.9$–1.5 g cm^{-3})[17] and those corresponding to fully dense hybrid frameworks ($E \approx 30$–100 GPa, $\rho \gtrsim 2$ g cm^{-3}).[10]

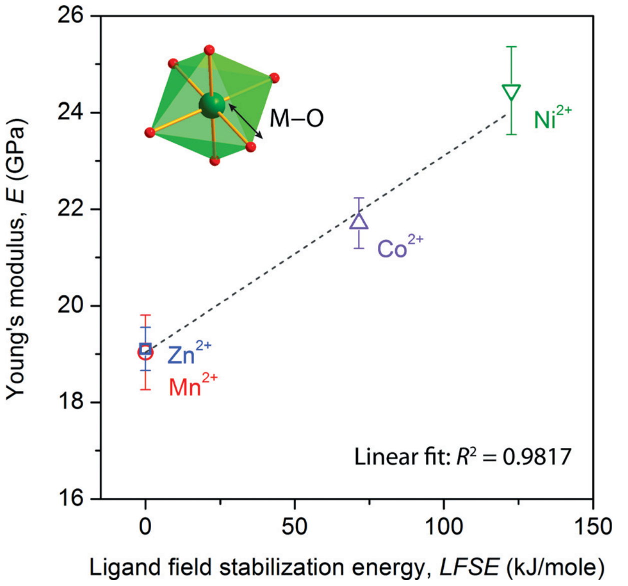


Fig. 5 Young's modulus of the isostructural DMMF structures as a function of LFSE (Table 1). The dotted line represents the best fit of the experimental data according to a linear correlation. Inset: M = Mn^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}. Correlations with respect to other chemical and thermodynamic properties are shown in Fig. S2.†

Table 1 Stabilization energy in octahedral fields corresponding to the different divalent cations in aquo complexes, in which their MO_6 coordination environment is reminiscent of those present in the DMMF compounds

Ion	Number of d-electrons	Octahedral field ground state	Stabilization energy[a] (kJ mole^{-1})
Mn^{2+}	5	$t_{2g}^3\ e_g^2$	0
Co^{2+}	7	$t_{2g}^5\ e_g^2$	71.5
Ni^{2+}	8	$t_{2g}^6\ e_g^2$	122.6
Zn^{2+}	10	$t_{2g}^6\ e_g^4$	0

[a] Crystal field theory data adapted from ref. 20.

The correlation between the elastic moduli of isostructural DMMF compounds and the identity of the divalent cation is presented in Fig. 4. The relationship is not as straightforward as expected. A simple dependence of the elastic moduli on the ionic radius was anticipated, but this is not found in DMMF. For example, it can be seen that Mn^{2+} and Zn^{2+} possess very different radii (the former is larger by ~9%), but both the DMZnF and DMMnF structures display almost identical stiffnesses (see Fig. 4). We have therefore focused on the role of ligand field stabilization energy (LFSE), as listed in Table 1; we note that the Young's modulus (E) of the Co^{2+} and the Ni^{2+} structures compared with Mn^{2+} and Zn^{2+} frameworks correlate very well with their respective stabilization energies. Fig. 5 further demonstrates the excellent correlation between the differential framework stiffnesses and the LFSE. It is also worth noting that as a consequence of ligand field stabilization, a distinct rise in the Young's modulus (~16%) between the Zn^{2+} and the Co^{2+} frameworks has been detected although their cation size differ by only ~1% (Fig. 4).

The elastic deformation of the DMMF frameworks includes contributions from distortions of the formate linker ($HCOO^-$), the MO_6 octahedra and the M–O–C bridging angle. However, with the exception of the MO_6 octahedra, these are the same in all four isostructural systems. The LFSE in the octahedral environment can therefore be thought of as representing a resistance against distortion of the MO_6 octahedra, thereby increasing the elastic stiffness of the framework structure. It is also worth highlighting that our current findings do not parallel the general trend established for silicate glasses, for which their elastic moduli (*i.e.* Young's, shear and bulk moduli) were found to systematically increase by decreasing the size of the divalent cations.[21] In this instance, the difference arises mainly because the cation in silicate glasses does not form part of the 3-D framework.

In conclusion, this study represents the first attempt to elucidate the mechanical behaviour of DMMF – a new class of multiferroic MOFs incorporating the ABX_3 perovskite architecture. Our study will complement the increasing number of reports[4,9,11] that hitherto focus only on their functional properties. Here we obtained the unexpected results that the elastic moduli of isostructural DMMF compounds are not straightforwardly correlated to the cation radius, but instead can be explained by taking into account their LFSE. We demonstrate that the Ni^{2+} structure exhibits the greatest mechanical stability (in elastic domain) by virtue of its strongest ligand field stabilization. Our current findings provide the fundamental understanding required for future investigations focusing on: (a) the effects of temperature and phase transitions on the mechanical response, (b) direct measurements of the elastic stiffness tensor (C_{ij}'s) for establishing the shear and bulk moduli, as well as the Poisson's ratio, (c) elastic–plastic transition by means of spherical nanoindentation, and (d) determination of fracture characteristics.

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