

Supporting Information

for

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

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Fig. S1 Optical micrographs showing the typical DMMnF single crystals with pseudo-cubic morphologies. Single crystals of other isostructural DMMF compounds also exhibit a similar crystal habit and dimensions (ca. 200–300 μm). The orientation of the crystals were established *via* single-crystal X-ray diffraction, with which $\{012\}$ was found to be the predominant facet. The method for mounting and preparing the crystals for nanoindentation studies, as well as detailed descriptions concerning the analysis of indentation data are available elsewhere.¹

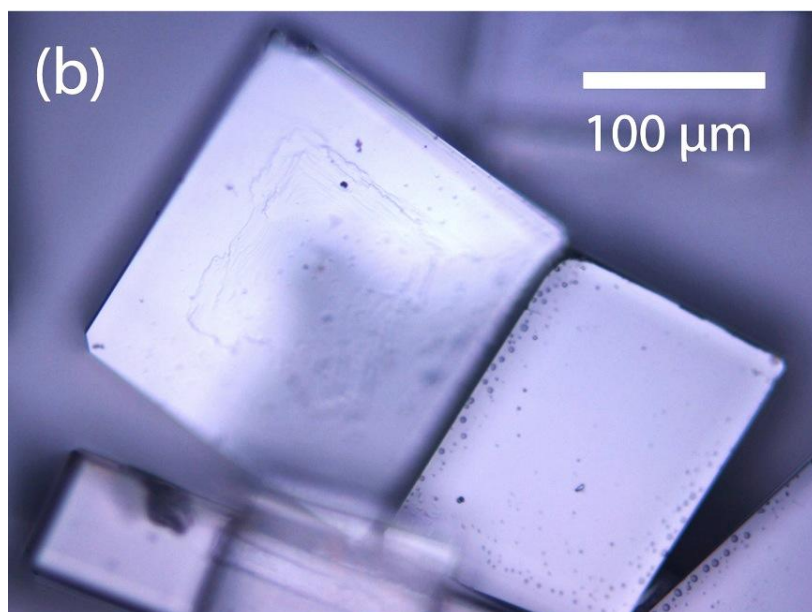
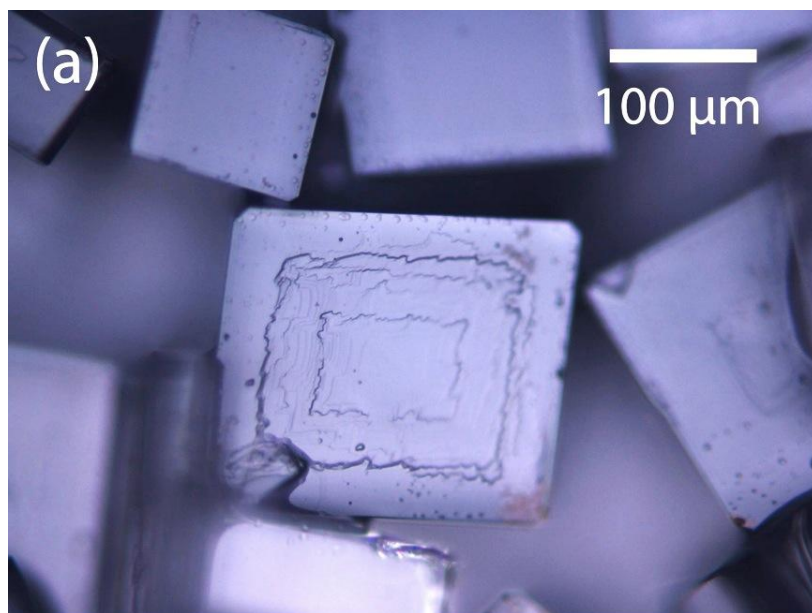
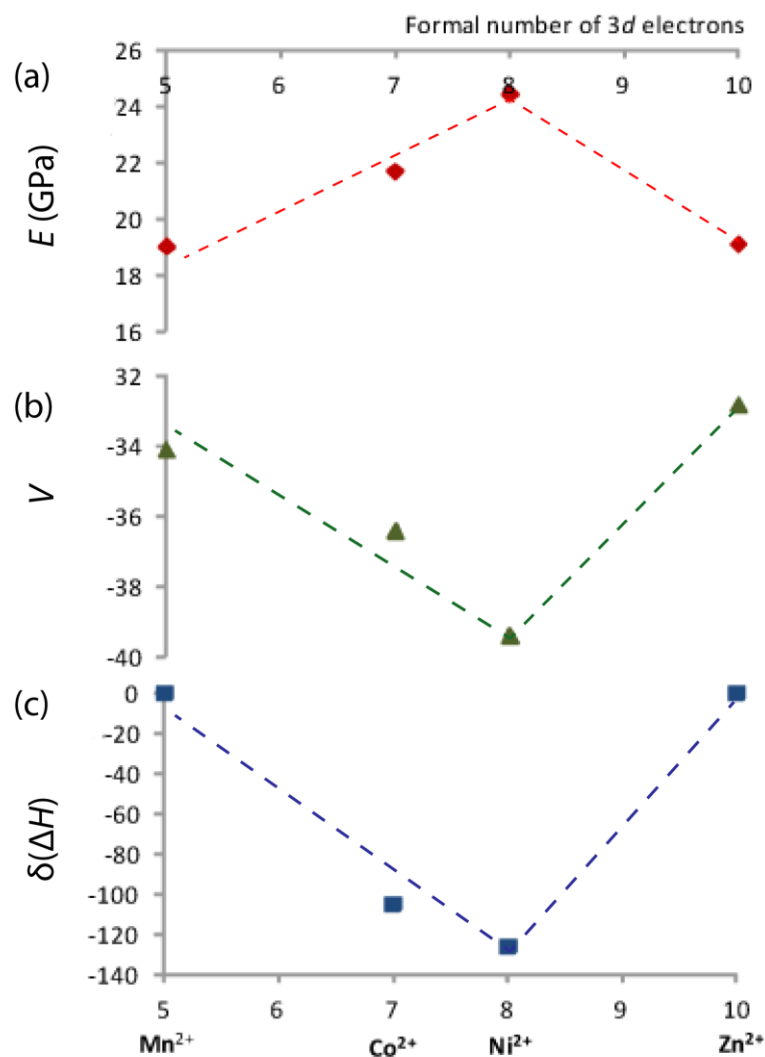


Fig. S2 (a) Young's moduli, E , of DMMF as a function of formal 3d orbital occupancy, presented alongside (b) partial molar volumes of $M(\text{DMSO})_6^{2+}$ solvates, V , and (c) ligand field contribution to the enthalpy of solvation, $\delta(\Delta H)$. The dotted lines serve as guides to the eye. *NB.* Plots and correlations presented below were contributed by Dr. M. Kosa.



It is interesting to compare the elastic mechanical response to other chemical and thermodynamic properties that are related to the nature of the metal-oxygen interactions in octahedral environment. For example, the partial molar volumes (V) of solvated octahedral cations, $M(\text{DMSO})_6^{2+}$ depend primarily on the metal-ligand interactions and thus are distinct for each member of the late 3d elements. The enthalpy of solvation, $\delta(\Delta H)$, could be correlated to the LFSE. The bonding scheme within the late 3d transition metal series is rather complex; in addition to LFSE, other factors such as the bond energetics, ionic vs. covalent contributions, and the energy curvature around the equilibrium can also contribute to the metal-ligand bond pattern, and thus to the differential elastic response.²

As shown in Fig. S2, the increasing stiffness of the metal-oxygen coordination environment upon going from Mn^{2+} to Ni^{2+} apparently results in greater enthalpy of solvation and this is accompanied by the decreasing solvate volumes. The Zn^{2+} octahedral environment is as compliant as that of Mn^{2+} , and this “softening” is reflected also in the molar volume and solvation energy of $\text{Zn}(\text{DMSO})_6^{2+}$.

References

1. J. C. Tan, C. A. Merrill, J. B. Orton and A. K. Cheetham, *Acta. Mater.*, 2009, **57**, 3481-3496; T. D. Bennett, A. L. Goodwin, M. T. Dove, D. A. Keen, M. G. Tucker, E. R. Barney, A. K. Soper, E. G. Bithell, J. C. Tan and A. K. Cheetham, *Phys. Rev. Lett.*, 2010, **104**, 115503; J. C. Tan, J. D. Furman and A. K. Cheetham, *J. Am. Chem. Soc.*, 2009, **131**, 14252-14254.
2. S. I. Gorelsky, L. Basumallick, J. Vura-Weis, R. Sarangi, K. O. Hodgson, B. Hedman, K. Fujisawa and E. I. Solomon, *Inorg. Chem.*, 2005, **44**, 4947-4960.