Giant Ferrimagnetism and Polarization In A Mixed Metal Perovskite Metal-Organic Framework

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Perovskite metal-organic frameworks (MOFs) have recently emerged as potential candidates for multiferroicity. However, the compounds synthesized so far possess only weak ferromagnetism and low polarization. Additionally, the very low magnetic transition temperatures (T_c) also pose a challenge to the application of the materials. We have computationally designed a mixed metal perovskite MOF -[C(NH_2)_3][Cu_0.5Mn_0.5(HCOO)_3]- that is predicted to have magnetization two orders of magnitude larger than its parent ([C(NH_2)_3][Cu(HCOO)_3]), a significantly larger polarization (9.9 μC/cm²), and an enhanced T_c of up to 56 K, unprecedented in perovskite MOFs. A detailed study of the magnetic interactions revealed a novel mechanism leading to the large moments as well as the increase in the T_c. Mixing a non-Jahn-Teller ion (Mn²⁺) into a Jahn-Teller host (Cu²⁺) leads to competing lattice distortions which are possibly responsible for the enhanced polarization. The MOF is thermodynamically stable as evidenced by the computed enthalpy of formation, and can likely be synthesized. Our work represents a first step towards rational design of multiferroic perovskite MOFs through the largely unexplored mixed metal approach.

Multiferroics are materials which possess ferromagnetic (FM), ferroelectric (FE) and structural order parameters within a single phase[1][8]. These are highly promising not only for their use in multi-functional device applications but also for the interesting physics they reveal. Much of the research in the field has so far focussed on multiferroics based on inorganic transition metal oxides. In the last decade, there has been growing interest in metal-organic frameworks (MOFs) consisting of metal ions interconnected by organic linkers. The organic-inorganic duality in MOFs leads to many interesting physical properties[9][10] that can be exploited in applications such as gas storage and separation, catalysis, nonlinear optics, photoluminescence, magnetic and electric materials, and so on[11][12]. The hybrid nature of these materials offers vast chemical space for synthetic chemists to explore and, hence, also affords tunability of properties. MOFs with the perovskite ABX₃ structure are of great interest, particularly those with multiferroic behavior arising due to hydrogen-bonds[13][14]. In the case of magnetic MOFs, for instance, one can control the nature of magnetic coupling through the variety of possible metal ions in the B-site, short ligands, co-ligands and radical ligands carrying spin degrees of freedom[15]. Recently, it has been shown that one can tune the magnitude of the ferroelectric polarization by carefully choosing different A-site cations in these MOFs[16].

In recent past, a new class of ABX₃ metal formates [C(NH₂)_3][M(HCOO)₃] (abbreviated below as M-MOF, M=divalent Mn, Fe, Co, Ni, Cu, and Zn), was experimentally synthesized[17]. Of these only the Cu-MOF crystallizes into a polar space group (Pnma₂) and exhibits multiferroic and magnetoelectric behavior. It has been reported that the Cu-MOF shows canted-spin anti-ferromagnetism with a Neel temperature of 4.6 K. Using first-principles calculations, Stroppa et al.[13] showed that this polar Cu-MOF has a polarization of 0.37 μC/cm² along with a weak magnetization. The polarization originates mainly from the displacements of the A-site organic cation induced by hydrogen-bonds between the guanidinium hydrogens and the oxygens of the formate linkers. The magnetization arises from the transition metal (TM) ion at the B-site, where in-plane anti-ferro orbital (AFO) ordering of Cu d-orbitals results in an anti-ferromagnetic (AFM) ground state with A-type spin ordering. The low values of the polarization and magnetization along with its low magnetic transition temperature (T_c) prevents the Cu-MOF from being practically useful. These intrinsic drawbacks can, in principle, be overcome by varying the A-site or B-site composition of the MOF. A mixed metal strategy for the B-site ion (or B-site doping) has proven to be successful in improving magnetic properties in inorganic multiferroic compounds[18][19]. The double-perovskites thus formed, with TM ions of differing d-orbital configurations, can not only result in larger magnetization but can also enhance the strength of the exchange coupling interactions pushing the transition temperature higher. However, only a few studies have so far appeared that explore this strategy[20][23]. In particular, B-site doping in perovskite MOFs aimed at improving ferroic properties is nascent[24][26]. Moreover, to the best of our knowledge, there are no theoretical predictions of mixed metal perovskite MOFs. First-principles based theory can not only help identify potential candidates but also elucidate the key mechanisms driving ferroic orders in these MOFs.

In this study, we have employed first-principles DFT-based techniques to investigate the potential of mixed metal perovskite MOFs - (M₀.₅M₀.₅)-MOF- as multiferroic materials. In particular, we propose a novel mixed metal MOF - (Cu₀.₅Mn₀.₅)-MOF - which not only yielded a magnetic moment two orders of magnitude larger than the parent Cu-MOF but also a significantly larger transition temperature. The combination of Mn²⁺ and Cu²⁺ was chosen deliberately keeping in mind the similarity in sizes of the ions as well as the fact the pair represents the largest different in magnetic moments possible on a ferrimagnetic lattice. Indeed, the proposed MOF was found to have a magnetization of 4 μB per Cu-Mn pair (or 2μB/TM) which is the largest among mixed metal magnetic MOFs synthesized so far. Since the parent Cu-MOF has a Jahn-Teller (JT) ion (Cu²⁺), mixing in a non-JT
ion (Mn$^{2+}$) would lead to competing lattice distortions which could significantly influence the dielectric properties as has recently been suggested [24]. Surprisingly, the polarization in the compound was significantly enhanced (9.9 $\mu$C/cm$^2$) compared to its parent. Furthermore, doping with Mn$^{2+}$ ions resulted in an enhancement of the exchange coupling between the TM ions. This in turn increased the magnetic transition temperatures to 24 K and 56 K, respectively, depending on the cation-ordering at the B-site. The computed formation energy indicates that the (Cu$_{0.5}$Mn$_{0.5}$)-MOF is thermodynamically stable and, in principle, can be synthesized. Our work highlights the potential of the largely unexplored mixed metal strategy towards improving the ferroic properties of perovskite MOFs.

Our spin-polarized DFT calculations employed a generalized gradient approximation (GGA) to the exchange-correlation functional through the PBE functional [27, 28]. We accounted for correlation effects in the 3$d$ TM ions using the plane-wave basis Quantum-ESPRESSO code [36] (see SI for details). All structures were fully optimized until forces were less than 0.26 meV/Å on each atom. In the results presented below all bond lengths are in angstrom (Å) and energies are reported in meV per TM (meV/TM).

The unit cell of Cu-MOF contains four formula units. We produced the (Cu$_{0.5}$Mn$_{0.5}$)-MOF by replacing two of the formula units by their Mn analogues. This can result in three kinds of cation ordering (D0, D1 and D2) as shown in Figure 1. Optimized energies of (Cu$_{0.5}$Mn$_{0.5}$)-MOF with all possible spin orderings were plotted with respect to various types of cation orderings. The following symbols are used for different types of cation orders: circles for the D0, squares for the D1, and diamonds for the D2 structures. A, C and G-type refer to various antiferromagnetic spin orderings while FM refers to a ferromagnetic one.

![Figure 1](image1.png)

FIG. 1. Optimized energies of (Cu$_{0.5}$Mn$_{0.5}$)-MOF with all possible spin orderings were plotted with respect to various types of cation orderings. The following symbols are used for different types of cation orders: circles for the D0, squares for the D1, and diamonds for the D2 structures. A, C and G-type refer to various antiferromagnetic spin orderings while FM refers to a ferromagnetic one.

Figure 1(a) shows the displacement of NH$_2$ groups providing charge balance in the compound. Like the parent Cu-MOF, each distorted Cu-O octahedron possesses two short (2.02, 1.99) and two long (2.44, 2.36) equatorial Cu-O$_{eq}$ bonds; and two medium (2.04, 2.02) axial Cu-O$_{ax}$ bonds. However, the Mn-O octahedra, with two long (2.22, 2.22) and two short (2.17, 2.21) equatorial bonds, are only slightly distorted. Thus, the Mn-O octahedra in D1-A closely resemble those in the parent Mn-MOF which crystallizes in a non-polar Pnma

![Figure 2](image2.png)

FIG. 2. Ball-and-stick model of two feasible structures of (Cu$_{0.5}$Mn$_{0.5}$)-MOF in different cation orderings: (a) the D1-A structure with alternating Cu and Mn planes perpendicular to the c-axis, and (b) the D0-G structure with rock-salt ordering of Cu and Mn. The Cu and Mn sublattices have opposite spins in either case, and units are connected by HCO$_{ax}$O$_{ax}$ and HCO$_{eq}$O$_{eq}$ units in the axial and equatorial directions, respectively. The two dashed line shows the displacement of NH$_2$ group of A-site cation forming two unequal (H(1)$_{eq}$O$_{eq}$ and H(2)$_{eq}$O$_{eq}$) bonds with the Cu and Mn octahedra sites, partially responsible for A-site polarization.

For each cation ordered structure we also investigated different collinear magnetic ordering of the Mn ($\mu_B$) and Cu ($\mu_B$) spin moments. These included three AFM arrangements (A, C, and G-type) and the ferromagnetic arrangement (FM) (SI-Figure S1(b)). The optimized energies for the various structures considered are summarized in the plot shown in Figure 1. The lowest energy structure consists of layers of Mn and Cu alternating along the c-axis with an A-type AFM arrangement of spins (referred to below as D1-A). A structure with rock-salt ordering of the TM ions and with a G-type AFM arrangement of their spins (referred to below as D0-G), was found to be higher in energy than D1-A by just 4.75 meV/TM. The formation energies computed for the D1-A and D0-G structures (-101 and -96.25 meV/TM, respectively) suggest that both can likely be synthesized. We focus on these two structures as they are magnetic in nature with moments comparable to inorganic compounds as shown below.
space-group. In the case of D0-G (Figure 2(b)), the bond-length variation around the Cu is the same as in D1-A. However, unlike in D1-A, the octahedra around Mn are strongly distorted with two short (2.03, 2.06), two long (2.18, 2.23) and two medium (2.08, 2.10) bonds. This is in contrast with the parent Mn-MOF where octahedral distortions arise only when the A site cation is changed[37]. Thus, compared to D0-G, D1-A is more stable since its layered structure allows the Mn-O octahedra to retain the undistorted structure seen in the parent.

The magnetic TM ions in the structure, linked by formate groups, interact with each other through long-distance super-exchange [38]. The density-of-states (DOS) plots for both D0 and D1 structure (see SI) shows Mn to be in the high-spin Mn$^{2+}$ ($d^5$) and Cu to be in the Cu$^{2+}$ ($d^9$) valence configurations. In both cases, the hole state from Cu forms a narrow band indicating spatial localization. Partial cancelation of moments between the two TM ions leads to a net magnetic moment of 4$\mu_B$/per Cu-Mn pair (or 2 $\mu_B$/TM) in both D1-A and D0-G. The predicted value is comparable to inorganic ferromagnets and higher than those generally seen in magnetic MOFs. In D1-A, the FM interaction in the Cu layer arises due to the AFO ordering of the Cu $d$-orbitals caused by the Jahn-Teller (JT) effect[13]. As a result, the hole in Cu alternates between the two $e_g$ orbitals from one Cu to its nearest neighbour, an effect also seen in the parent Cu-MOF. FM super-exchange interaction is mediated via a half-filled $e_g$ orbital on a Cu and a completely filled one on its neighbour in the same layer, as predicted by the Goodenough-Kanamori (GK)[39] rules. Surprisingly, however, the Mn layer also displays FM order defying the GK rules for a $d^5-d^9$ TM ion pair. Moreover, in the D0-G case, despite the octahedral distortions around both TM ions only AFM interactions prevail.

The predicted magnetic states for D0 and D1 structures can be rationalized with the help of the exchange coupling constants calculated[40] (see SI for details) for all TM pairs in the structures. The intra- and inter-plane coupling constants for D0-G are $J_{Cu-Mn}$ $\approx$ 4.6 meV and $J_{Cu-Mn}$ $\approx$ 2.53 meV, respectively. In D1-A, there are two in-plane ($J_{Cu-Cu}$ $\approx$ -0.9 meV, $J_{Cu-Mn}$ $\approx$ -0.5 meV) and one out-of-plane ($J_\perp$ $\approx$ 3.9 meV) coupling constants. We note that the Cu-Mn interactions are strongly AFM, consistent with the GK rules for a $d^5-d^9$ pair. Thus we get a G-type AFM ordering for the D0 structure irrespective of the JT distortions around Cu. In D1, the strong out-of-plane AFM exchange along with the AFO-driven FM ordering in the Cu layer, drives the Mn layer to be FM. This leads to the predicted A-type AFM ground state. The FM coupling between Cu ions is key to establishing such a ground-state.

From the magnitude of the coupling constants we anticipated a significant increase in the magnetic transition temperature ($T_c$) as the coupling constant is directly proportional[41] to $T_c$. Using classical Monte-Carlo simulations (see SI for details), we can predict the $T_c$ for the $Pmn2_1$-like phase of (Cu$_{0.9}$Mn$_{0.1}$)-MOF. Figure 5 shows the magnetic moment as well as the magnetic susceptibility plotted as a function of temperature for both structures. The plots indicate that the magnetic transition occurs at 24 K and 56 K for D1-A and D0-G, respectively. Thus the $T_c$ could be pushed up to 56 K through this mixed metal strategy. The predicted $T_c$ is a remarkable increase over that of the parent compound and is indicative of the enhanced stability of the ferrimagnetic phase in the (Cu$_{0.9}$Mn$_{0.1}$)-MOF relative to most other magnetic MOFs seen so far.

First-principles calculations on Cu-MOF have estimated a c-axis electric polarization of 0.37 $\mu C/cm^2$[13], while Mn-MOF was found to crystallize in a non-polar structure[17]. It has been suggested that the weak polarization can be tuned by varying the organic A-site cation[16] or by strain field[42].
Indeed, [CH$_3$CH$_2$NH$_3$][Mn(HCOO)$_3$] was found to yield a theoretical polarization of 1.6 $\mu$C/cm$^2$[10] with some contribution arising from octahedral distortion around Mn cations. While the B-site mixing strategy proposed here was aimed mainly at improving the magnetic moments, we also investigated the polarization of the predicted compounds. We calculated the electric polarization using a Berry phase approach[43] ensuring the convergence of the computed numbers with the relevant parameters (see SI). Surprisingly, we found that both D0-G and D1-A yielded a significantly enhanced c-axis polarization of -9.93 and -9.78 $\mu$C/cm$^2$, respectively, much higher than that (0.37 $\mu$C/cm$^2$) in the parent Cu-MOF. Both polar phases are more stable than their corresponding centric phase (assumed to be Pmna-like) by 1.5 and 1.8 eV/TA, respectively.

In Cu-MOF, it was shown[13] that the displacements of NH$_2$ groups of the guanidinium cations result in the dominant contribution to the ferroelectric polarization. In the ground-state of the (Cu$_{0.5}$Mn$_{0.5}$)-MOF, we also found that a large contribution arises from the A-site in addition to that from the B-site and formates. In order to estimate their relative magnitudes, we calculated the polarization arising from A-site displacements ($P_A$), B-site distortion ($P_B$) and the formates ($P_{X_3}$) separately by displacing each group towards its polar configuration keeping the others fixed in the non-polar geometry. We found the values $P_A = -7.8$, $P_B = -1.5$ and $P_{X_3} = 2.0 \mu$C/cm$^2$, respectively, indicating that the largest contribution is made by the distortions at the A-site. The discrepancy between the polarization estimated from these contributions (-7.3 $\mu$C/cm$^2$) and the exact value is likely due to the neglect of relaxation effects in the former. The precise origin of the large polarization is as yet unclear and currently under investigation.

In conclusion, we have designed, from first-principles, a mixed metal perovskite MOF, [C(NH$_3$)$_2$][Cu$_{0.5}$Mn$_{0.5}$](HCOO)$_3$] with significantly enhanced magnetization and a polarization compared to its parent Cu-MOF as well as other mixed metal MOFs synthesized so far[24]. We also predict that the ground state MOF would have a magnetic transition temperature of around 24 K which can be enhanced up to 56 K by altering the cation ordering in the B-site. This is a remarkable improvement over multirotro MOFs synthesized so far. Our calculations indicate large formation enthalpies for the compound in two lowest energy structures suggesting feasibility of laboratory synthesis. The ground-state structure is composed of layers of Mn and Cu alternating along the c-axis. A strong AFM Cu-Mn exchange coupling along with FM ordering in the Cu layer, driven by Jahn-Teller distortion, forces FM coupling in the Mn layer as well. This results in an A-type AFM ordered state with a magnetic moment of 2 $\mu_B$/TM. Changes in hydrogen-bonds at the A-site, distortions of the oxygen octahedra around Cu and Mn, as well as displacements of the formates contribute to the polarization enhancement. The competing magnetic interactions between the Cu and Mn layers suggest the possibility of magnetic and structural transitions with variation of relative composition[24] of the two TM ions as well as epitaxial strain. These will be the subjects of a future study.

Our choice of the TM ions as well as the feasibility of the mixed metal approach are motivated by the facts that, (i) polar [C(NH$_3$)$_2$][Cu(HCOO)$_3$] and [CH$_3$CH$_2$NH$_3$][Mn(HCOO)$_3$] have already been experimentally synthesized, and (ii) very recently[23], a mixed metal MOF with the same framework has been synthesized. Therefore, we expect that [C(NH$_3$)$_2$][Cu$_{0.5}$Mn$_{0.5}$](HCOO)$_3$ can also be realized. The strategy can be used to further explore other metal combinations in the (A$_2$BB$'X_6$) structure, along with variations in their compositions, to engineer the magnetic, electric[24] and even elastic[43] properties in this class of MOFs.

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