Ferroics

Coexistence of Three Ferroic Orders in the Multiferroic Compound [(CH₃)₄N][Mn(N₃)₃] with Perovskite-Like Structure

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Abstract: The perovskite azido compound $[(CH_3)_4N]$ $[Mn(N_3)_3]$, which undergoes a first-order phase change at $T_t = 310$ K with an associated magnetic bistability, was revisited in the search for additional ferroic orders. The driving force for such structural transition is multifold and involves a peculiar cooperative rotation of the $[MnN_6]$ octahedral as well as order/disorder and off-center shifts of the $[(CH_3)_4N]^+$ cations and bridging azide ligands, which also bend and change their coordination mode. According to DFT calculations the latter two give rise to the appearance of electric di-

Introduction

In the last ten years, obtaining new materials in which at least two ferroic orders (magnetic, electric, or elastic) coexist in the same phase has been a hot topic in solid-state chemistry and materials science.^[1] The reason for this interest lies not only in

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D	Supporting information (X-ray crystallographic data with selected bond length and angles, DSC curve as a function of temperature, details of the low-temperature crystal structure, magnetic susceptibility data versus tem- perature, and LeBail refinement of the powder X-ray diffraction pattern at room temperature) and the ORCID identification numbers for the authors of this article can be found under http://dx.doi.org/10.1002/ chem.201503445.

poles in the low-temperature (LT) polymorph, the polarization of which nevertheless cancels out due to their antiparallel alignment in the crystal. The conversion of this antiferroelectric phase to the paraelectric phase could be responsible for the experimental dielectric anomaly detected at 310 K. Additionally, the structural change involves a ferroelastic phase transition, whereby the LT polymorph exhibits an unusual and anisotropic thermal behavior. Hence, $[(CH_3)_4N]$ $[Mn(N_3)_3]$ is a singular material in which three ferroic orders coexist even above room temperature.

the scientific challenge they pose, but especially also in the huge technological potential of these multiferroic materials for applications such as information storage, spintronics, novel circuits, sensors, and high-power microwave applications.^[2,3] Nevertheless, because the conventional mechanisms for long-range electric order and cooperative magnetic ordering are mutually exclusive, examples of single-phase multiferroics are few.^[4,5]

These properties were traditionally sought in oxide materials. More recently, research has been extended to metal-organic frameworks (MOFs) and coordination polymers,^[6,7] since it is possible to construct frameworks by combination of different metal cations with bridging ligands and to include different guest molecules inside the cavities of the framework. Thus, such compounds can provide new and interesting properties that can coexist in the same material.

Dense MOFs with perovskite-like structure and formula [AmineH][$M(HCOO)_3$] (M^{2+} : divalent transition metal cation, AmineH⁺: mid-sized protonated amine) have been intensively studied as promising type-I multiferroic materials, as they simultaneously show electric and magnetic order. In these formates the former arises from order/disorder phenomena of the polar cations occupying the A sites of the perovskite architecture, which are linked to the framework through hydrogen bonds.^[8-12] The framework, based on [MO_6] octahedra that are connected through the short formate ligands, is responsible for their weak ferromagnetism at low temperatures.^[13-15]

Another related, yet much less explored, family of potentially interesting compounds is that of azido-bridged transition metal perovskites of formula [AmineH][$M(N_3)_3$]. In these compounds, the azide groups act as end-to-end (EE, μ -1,3-N₃)

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bridging ligands between the M cations (up to now monometallic with $M^{2+} = Mn^{2+}$, Ca^{2+} , $Cd^{2+[16-19]}$ or bimetallic with $M^{3+} = Cr^{3+}$, Fe^{3+} and M^+ : Na⁺, K⁺),^[20] giving rise to a 3D framework. The protonated amines (so far [(CH₃)_nNH_{4-n}]⁺, n = 1-4) are located in the resulting "pseudo"-cuboctahedral cavities.^[21,22]

In this family of azido perovskites, the Mn compounds $[(CH_3)_n NH_{4-n}][Mn(N_3)_3]$ (n = 1-4) show interesting magnetic properties: long-range antiferromagnetic order at considerably higher temperatures than the corresponding metal formate perovskites ($T_N \approx 66-96$ K, depending on the ammonium cation),^[17,18,21] and magnetic bistability near room temperature, related to a structural phase transition.^[21] On the other hand, the Cd compound [(CH₃)₄N][Cd(N₃)₃] displays a ferroelastic phase transition and dielectric relaxation,^[19] which has been related to dynamics of the guest molecules inside the framework. In addition, the bimetallic compounds $[(CH_3)_4N]_2[M'M''(N_3)_6] \ (M': \ Cr^{3+}, \ Fe^{3+}; \ M'': \ Na^+, \ K^+) \ exhibit$ a solid/solid structural phase transition induced by the successive displacements of the $[(CH_3)_4N]^+$ (TMA) guest cations and a subsequent abrupt order/disorder process of both the guest cations and the framework.^[20]

The above findings motivated us to revisit $[(CH_3)_4N][Mn(N_3)_3]$ in the search for additional ferroic orders. This Mn compound, which was one of the first members of this family of azido perovskites to be synthesized,^[17] is known to undergo a reversible structural transition at a rather high temperature (≈ 303 K). The high-temperature (HT) phase, which could not be initially solved,^[17] is cubic (space group (SG): $Pm\bar{3}m$) according to recent studies,^[21] and the LT phase is monoclinic. It was first described as noncentrosymmetric (SG: $P2_1$)^[17] and more recently as centrosymmetric (SG: $P2_1/m$).^[21] Such structural phase transition additionally induces a magnetic bistability at 303 K, which has been related to changes in the existing magnetic exchange interactions.^[20] This compound also shows 3D antiferromagnetic order below 70 K.^[17]

Moreover, the results we report herein, which we obtained mainly by means of variable-temperature single-crystal X-ray diffraction, DFT calculations, and dielectric measurements, reveal that $[(CH_3)_4N][Mn(N_3)_3]$ is a singular multiferroic material in which three ferroic orders (antiferroelectric, ferroelastic, and magnetic bistability) coexist even above room temperature.

Results and Discussion

Phase transition and structural details of the LT and HT polymorphs

Differential scanning calorimetry (DSC) confirmed that [(CH₃)₄N] [Mn(N₃)₃] undergoes a first-order reversible phase transition at $T_t \approx 303$ K on cooling and $T_t \approx 307$ K on heating (see Figure S1 of the Supporting Information), in agreement with the literature.^[18] The associated changes in enthalpy and entropy are $\Delta H \approx 6.33$ (heating), -6.45 J mol⁻¹ (cooling) and $\Delta S \approx 20.61$ (heating), -21.25 J mol⁻¹ K⁻¹ (cooling), respectively. Considering that for an order/disorder transition $\Delta S = R \ln N$, where *R* is the gas constant and *N* the ratio of the number of configura-

tions in the disordered and ordered system, $N \approx 12$ is obtained. This value is close to that reported for the related Cd compound [(CH₃)₄N][Cd(N₃)₃], which has $N \approx 11$.^[19]

Detailed single-crystal X-ray studies carried out at different temperatures above and below the phase transition revealed interesting new features of the HT and LT polymorphs, which are important to establish structure–property relationships for this compound. As expected, above T_t [(CH₃)₄N][Mn(N₃)₃] has a cubic perovskite structure (SG: $Pm\bar{3}m$), with cell parameter a_c =6.445(5) Å at 317 K (Figure 1a). In this HT structure the



Figure 1. Crystal structures of $[(CH_3)_4N][Mn(N_3)_3]$. a) HT polymorph (SG: $Pm\bar{3}m$). b) LT polymorph (SG: $P2_1/m$) with important structural changes that occur in the phase transition highlighted: the cooperative off-center shift of the TMA cations and *cis*-azide ligands, the cooperative rotation of the [MnN₆] octahedra, and the decrease of the *a* and *c* cell parameters with increase in *b*.

 Mn^{2+} cations, which occupy the B sites, sit at cube corner positions (0,0,0). The N atoms of the TMA cations (A cations) occupy the body-center position (1/2, 1/2, 1/2), and the C atoms show a large disorder over twelve different positions around the N atom. The bridging N₃⁻ ligands are linear, coordinate the Mn^{2+} cations in a *trans*-EE mode, and sit over the cubic edges of the unit cell with the central N atom in the mid-edge position (0,1/2,0), and the terminal N atoms are disordered over four positions. The obtained structural data, summarized in Tables SI and SII of the Supporting Information and in Figure 1a, are in agreement with those previously reported in the literature.^[21]

On crossing T_t (Figure S1 of the Supporting Information) the cubic HT phase transforms into the LT polymorph, which is monoclinic with SG $P2_1/m$ (no. 11), in agreement with the liter-



ature.^[21] As shown in Figure 1b, the unit cell of The LT polymorph shows a twofold superstructure along the *b* axis (cell parameters: $a_c \times 2a_c \times a_c$) and a small deviation of the angle β from 90°(β =90.013(3) at 290 K). The asymmetric unit contains one independent metal cation, three azide ligands, and one TMA cation. The obtained structural data, which are summarized in Figure 1 b and in Tables SI and SII of the Supporting Information, reveal that the LT polymorph exhibits remarkable changes compared to the HT polymorph. In contrast to the HT phase, in the LT polymorph the C atoms of the TMA cations are ordered and sit on a single crystallographic position (Figure 1 b). In addition, and most remarkably, the N atoms of these TMA cations are no longer located at the centers of the cavities but are shifted off-center inside the cavity along the $\langle 40\bar{7} \rangle$ and $\langle 407 \rangle$ directions by about 0.339 Å (see Figure 2 and Table SIII of the Supporting Information).



Figure 2. Visualization of the LT crystal structure of $[(CH_3)_4N][Mn(N_3)_3]$ as stacking of A and B slabs. a) Projection along the *b* axis showing the cooperative displacement of the TMA cations and the azide ligands along the same direction (ferrodisplacement) in the *ac* plane and b) projection along the *c* axis showing that the alternating stacking of A and B slabs along the *b* axis results in an antiferrodisplacement.

The magnitude of this displacement is more than five times larger than that reported for classical ferroelectric oxides such as $BaTiO_3$ and related compounds, even though in these oxides the B-site transition metal ion is the one that shifts.^[23] Furthermore, the displacement of the TMA cations in the structure is cooperative and follows an antiferrodistorsive pattern along the *b* axis and a ferrodistorsive one in the *ac* plane (see Figure 2).

Another interesting feature is that in the LT structure the $[Mn(N_3)_3]^-$ framework is considerably distorted. The octahedral environment of the Mn^{2+} cations is slightly elongated with

three different Mn–N distances (Table SII of the Supporting Information). Moreover, there is a very peculiar and interesting cooperative tilting of the [MnN₆] octahedra, which cannot exist in conventional ABO₃ perovskites and would correspond to a^+ b^-c^+ in the Glazer tilting system:^[24] adjacent octahedra display a cooperative in-phase rotation in the *ac* plane (all of them are rotated clockwise or counterclockwise), while along the *b* axis adjacent octahedra are oppositely rotated (alternating clockwise and counterclockwise rotations; see Figure 1 b).

Such tilting is possible because the azido bridges in EE mode (μ -1,3-N₃) allow for both *cis*-EE (as in conventional oxide perovskites) and *trans*-EE coordination to the metal cations, and therefore new degrees of freedom for rotation of the [MN₆] octahedra are introduced.^[25] In fact, and as is shown in Figure S2 of the Supporting Information, in this LT polymorph the coordination of the azide ligands has changed to *cis*-EE along the *b* axis, whereas it has remained *trans*-EE in the *ac* plane. Also, none of these ligands shows disorder.

In addition, in this LT phase the *cis*-EE azide bridging ligands are slightly bent (\approx 176°, see Table SII of the Supporting Information) and show an increased intraligand N5–N6 bond length on cooling. Such features are probably related to the presence of a certain interaction between the N atom of the *cis*-EE azide ligands and the H atom of the TMA cation that is close enough ($d(H_{TMA}-N_{azide}) \approx 2.6$ Å, see Figure S3 of the Supporting Information), which in turn weakens the intra-azide N–N bond.

The *cis*-EE azide ligands are cooperatively shifted off-center from the *b* axis by about 0.51 Å in the $\langle 205 \rangle$ and $\langle 205 \rangle$ directions (Figures 1 b and 2 and Table SIII of the Supporting Information), whereas the central N atoms of the *trans*-EE azide ligands remain invariant compared to the HT phase (Figure 2 and Figure S2 of the Supporting Information). Therefore, the herein-described phase transition involves cooperative rotation of the [MnN₆] octahedra, cooperative off-center shifts of both the TMA cations and the *cis*-azide ligands, and order/disorder phenomena that affect both the TMA cations and the *cis*-azide ligands. In fact, the value of $N \approx 12$ obtained from the DSC data is already close to the calculated value if the disorder/ order ratio of the [(CH₃)₄N]⁺ and N₃⁻ ligands in the HT and LT polymorphs (N = 12/4 + 2(4/1) = 11) are taken into account.

The structural transition from monoclinic (LT phase) to cubic symmetry (HT phase) involves a pronounced change in the volume of the cuboctahedral cavity (Figure S4 of the Supporting Information). The volume of the empty cavity in the LT phase (calculated by PLATON software^[26] without the TMA cation) of 133 Å³ increases by more than 16% in the HT phase, in which $V_{cavity}(317 \text{ K}) = 155 Å^3$. In addition, this phase transition also implies an unusual and anisotropic thermal expansion of the unit cell, which is positive along the *a* and *c* axes but negative along the *b* axis (negative thermal expansion; see Figure 3).

From the obtained data, the following linear thermal expansion coefficients were calculated for $[(CH_3)_4N][Mn(N_3)_3]$: $\alpha_a =$ 144(7) MK⁻¹, $\alpha_b = -20(2)$ MK⁻¹, and $\alpha_c = 80(3)$ MK⁻¹. Such anisotropic behavior is directly related to the different thermal evolutions of the *cis*-EE and *trans*-EE azide ligands in the structure,



Figure 3. Thermal evolution of the *a*, *b* and *c* cell parameters.

which in turn depend on the templating effect of the TMA cations in the cavities.

In this regard, the *trans*-EE ligands remain linear in the whole temperature interval studied, and the main change they experience is closing in the angle θ between the *trans*-EE ligand and the *a* or *c* axis as the temperature increases. This leads to a larger separation between the nearest-neighbor Mn ions and thus to positive thermal expansion along the *a* and *c* axes (see Figure 4a and S5 of the Supporting Information).



Figure 4. Representation of the evolution of the azide ligands as a function of temperature. a) *trans*-EE azide ligands, responsible for the positive thermal expansion observed along the *a* axis, and b) *cis*-EE azide ligands, responsible for the negative thermal expansion along the *b* axis.

In the case of the *cis*-EE ligands the predominant effect that accounts for the observed negative thermal expansion along the *b* axis is the above-mentioned decrease in the intra-azide N–N bond length with increasing temperature (see Table SII of the Supporting Information). This apparently anomalous behavior can be explained on the basis of the weakening of the interaction between this ligand and the TMA cation as the temperature increases (see Figure S3 of the Supporting Information), which in turn reinforces and shortens the intra-azide N–N bonds. Eventually, the change in the coordination mode of this azide ligand from *cis*-EE to *trans*-EE at the phase transition provokes further approach of the nearest-neighbor Mn centers along the *b* axis and further contraction of that axis (see Figure 4b).

The phase transition from the HT polymorph (SG: $Pm\bar{3}m$) to the LT polymorph (SG: $P2_1/m$) is m3mF2/m(p) according to Aizu notation,^[27] and thus belongs to one of the 94 ferroelastic phase transitions. This means that this compound shows ferroelasticity, as is also the case for the related Cd compound [(CH₃)₄N][Cd(N₃)₃].^[19]

Theoretical calculations

In view of the structural characteristics displayed by $[(CH_3)_4N]$ [Mn(N₃)₃], we explored the possibility that it shows polar/nonpolar order by means of DFT calculations. First, we performed the following computational experiment (see Figure 5): starting from the LT phase, we centrosymmetrized the $[Mn(N_3)_3]^$ framework, for simplicity hereafter called BX₃. Furthermore, we considered an ideal, that is, undistorted, TMA cation in the center of each perovskite unit (Figure 5 a). The two TMA cations are related by an inversion symmetry center at (1/2, 1/2, 1/2). Each subsystem is nonpolar (the BX₃ framework is centric and the TMA cation is nonpolar). When we allowed relaxation of all



Figure 5. DFT calculations on the LT structure of $[(CH_3)_4N]Mn(N_3)_3$. a) Centrosymmetric $[Mn(N_3)_3]^-$ framework and $[N(CH_3)_4]^+$ cations related by inversion center at $(^1/_2,^1/_2,^1/_2)$. After atomic relaxation (b), bending of the ligands occurs along the *b* axis, as shown by the curved symbol and the N-N-N angle deviates from 180°. When the $[N(CH_3)_4]^+$ cations are replaced by K⁺ (c) no distortion was observed in the system (d).

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atoms in the unit cell (Figure 5 b), atomic distortions were induced corresponding to an electrical ordering of the same type, as found in the experimental low symmetry structure. In particular the N-N-N angle of the *cis*-EE azide ligand deviates from the ideal 180° in the centrosymmetric structure to 177.67°, in good agreement with the angle obtained by singlecrystal XRD (Table SII of the Supporting Information). On the other hand, if the TMA cations are substituted with an alkali metal cation (Figure 5 c), such as K⁺, the "virtual" system KBX₃ does not show any distortion, that is, the N-N-N angles along the *b* axis remain 180° (Figure 5 d).

This finding clearly highlights the role of the TMA cations and their coupling with the framework, which induces an antipolar type of distortion, compatible with the presence of inversion symmetry. Interestingly, in the theory of ferroelectric liquids it is possible to induce an electrical ordering starting from nonpolar and achiral units.^[28] In our case, starting from nonpolar subsystems such as BX₃ and TMA cations, an antipolar order is induced, which, in this case, preserves the inversion symmetry.

In the second computational experiment (Figure 6) we evaluated the polarization in each perovskite subunit made of a centric BX₃ framework and an ideal TMA cation. The two subunits form a reference paraelectric structure, here called PARA structure.

Furthermore, we constructed two artificial structures, FERRO-A and FERRO-B. In the former, one perovskite subunit preserves its ideal atomic positions as in PARA, whereas the other perovskite subunit has the same atomic positions as in the LT phase, and vice versa for the latter. Clearly, in FERRO-A, one subunit makes no contribution to the polarization, but the other subunit does. This contribution is called P-A. Analogously, for FERRO-B, this contribution is termed P-B. We will show that P-A and P-B are nonzero, but P-A + P-B = 0. Note that, in this approach, we only evaluate the contribution from the



Figure 6. a) Reference centric structure (PARA). FERRO-B (b) and FERRO-A (c) are two different structures derived from PARA by including the atomic position of the low-symmetry structure only in one subunit, compatible with periodic boundary conditions. d) Obtained polarization P_a and P_c for FERRO-A and FERRO-B.

framework, while neglecting that from TMA. Although this simplification may affect the absolute numerical estimate of P-A and P-B, it will not change the main conclusion.

In Figure 6, we show the PARA structure (Figure 6a) and the two FERRO-A,B structures derived therefrom (Figure 6b,c). We also show the evaluation of the polarization for the structures along the distortion path that brings the PARA structure to the FERRO-A,B structures (Figure 6d). Clearly the two polarizations, which lie in the *ac* plane, are equal in modulus ($1.03 \ \mu C \ cm^{-2}$) but opposite in direction, and this confirms that each subunit carries a polarization opposite to that on the other subunit, that is, they correspond to what can be considered to be an antiferroelectric (AFE) phase.^[29]

The calculated polarization modulus for each subunit is very similar to that reported for other polar hybrid perovskites, such as $[NH_4][Cd(HCOO)_3]$ with a net polarization of 1.35 μ C cm⁻².^[30] Nevertheless, in $[(CH_3)_4N][Mn(N_3)_3]$, the antiparallel stacking of such ferroelectric planes along the *b* axis would finally result in an AFE phase.

Dielectric measurements

The temperature dependence of the real part of the complex dielectric permittivity ε'_r (the so-called dielectric constant) of $[(CH_3)_4N][Mn(N_3)_3]$ is shown in Figure 7. The ε'_r versus *T* curves show a small spike around $T \approx 330$ K, which is frequency-independent. Interestingly, the temperature at which this anomaly occurs is very close to that at which the HT polymorph transforms into the LT polymorph,



Figure 7. Temperature dependence of the dielectric constant of [(CH₃)₄N] [Mn(N₃)₃] measured at $\nu = 10$ and 100 kHz.

Taking into account that in the LT phase the cooperative offcenter shifts of the TMA cations and the *cis*-azide ligands give rise to electric dipoles that are arranged in an AFE pattern, which disappears in the HT phase, such a kink in the dielectric constant could be signaling the change from AFE order to noncooperative behavior at higher temperatures (>310 K). In any case, further experimental proof and/or theoretical calculations are needed to unambiguously corroborate this and to prove whether such an AFE phase can transform into a ferroelectric one when subjected to a sufficiently high external elec-

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tric field or other external stimuli (pressure, magnetic field, etc.).

There are significant differences in the driving force for the structural and dielectric transitions described in this work and those previously reported for another hybrid inorganic–organic compounds or coordination polymers with perovskite-like structures, such as the compounds of formula [AmineH] $[M(HCOO)_3]$, (AmineH⁺: mid-sized alkyl ammonium cation),^[8–10,12] $[(CH_3)_2NH_2]_2[KCo(CN)_6]$,^[31] and $[(CH_3)_2NH_2]$ $[Cd(N_3)_3]$.^[22]

Hitherto, all described hybrid perovskites with dielectric properties contain polar cations inside the cuboctahedral cavities and/or hydrogen bonds between the cations and the framework, and such structural phase and associated dielectric transitions arise from order/disorder processes of the polar guest molecules. In the case of [(CH₃)₄N][Mn(N₃)₃], in which the guest TMA cations are apolar, they have a completely different origin: they are due to a cooperative displacive mechanism of both the TMA cations and the *cis*-azide ligands, as well as bending of the latter. The former resembles that shown by ceramic ferroelectrics with perovskite structure, such as BaTiO₃, even though in those materials the B cation experiences the temperature-dependent reversible displacement and gives rise to the electric order.

Therefore, and for the first time in a hybrid inorganic–organic compound with perovskite structure, we have reported a structural phase transition and associated dielectric anomaly induced by a displacive mechanism affecting the A cations and in which the X ligands are also directly involved.

Conclusions

In summary, we have studied [(CH₃)₄N][Mn(N₃)₃], which experiences a sharp first-order structural change at T_t =310 K from a HT cubic phase (SG: $Pm\bar{3}m$) to an LT monoclinic one (SG: $P2_1/m$). The driving force for such structural phase transition is multifold and involves the order/disorder of the TMA cations inside the cavities and of the bridging azide ligands in the framework, the displacive transition of such A cations from off-center positions in the LT polymorph to centered positions in the HT phase, the displacive transition of the *cis*-azide ligands, with bending and change in coordination mode, along the *b* axis, together with cooperative tilting and rotation of the [MnN₆] octahedra.

All these processes are strongly correlated and take place simultaneously. Interestingly, this phase transition is associated with remarkable changes in the functional properties of $[(CH_3)_4N][Mn(N_3)_3]$. Structural changes that provoke negative thermal expansion along the *b* axis and positive thermal expansion along the *a* and *c* axes are coupled with a ferroelastic phase transition.

Additionally, a spike in the dielectric constant is observed very close to this phase transition, which could be related to the change from noncooperative behavior at higher temperatures (>310 K) to the AFE phase predicted by DFT below T_{t} . Such AFE order and thus the origin of such dielectric transition would be different from those reported up to now for other

perovskite-type hybrid compounds, in which typically the electric order arises from order/disorder phenomena of the polar cations occupying the A sites of the perovskite architecture, which is not the case here.

These findings allow the search field for new hybrid perovskites with dielectric and multiferroic properties to be enlarged, because it is no longer restricted to compounds containing polar cations at the A site, since appropriate combinations of apolar cations and ligands could also give rise to electric order. The structural changes in the framework also affect the magnetic exchange interactions in the compound, which provoke the appearance of magnetic bistability at the same temperature.

Hence, $[(CH_3)_4N][Mn(N_3)_3]$ is a singular multiferroic material in which the three ferroic orders coexist even above room temperature. Furthermore, to the best of our knowledge, it is the first and only hybrid inorganic–organic perovskite that exhibits these extraordinary features.

Experimental Section

Materials

 $MnCl_2 \cdot 4H_2O~(\geq 98\%,~Aldrich),~tetramethylammonium~chloride~(purum <math display="inline">\geq 98\%,~Fluka),~sodium~azide~(\geq 99\%,~Aldrich)~and~methanol~(99.5\%,~Panreac)~were~commercially~available~and~used~as~purchased~without~further~purification.$

Synthesis

The synthetic route was adapted from the solution-diffusion method used in the synthesis of formate compounds.^[14] In a typical experiment, solution of 0.5 M NaN₃ and 0.5 M tetramethylammonium chloride (CH₃)₄NCl in CH₃OH/H₂O (2.5 mL, 1:1) was placed at the bottom of a glass tube. Upon the NaN₃/(CH₃)₄NCl solution, 1 mL of methanol was carefully added, followed by carefully layering with a 0.10 m solution of MnCl₂·4 H₂O in 4 mL of methanol. The tube was sealed and kept undisturbed. After 3 d, colorless platelet-like single crystals and polycrystals were obtained. They were collected, washed with ethanol and dried at room temperature. This synthetic route has several advantages over that previously described:^[17,21] it can be carried out at room temperature, avoids the use of toxic HN₃, and an inert atmosphere is not necessary.

Caution! Although our samples never exploded during handing, metal azide compounds are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great caution.

Crystallographic structure determination

Single-crystal full data sets of the sample were collected at 317, 290, 250, and 200 K with a Bruker Kappa Apex II X-ray diffractometer equipped with a CCD detector by using monochromatic $Mo_{K\alpha 1}$ radiation ($\lambda = 0.71073$ Å). Cell parameters were determined for additional temperatures in the range of 297–317 K in steps of 2 K.

A suitable crystal of approximately $0.30 \times 0.32 \times 0.42$ mm was chosen and mounted on a MiTeGenMicroMountTM by using FOM-BLIN[®] YR-1800 perfluoropolyether (Lancaster Synthesis). The crystal was cooled at different rates by using a cold stream of nitrogen from an Oxford Cryosystems cooler. Data integration and reduction were performed with the APEX2 V2013.2-0 (Bruker AXS, 2013) soft-



ware suite. The collected intensity was corrected for Lorentzian and polarization effects and for absorption by semiempirical methods on the basis of symmetry-equivalent data by using the SADABS 2012/1 software suite. The structures were solved by the direct method with the SHELXS-97 program and refined by the least-squares method with SHELXL-97.^[32] CCDC 1420768–1420771 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

In addition, [(CH₃)₄N][Mn(N₃)₃] was studied by X-ray powder diffraction (XRPD) at room temperature with a Siemens D-5000 diffractometer by using Cu_{ka} radiation ($\lambda = 1.5418$ Å). The Le Bail refinement of the experimental PXRD pattern at room temperature confirmed that the obtained sample is single-phase (Figure S7 of the Supporting Information).

The linear thermal expansion coefficients of the LT phase were calculated from the obtained cell parameters by using the web-based tool PASCal.^[33]

Dielectric properties

The complex dielectric permittivity $\varepsilon_r = \varepsilon'_r - i\varepsilon''_r$ of the cold-press pelletized sample was measured as a function of frequency and temperature with a parallel-plate capacitor coupled to a Solartron 1260A Impedance/Gain-Phase Analyzer, capable of measuring in the frequency range 10 µHz to 32 MHz, with an amplitude of 2 V. The capacitor was mounted in a Janis SVT200T cryostat refrigerated with liquid nitrogen with a Lakeshore 332 temperature controller incorporated to control the temperature from 78 to 400 K. The data were collected on heating.

Pellets with an area of approximately 530 mm² and thickness of approximately 1 mm were prepared to fit into the capacitor, and gold was sputtered on their surfaces to ensure a good electrical contact with the electrodes. Additional measurements were performed on single crystals, but the high strain produced during the phase transition broke the crystal into pieces.

All the dielectric measurements were carried out in a nitrogen atmosphere, and several cycles of vacuum and nitrogen gas were performed to ensure that the sample environment was free of water. The impedance analysis software SMART (Solartron Analytical) was used for data acquisition and processing.

Thermal analysis

Differential scanning calorimetry was carried out with a TA Instruments MDSC Q-2000, with a liquid nitrogen cooling system by heating/cooling 15 mg of a polycrystalline sample at 10 Kmin^{-1} from 200 to 400 K under nitrogen atmosphere.

Magnetic properties

Magnetic properties were studied with a Quantum Design PPMS SQUID magnetometer on a collection of small single crystals randomly oriented in the magnetic field. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data were obtained in a 50 Oe magnetic field in the temperature range 5–350 K. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables,^[34] and an experimental correction for the sample holder was applied.

DFT calculations and symmetry analysis

The calculations were performed using the Vienna Ab initio Simulation Package (VASP), $^{\rm [35]}$ and projector augmented-wave (PAW) po-

tentials.^[36] The energy cutoff was fixed to 400 eV and the k-point mesh to $4 \times 2 \times 4$ with corresponding meshes for cubic cells. Berry phase theory was used for evaluating the ferroelectric polarization.^[37] The tools of BCS (Bilbao Crystallographic Server) were used for symmetry analysis.^[38]

Acknowledgements

The authors are grateful for financial support from Ministerio de Economía y Competitividad (MINECO, Spain) ENE2014-56237-C4-4-R and Xunta de Galicia under the project GRC2014/042. A.S. thanks the Bilateral Agreement CNR/RA (Joint Projects 2014-2016) N.0006436 (27.01.2014). L.M.Y. ac-knowledges support from startup funding from Huazhong University of Science and Technology. L.C.G.A. also wants to thank the UDC for a Predoctoral fellowship and S.Y.V. the Xunta de Galicia for a postdoctoral grant (Plan I2C). A. L. Llamas-Saiz from Unidad de Rayos X (USC) is acknowledged for his efforts with the single-crystal X-ray diffraction data.

Keywords: ab initio calculations · azides · ferroics · perovskites · phase transitions

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Received: August 29, 2015 Revised: February 16, 2016 Published online on April 13, 2016