Large ferroelectric polarization in the new double perovskite NaLaMnWO$_6$ induced by non-polar instabilities

T. Fukushima$^*$, A. Stroppa, and S. Picozzi

Consiglio Nazionale delle Ricerche - Institute for Superconducting and Innovative Materials and Devices (CNR-SPIN), 67100 L’Aquila, Italy

J. M. Perez-Mato

Departmento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 633, E-48080 Bilbao, Spain

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Based on density functional theory calculations and group theoretical analysis, we have studied NaLaMnWO$_6$ compound which has been recently synthesized [Phys. Rev. B 79, 224428 (2009)] and belongs to the AA$'$BB$'$O$_6$ family of double perovskites. At low temperature, the structure has monoclinic $P2_1$ symmetry, with layered ordering of the Na and La ions and rocksalt ordering of Mn and W ions. The Mn atoms show an antiferromagnetic (AFM) collinear spin ordering, and the compound has been reported as a potential multiferroic. By comparing the low symmetry structure with a parent phase of $P4/nmm$ symmetry, two distortion modes are found dominant. They correspond to MnO$_6$ and WO$_6$ octahedron tilt modes, often found in many simple perovskites. While in the latter these common tilting instabilities yield non-polar phases, in NaLaMnWO$_6$ the additional presence of the A-A$'$ cation ordering is sufficient to make these rigid unit modes as a source of the ferroelectricity. Through a trilinear coupling with the two unstable tilting modes, a significant polar distortion is induced, although the system has no intrinsic polar instability. The calculated electric polarization resulting from this polar distortion is as large as $\sim 16\ \mu$C/cm$^2$. Despite its secondary character, this polarization is coupled with the dominant tilting modes and its switching is bound to produce the switching of one of two tilts, enhancing in this way a possible interaction with the magnetic ordering. The transformation of common non-polar purely steric instabilities into sources of ferroelectricity through a controlled modification of the parent structure, as done here by the cation ordering, is a phenomenon to be further explored.

Perovskite oxides are one of the most interesting and studied classes of inorganic compounds. They show many interesting properties such as ferroelectricity, ferromagnetism, superconductivity, colossal magnetoresistance, etc.[1] The prototype structure is the simple ABO$_3$, where the three-dimensional framework of corner-sharing BO$_6$ octahedra form 12-coordinate cavities occupied by the larger A cations. The possibility of A- or B-site cations order rise to a large compositional range with different properties and symmetries. A well studied case is the 50:50 substitution of B-site in the double perovskites $A_2BB'O_6$, where the $B$ and $B'$ cations order in a rock-salt fashion.[2,3] Analogously, ordering of the A-cations can also occur, showing a strong preference for a layered arrangement.[4,5] Finally, simultaneous A- and B-site cation ordering can also occur in compounds of type AA$'$BB$'$O$_6$.[7] These compounds are interesting from a structural point of view since they exhibit rock-salt ordering of B-site cations and layered ordering of A-site cations. However, they are relatively unexplored, because this type of ordering is very rare.[7,8] Clearly, the presence of four different distinct cation sites greatly increases the possibility of functional design in this class of compounds. NaLaMnWO$_6$ that has been recently synthesized[9] belongs to the A and B ordered double perovskites. Mn and W ions are octahedrally coordinated to O ions and these octahedra are strongly tilted: the tilting is represented as $a^+a^+c^-$ in terms of Glazer notation[9]. It exhibits a polar crystal structure with monoclinic $P2_1$ symmetry and an AFM spin configuration with Néel temperature $T_N = 10$ K [6,8]. $P2_1$ is a polar group where electric polarization is allowed. Therefore, the magnetic ordering at low temperature, suggests a possible multiferroic behavior [4,8], showing both spontaneous ferroelectric and magnetic order.[10,13]. Typical multiferroics belong to the group of perovskite transition metal oxides, and include rare-earth manganites and ferrites (e.g. TbMnO$_3$, HoMnO$_3$, HoMn$_2$O$_5$, LuFe$_2$O$_4$). Other examples are bismuth compounds BiFeO$_3$ and BiMnO$_3$, non-oxides, such as BaNiF$_4$, and spinel chalcogenides, e.g. ZnCr$_2$Se$_4$.[14,28]. In these compounds ferroelectricity is either an independent phenomenon (like in BiFeO$_3$, where ferroelectricity can be caused by an intrinsic polar instability, or its existence is an induced effect of the magnetic ordering (as in TbMnO$_3$), where

$^*$Present address: Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan
produced by local rotational modes in SrTiO$_3$.

In particular, a coupling between polarization and two of them associated to unstable or nearly-unstable modes. In particular, a coupling between polarization and two rotational modes has been described.

More recently, Bousquet et al. have demonstrated that ferroelectricity is produced by local rotational modes in a SrTiO$_3$/PbTiO$_3$ superlattice. Following this work, Benedeck and Fennie proposed that magnetoelectric coupling, weak ferromagnetism, and ferroelectricity can develop from the combination of two lattice rotations, neither of which produces ferroelectric properties individually. In other words, separate lattice distortions can not only produce ferroelectricity, but also modify the magnetic order and favor magnetoelectricity.

In this paper, we will demonstrate that, by means of ab initio density functional theory (DFT) calculations and group theoretical analysis, a similar mechanism works in the case of NaLaMnWO$_6$ producing a relatively large $\sim 16 \mu C/cm^2$ polarization: two tilting instabilities are not enough to induce ferroelectric polarization by themself, but their coupling is sufficient to induce a polar instability and, therefore, ferroelectricity. To this end, we will show that the additional degree of freedom provided by the cation $A$-$A'$ ordering has an important role. The mechanism explained in the article by Fennie et al. and termed “hybrid improper ferroelectricity” is basically the same as the one discussed here, although for other type of systems. The calculated polarization is large here, due to the intrinsic softness of the polar mode in NaLaMnWO$_6$. The condensation of a hard mode through a trilinear coupling with two unstable modes is in fact a quite common mechanism in perovskite-related compounds and other materials, and can also be the origin of the simultaneous condensation of several distinct soft-modes, effectively acting as a single order parameter.

Electronic structure calculations and structural optimizations were performed by using the “Vienna Ab initio Simulation Package” (VASP) and Projector Augmented Wave (PAW) pseudopotentials. The Perdew-Burke-Ernzerhof (PBE) was employed for the exchange-correlation potential. The DFT+$U$ method was used to properly take into account correlation effects using $U=4$ eV. We used experimental lattice constants and we relaxed the internal coordinates. The magnetic structure is an AFM collinear spin configuration with propagation vector $k = (0.5, 0, 0.5)$ (see Fig. 1).

Monkhost-Pack $k$-point grid in the Brillouin zone was used. The Berry phase approach was employed to calculate the electric polarization.

A relaxed structure within the experimentally observed $P2_1$ symmetry was first calculated. The relaxed atomic positions are in good agreement with experimental values, as shown in Table I. Mn-O and W-O corner sharing octahedra are strongly tilted and rotated due to the GdFeO$_3$-type distortion. It is well known that when the ionic radius of the $A$ and $A'$ cation is small ($r_{Na} = 1.22 \ \AA$, $r_{La} = 1.24 \ \AA$), this distortion is enhanced. In fact, in our case, the Goldschmidt tolerance

| Atom   | Exp.[6] x | Exp.[6] y | Exp.[6] z | GGA+$U$ x | GGA+$U$ y | GGA+$U$ z |
|--------|-----------|-----------|-----------|------------|------------|------------|
| Na (2a) | 0.2514    | 0.2289    | -0.0008   | 0.2489     | 0.2223     | 0.0004     |
| La (2a) | 0.2556    | 0.2755    | 0.4984    | 0.2574     | 0.2845     | 0.5003     |
| Mn (2a) | 0.7571    | 0.2507    | 0.2389    | 0.7517     | 0.2526     | 0.2392     |
| W (2a)  | 0.7581    | 0.2494    | 0.7652    | 0.7547     | 0.2451     | 0.7664     |
| O$_1$ (2a) | 0.5345 | 0.5017    | 0.6944    | 0.5461     | 0.5118     | 0.6973     |
| O$_2$ (2a) | 0.5136 | 0.5364    | 0.3017    | 0.5222     | 0.5365     | 0.3021     |
| O$_3$ (2a) | -0.0205 | -0.0584   | 0.2250    | -0.0362    | -0.0681    | 0.2197     |
| O$_4$ (2a) | -0.0669 | -0.0358   | 0.7819    | -0.0692    | -0.0482    | 0.7840     |
| O$_5$ (2a) | 0.8279  | 0.2285    | 0.5111    | 0.8320     | 0.2252     | 0.5090     |
| O$_6$ (2a) | 0.6684  | 0.2565    | -0.0166   | 0.6664     | 0.2718     | -0.0127    |

FIG. 1: Magnetic unit cell of NaLaMnWO$_6$ with propagation vector $k = (0.5, 0, 0.5)$ which doubles the nuclear unit cell along $a$ and $c$ directions. The orange arrows indicate the spins of Mn atoms.
This idealized prototype structure can be found using the AMPLIMODES software.\[45\], one can decompose the distortion relating the relaxed monoclinic structure with this prototypical structure into symmetry-adapted distortion modes. Three symmetry-breaking distortions can be distinguished with symmetries labelled as $\Gamma^+_5$, $\Gamma^-_1$ and $\Gamma^-_5$. Figure 2(b, c and d) show the pattern of atomic displacements associated with these three different distortion modes. The $\Gamma^+_5$ and $\Gamma^-_5$ distortion modes can be seen to be essentially two tilting modes of the octahedron framework. They correspond to the so-called rigid unit modes (RUMs)\[46\], that are frequently unstable in simple perovskites. Their usual labels when described with respect to a $Pm\overline{3}m$ perovskite are $R4^+$ and $M3^+$ and would yield a distorted non-polar structure of $Pnma$ ($Pbnm$) symmetry. Here, the structure of the modes is the same, but the cation ordering implies that the reference parent structure has a smaller tetragonal symmetry with a larger unit cell, so that they correspond to $\Gamma$ modes for this larger tetragonal supercell. The third distortion mode labelled $\Gamma^-_5$ and shown in Figure 2(d) is the polar mode frozen, which should be responsible for the ionic spontaneous polarization present in this compound. The atomic displacements for this mode are mostly along the crystallographic $b$ direction (polar axis). Na and La atoms displace in opposite directions by 0.055 and 0.108 Å respectively, while Mn and W atoms remain essentially fixed. The maximum oxygen displacement along the polar axis is 0.136 Å.

FIG. 2: (Color online) (a) Group-subgroup tree connecting the paraelectric $P4/nmm$ phase to ferroelectric $P2_1$ phase. (b), (c), and (d) are the pattern of atomic displacements for the $\Gamma^+_5$, $\Gamma^-_1$, and $\Gamma^-_5$ distortion mode, respectively. Yellow, green, purple, grey, and red spheres indicate Na, La, Mn, W, and O atoms, respectively.

The tiltings present in NaLaMnWO$_6$ can be described using the Glazer notation\[36\]. In our case, $Q_{\Gamma^-_5}$ and $Q_{\Gamma^-_1}$ are equal to 1.34 and 0.94 Å, respectively. On the other hand, the polar distortion $\Gamma^-_5$ has much smaller amplitude of 0.51 Å. The relative size of symmetry-adapted mode amplitudes offer a valuable clue to interpret the mechanism giving rise to the polarization. The fact that $Q_{\Gamma^+_5}$ and $Q_{\Gamma^-_1}$ are much larger than $Q_{\Gamma^-_5}$, suggests that the two first distortion modes are the primary structural distortions with respect to the prototype phase, acting as order parameters, while the polar mode is a secondary induced distortion. Indeed, the $\Gamma^+_5$ and $\Gamma^-_5$ distortion modes lower the symmetry to $P2_1/m$ and $P42_2$, respectively (isotropy subgroups). Note that none of them is a polar subgroup, although the second one breaks the inversion symmetry. This means that the structure resulting from these two dominant distortions, which is very close to the real structure, is a non-polar structure. However, these two modes are sufficient to reduce the symmetry to $P2_1$, which allows the presence of a secondary induced polar distortion. This can be understood considering the graph representing the group-subgroup relations connecting the high-symmetry $P4/nmm$ to the observed $P2_1$, as shown in Fig 2(a). It can been seen that the intersection of the two mentioned isotropy subgroups is the observed $P2_1$ group, as it is their largest common subgroup. This means that the combination of these two tilting modes are able to induce a polar phase (although they don’t produce a polarization by themselves). It must be stressed that the original $R4^+$ and $M3^+$ unstable modes in pure $Pm\overline{3}m$ perovskites preserve in all cases a non-polar symmetry. It is only the fact that the cation ordering reduces the parent high symmetry to $P4/nmm$, which permits, in this compound, that two typical unstable non-polar per-
ovskite tilting modes produce a polar structure, and, as a consequence, an improper ferroelectric. To confirm this scenario we have investigated the stability of each of the three distortion modes present in the relaxed structure of NaLaMnWO$_6$. We have calculated the energy variation as a function of the amplitude of each mode, separately. The results are shown in Fig. [3] For the $\Gamma^+_5$ and $\Gamma^-_1$ modes, we have a characteristic double-well shape, clearly indicating that they are unstable modes. On the other hand, the total energy variation of $\Gamma^-_5$ mode is a positive parabola, showing that the mode is stable. As shown in the inset of Fig.[3(c), there are minima around $Q = 0.5$ and -0.5 for the $\Gamma^-_5$. In this sense, this mode is also unstable. However, the amplitude of the $\Gamma^-_5$ is 0.5086 Å and corresponds to $Q = 1$. Therefore, in order to achieve this amplitude, the $\Gamma^-_5$ distortion needs to combine with primary distortions ($\Gamma^+_5$ and $\Gamma^-_1$ modes).

The presence of the $\Gamma^-_5$ distortion with a quite significant amplitude can be explained as an induced effect through a symmetry-allowed anharmonic trilinear coupling with the primary tilting non-polar distortion modes ($\Gamma^+_5$ and $\Gamma^-_1$) $Q_{\Gamma^+_5} Q_{\Gamma^-_1} Q_{\Gamma^-_1}$. This simple coupling is sufficient to explain the presence of a non-zero amplitude $Q_{\Gamma^-_5} \propto (Q_{\Gamma^+_5} Q_{\Gamma^-_1} Q_{\Gamma^-_1})$ in order to minimize the energy, despite the mode itself being essentially stable. More importantly, this trilinear coupling will correlate the possible switching of polarization and tilting modes. For a fixed orientation of the polar axis, the number of domains is four and will be characterized by independent changes of sign of the two tilting modes, while the secondary polarization correlates with them according to the proportionality law indicated above. Therefore, polarization switching will imply necessarily a change of sign of one of the two rotational modes. This may be important to enhance the coupling of polarization with the magnetic ordering. Our results demonstrate that NaLaMnWO$_6$ can be considered an improper ferroelectric.

We now turn our attention to the estimate of the value of spontaneous polarization in NaLaMnWO$_6$. For the calculation, the $P2_1/m$ phase resulting from the sole presence of the $\Gamma^+_5$ distortion is employed as a virtual paraelectric state and $\lambda$ is used as a scaling parameter of all ionic displacements, i.e. $\lambda = 0$ for the paraelectric state ($P2_1/m$) and $\lambda = 1$ for the sum of the two distortion components $\Gamma^+_1 + \Gamma^-_5$ leading to the relaxed structure ($P2_1$). The negative $P$ ($\lambda = -1$) state is built by ionic displacements opposite to the positive $P$ state, with respect to the $\lambda = 0$ structure. This corresponds to a correlated switch of the two distortion modes $\Gamma^+_1$ and $\Gamma^-_5$, as discussed above. Figure [4] shows (a) the total energy difference and (b) the variation of polarization as a function of $\lambda$. The total energy difference $\Delta E_{\lambda=-1} = E_{\lambda = 1} - E_{\lambda = -1}$ shows convex and symmetrical shape between positive and negative $P$ states, thus reproducing the bi-stable shape characteristic of ferroelectric materials. The energy barrier between the paraelectric and ferroelectric states $\Delta E = 890$ meV/unit cell corresponding to 110 meV/formula unit (f.u.) is two times larger than in the YMnO$_3$ case, where $\Delta E \approx 60$ meV/f.u. [47] Spontaneous ferroelectric polarization $\Delta P$ calculated by the Berry phase method is $\sim 16 \mu C/cm^2$, as shown in Fig [4b). This value is very close to the polarization value $\sim 14 \mu C/cm^2$ obtained by the point charge model with nominal charges (i.e. +1e for Na, +3e for La, +2e for Mn, +6e for W, and -2e for O). This means that electronic effects are are negligible and ionic displacements are the main contribution to ferroelectric polarization. The relatively large value of polarization is consistent with the softness of the polar mode shown in Fig. [5] We have also checked that, by reducing the on-site Coulomb interaction $U$ to zero in our calculation, the polarization is not significantly affected. This suggests that Mn-3$d$ states do not play an important role in the ferroelectricity in NaLaMnWO$_6$.

Finally, we feel important to discuss two points, although they go beyond the purpose of the present study.
However, we believe that they may stimulate further studies in this interesting class of compounds. First, we have argued that the primary order parameters driving the transition in this compound are the two rotation modes, and not the polar mode, which happens to also be unstable. For example, as in the Bousquet’s work on PbTiO3/SrTiO3,[31] one rotation mode completely suppresses the other rotation mode, and it is required that the polar mode and a rotation mode be present in order for the second rotation mode to freeze in, i.e., the two rotation modes actually compete with each other and only one wins. In the work of Benedek and Fennie on Ca3Mn2O7,[33] the polar mode is hard and the two rotation modes are compatible with each other, i.e., true rotation driven ferroelectricity. In our case, we did not investigate whether the two rotation modes compete with each other or they are compatible: to properly address this question, a detailed study of the anharmonic couplings is needed. Second, a peculiar property arise by studying the magnetoelectric coupling in this compound. By symmetry considerations, not reported here, one can show that: i) a weak AFM magnetic moment M_y should exist in this compound with the same propagation vector of the M_x and M_z components; ii) the magnitude of the M_y component should be proportional to the product of the amplitudes of the polar distortion and of the primary frozen magnetic mode in the plane xz. This means that one should be able to see that this y antiferromagnetic component switches by switching the sign of the polar mode and one could expect that it increases linearly with an increase of the amplitude of the polar mode. In this way, one can simulate the effect of an electric field along y, and if the y-AF component responds linearly, this would correspond to a quite peculiar magnetoelectric effect: namely an AF ordering responding linearly to an electric field. These considerations reinforce the idea of interesting physics in this novel class of compounds.

In conclusion, we have studied a new multiferroic material, NaLaMnWO_6, and shown that the compound is an improper ferroelectric. The estimated ferroelectric polarization is \( \sim 16 \, \mu C/cm^2 \), a relatively high value compared with ferroelectrics of this type. A negligible polar instability does exist [see inset of Fig. 3(c)], but the additional A' cation layer ordering of this double perovskite is sufficient to make ferroelectrically active some tilting modes of the octahedra that in simple perovskites and in B-ordered double perovskites only give place to non-polar phases. Through a trilinear coupling with the two unstable tilting modes, a significant polarization is induced. We hope that this study will stimulate further investigation of cation ordering as a tool to convert ubiquitous well-known steric non-polar instabilities into mechanisms for producing improper ferroelectrics, as well as new multiferroics.

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