Pressure-induced ferroelectric phase of LaMoN₃

Churen Gui 💿 and Shuai Dong 💿*

School of Physics, Southeast University, Nanjing 211189, China

(Received 13 October 2020; accepted 18 November 2020; published 30 November 2020)

Nitride perovskites are supposed to exhibit excellent properties as oxide analogs and may even have a better performance in specific fields for their more covalent characters. However, until now, very limited nitride perovskites have been reported. In this Rapid Communication, a nitride perovskite LaMoN₃ has been systematically studied by first-principles calculations. The most interesting physical property is its ferroelectric *R*3*c* phase, which can be stabilized under a moderate hydrostatic pressure (~1.5 GPa) and probably remain metastable under an ambient condition. Its ferroelectric polarization is considerably large, 80.3 μ C/cm², driven by the nominal 4*d*⁰ rule of Mo⁶⁺, and the covalent hybridization between Mo's 4*d* and N's 2*p* orbitals is very strong. Our calculation not only predicts a ferroelectric material with prominent properties, but also encourages more studies on the pressure engineering of functional nitrides.

DOI: 10.1103/PhysRevB.102.180103

Introduction. Oxides are important quantum materials, which host many exotic emergent physical properties such as high-temperature superconductivity, colossal magnetoresistance, multiferroicity, etc. Thus, these oxide families have been extensively investigated in the past decades. Comparing with these widely studied oxides, nitrides have been much less explored. The crucial reasons are their high formation enthalpies and the low chemical potential of N₂ molecules [1], which make stable nitrides not as common as oxides.

Regardless, nitrides remain highly valuable for their physical properties and promising applications. For example, the blue light-emitting diodes (LED) were based on nitrides [2–4], and nowadays devices based on GaN and related materials have been commercially applied widely, which boosts further research on nitrides.

Very recently, a stability map of inorganic ternary metal nitrides was constructed using the data-mined structure prediction algorithm [5], which provided a useful guide for further explorations of nitrides. A perovskite with the chemical formula *ABX*₃ is the most common crystal structure for ternary metal oxides, and holds a variety of excellent properties for applications. However, the oxidation state of -3 for nitrogen requires very high oxidation states for cations at the *A* site and *B* site. However, a few nitride perovskites, e.g., LaWN₃ and LaMoN₃, have been predicted theoretically [6,7], and ThTaN₃ has been synthesized [8]. More oxynitride perovskites, e.g., SrTaO₂N, LaTaON₂, and LaWO_{δ}N_{3- δ}, have been experimentally synthesized [9–12].

Among these nitride perovskites, LaWN₃ was predicted to be ferroelectric with a spontaneous polarization ~66 μ C/cm² and a small band gap [local density approximation (LDA) result: 0.81 eV] [13]. Such a small band gap, due to the spatial-extending 5*d* orbitals, will be an obstruction for experimental verification of its ferroelectricity. In fact, most applied ferroelectric perovskites are based on 3*d* metal oxides, e.g., BaTiO₃ and Pb(Zr, Ti)O₃, whose *d* orbitals are more localized, leading to larger band gaps. Thus, the continuous search for more ferroelectric nitride perovskites remains crucial, especially for those with larger band gaps. A natural idea is to replace the *B*-site W⁶⁺ cation using 3*d* or 4*d* cations. However, unluckily, the structure of LaMoN₃ was predicted to be a nonpolar and nonperovskite C2/c phase [6,14].

In this Rapid Communication, based on first-principles calculations, we predict a pressure-induced structural transition of LaMoN₃, from the nonpolar nonperovskite C2/c phase to the ferroelectric perovskite R3c phase. Also, the ferroelectric properties of LaMoN₃ can be superior to those of LaWN₃.

Methods. Density functional theory (DFT) calculations are performed based on the projector augmented-wave (PAW) pseudopotentials implemented in the Vienna *ab initio* simulation package (VASP) [15,16]. The plane-wave cutoff energy is fixed to 500 eV. A $7 \times 7 \times 7$ Monkhorst-Pack Γ -centered *k*-point mesh has been used for structural relax and the Hellmann-Feynman force convergent criterion is set to 10^{-3} eV/Å. The ferroelectric polarization is calculated using the Berry phase method [17,18], and compared with the point-charge model. To acquire accurate band gaps, the hybrid functional calculation is performed based on the Heyd-Scuseria-Ernzerhof (HSE06) method [19–21].

Positive hydrostatic pressure is applied on LaMoN₃ with a stress tensor smaller than 0.1 GPa throughout our calculations. The enthalpy, which equals the Gibbs free energy at zero temperature, is used to identify the ground state. The dynamic stability of certain structures is verified by the vibrational properties using the density functional perturbation theory (DFPT) [22]. PHONOPY is adopted to calculate the phonon band structures [23], and AFLOW is used to seek and visualize the dispersion paths in the Brillouin zone [24].

Enthalpy-driven structural transition. As sketched in Fig. 1(a), the structure of the C2/c phase is quite loose, about 26% larger than a compact perovskite one [Figs. 1(b) and 1(c)]

^{*}Corresponding author: sdong@seu.edu.cn



FIG. 1. Crystal structures of LaMoN₃ in (a) the C2/c phase and (b) the R3c phase. (c) The corresponding pseudocubic cell of the R3c phase.

[14]. The energy difference between the C2/c phase and perovskite R3c phase is only 180 meV/f.u. [14]. Inspired by the recent progress of pressure-driven phase transitions in oxides [25], we naturally expect a high possibility of a phase transition by applying an external pressure to LaMoN₃.

Referring to the Materials Project database [26] and the previous study on LaWN₃ [13], a total of seven possible structures of LaMoN₃ are considered in our calculations: Including the pervoskites R3c, $R\overline{3}c$, $Pna2_1$, P4mm, and nonperovskites C2/c, Ama2, $P2_1/m$.

To validate the correctness of our calculation, we first optimized the structure of the C2/c phase. Our optimized lattice constants reach good agreement with previous studies [listed in Table S1 of the Supplemental Material (SM)] [27]. Then various phases have been optimized and their energies are compared. Indeed, the C2/c phase has the lowest energy among all these structures, in agreement with previous structural predictions [6].

Next, the hydrostatic pressure is applied to all phases. The volumes per formula as a function of pressure are plotted in Fig. 2(a). In general, the pressure compresses the lattices, and different phases show distinct stiffnesses. Naturally, those loose structures (e.g., the C2/c one) are softer upon pressure. The energy versus volume curves are shown in Fig. 2(b).

The enthalpies under pressure are shown in Fig. 2(c), with reference to the C2/c phase. In principle, the lowest enthalpy value at a given pressure indicates the most stable structure. Thus, a phase transition from the nonpolar C2/c phase to the polar R3c phase is expected to occur between 1 and 1.5 GPa, a moderate pressure easy to reach in experiment. It is to be expected since a compact perovskite is more favorable under pressure than a loose C2/c one. A higher pressure up to the 40 GPa region is also tested, and the R3c phase always has the lowest enthalpy, as shown in the inset of Fig. 2(c). In other words, no other structural transition exists in this region.

Since the C2/c phase is a nonperovskite which cannot continuously change to the perovskite one, the phase transition between C2/c and R3c must be the first-order one. Thus the R3c phase, synthesized under pressure, may be metastable at the ambient condition after the formation.

More structural details of the C2/c phase at 0 GPa and R3c phase at 0/3 GPa can be found in Table S2 in SM [27].

Dynamic stability. The stability of a structure not only depends on energy/enthalpy, but also needs dynamic stability. The existence of imaginary vibration mode(s) in the phonon band structure indicates dynamic instability. Here, the dynamic properties of LaMoN₃ structures are studied using the DFPT calculations.

First, the phonon spectra of C2/c at 0 and 3 GPa have been calculated, as shown in Fig. S1 of SM and Fig. 3(a), respectively. No imaginary vibration mode exists in both spectra, indicating dynamic stability. In particular, the dynamic stability of the C2/c phase at 3 GPa implies its metastability under pressure, a character of a first-order phase transition.

Next, the $R\bar{3}c$ phase is considered, which is the parent group of R3c, i.e., the paraelectric state. As shown in Fig. 3(b), some unstable phonon modes appear around the Γ point, which is evidence of a ferroelectric transition. Following the eigenvector of the most unstable phonon mode, i.e., the one with the highest imaginary frequency, the R3c phase with a lower symmetry is obtained. Then the phonon bands of R3cat 3 GPa have been calculated, which show dynamic stability [Fig. 3(c)]. Furthermore, after removing the pressure, no serious imaginary mode exists in the phonon spectrum of the R3cone at 0 GPa, implying the metastability of this ferroelectric phase at the ambient condition.

Ferroelectricity and electronic structure. To explore the ferroelectricity of the R3c phase, the spontaneous polarization and ferroelectric switching barrier are calculated, as shown in Fig. 4(a). At 0 GPa, the polarization estimated by the Berry



FIG. 2. (a) The volumes per formula as a function of pressure. The lines of R_{3c} and $Pna2_1$ almost overlap (highlighted in the reddashed square). At 0 GPa, the volume of the C2/c phase is about ~25% larger than the R_{3c} one. (b) The energies of different phases as a function of volume under pressure. The curves are fitted by the Murnaghan equation of state [28]. (c) The enthalpies of different phases as a function of pressure. The C2/c phase is taken as the reference (i.e., 0). The R_{3c} phase becomes more stable from ~1.5 GPa.

phase method is 80.3 μ C/cm², larger than that of LaWN₃ (66 μ C/cm² [13]) and comparable to PbTiO₃ (a famous





FIG. 3. Phonon spectra for LaMoN₃. (a) The C2/c phase at 3 GPa, which is metastable. (b) The $R\bar{3}c$ phase at 3 GPa, which is unstable. (c), (d) The R3c one at 3 and 0 GPa, respectively. (e), (f) The corresponding dispersion paths between high-symmetric points of the Brillouin zone for the C2/c and rhombohedral (R3c and $R\bar{3}c$), suggested by AFLOW [24].

large-polarization ferroelectric oxide whose polarization reaches $\sim 80 \ \mu C/cm^2$ [29]).

By analyzing the structural distortion, it is clear that such ferroelectric polarization originates from the displacement of the Mo^{6+} ion towards the diagonal direction of the N₆ octahedron, as shown in Fig. 4(b). This mechanism is called the d^0 rule, according to the experience of ferroelectric perovskite oxides. However, in typical ferroelectric perovskite oxides, e.g., BaTiO₃, the d^0 rule usually drives a ferroelectric



FIG. 4. (a) The energy difference between R3c and $R\bar{3}c$ as the barrier for polarization switching under different pressures. (b) The ferroelectric displacement (defined as Δd) of the Mo ion along the [111] direction. Magenta lines: The (111) planes for Mo and N₃ ions. Black line: The original mirror plane of the paraelectric state. (c) Polarization (left) and ferroelectric displacement (right) as a function of pressure. The polarization calculated by the Berry phase method is accurate, which is slightly larger than the intuitional one estimated by the point-charge model. The ferroelectric displacement is suppressed by pressure, which is the reason for the reduced polarization and ferroelectric switching barrier.

distortion toward one neighbor oxygen anions, instead of the diagonal direction of the O_6 octahedron.

The ferroelectric structure of LaMoN₃ is somewhat similar to BiFeO₃ which also has an *R*3*c* structure [30]. However, the ferroelectric polarization in BiFeO₃ is driven by the $6s^2$ lone pair of Bi³⁺, not the *B*-site cation. However, the plentiful experience of ferroelectricity from BiFeO₃ can be applied to LaMoN₃. For example, for such an *R*3*c* perovskite, the polarization is along the eightfold (111) directions of the pseudocubic cell, which leads to the possible 71°, 109°, and 180° domain walls [31].

The polarization is suppressed moderately by pressure, as shown in Fig. 4(c), e.g., \sim 74.8 μ C/cm² at 3 GPa. The energy barrier, i.e., the energy/enthalpy difference between the ferro-electric and paraelectric state, is about 0.3 eV/Mo (the upper limit in the real switching process while another lower-energy path may be possible), which is also suppressed continuously by pressure [Fig. 4(a)].

Another interesting result is that the polarization estimated using the point-charge model is slightly lower than the Berry phase one, as compared in Fig. 4(c). This is not common but suggests the deviation from an ideal ionic crystal. Due to the weak electronegativity of N and the high valences of N/Mo, there must be many electrons being distributed in the partially



FIG. 5. (a) The electronic DOS under 0 and 3 GPa. The Fermi level is set at 0 eV. The strong hybridization between N's and Mo's orbitals occurs mainly in the [-5.5, -2.75] eV region. (b) The spatial electron distributions for the [-5.5, -2.75] eV and [-2.75, 0] eV energy windows. The strong covalent Mo-N bonds can be evidenced in the [-5.5, -2.75] eV case. (c) The GGA and HSE06 band gaps as a function of pressure.

covalent N-Mo bonds, instead of staying in the N and Mo sites locally. Then the deformation of an electron cloud can

contribute much to the total polarization, even the ions that do not move too much.

The partially covalent characteristic of Mo-N bonds can also be evidenced in the electronic density of states (DOS), as shown in Fig. 5(a). There is strong hybridization between N's 2p and Mo's 4d orbitals, although nominally the 4dorbitals should be empty in the ionic crystal limit. Such hybridization and covalent characteristic of Mo-N bonds can be also visualized by the electron spatial distribution, as shown in Fig. 5(b).

According to Fig. 5(a), the pressure can slightly reduce the band gap, which can be understood as the enhanced bandwidth of a more compact lattice. The band gap of the *R*3*c* phase is plotted in Fig. 5(c) as a function of pressure. Although the band gap at 0 GPa is only 1.25 eV for the GGA calculation, the hybrid functional calculation based on HSE06 gives 1.96 eV, which is certainly larger than that of LaWN₃ (0.81 eV for the LDA calculation and 1.72 eV for the HSE06 calculation [13]).

Last, the magnetism is also tested considering the fact that Mo's 4*d* orbitals are partially "occupied" in a shared manner.

- [1] A. Zakutayev, J. Mater. Chem. A 4, 6742 (2016).
- [2] I. Akasaki, Rev. Mod. Phys. 87, 1119 (2015).
- [3] H. Amano, Rev. Mod. Phys. 87, 1133 (2015).
- [4] S. Nakamura, Rev. Mod. Phys. 87, 1139 (2015).
- [5] W. Sun, C. J. Bartel, E. Arca, S. R. Bauers, B. Matthews, B. Orvañanos, B. R. Chen, M. F. Toney, L. T. Schelhas, W. Tumas, J. Tate, A. Zakutayev, S. Lany, A. M. Holder, and G. Ceder, Nat. Mater. 18, 732 (2019).
- [6] R. Sarmiento-Pérez, T. F. T. Cerqueira, S. Körbel, S. Botti, and M. A. L. Marques, Chem. Mater. 27, 5957 (2015).
- [7] S. Körbel, M. A. Marques, and S. Botti, J. Mater. Chem. C 4, 3157 (2016).
- [8] N. E. Brese and F. DiSalvo, J. Solid State Chem. 120, 378 (1995).
- [9] A. Fuertes, J. Mater. Chem. 22, 3293 (2012).
- [10] K. R. Talley, J. Mangum, C. L. Perkins, R. Woods-Robinson, A. Mehta, B. P. Gorman, G. L. Brennecka, and A. Zakutayev, Adv. Electron. Mater. 5, 1900214 (2019).
- [11] L. Clark, J. Oró-Solé, K. S. Knight, A. Fuertes, and J. P. Attfield, Chem. Mater. 25, 5004 (2013).
- [12] Y. Hinuma, H. Moriwake, Y. R. Zhang, T. Motohashi, S. Kikkawa, and I. Tanaka, Chem. Mater. 24, 4343 (2012).
- [13] Y.-W. Fang, C. A. J. Fisher, A. Kuwabara, X.-W. Shen, T. Ogawa, H. Moriwake, R. Huang, and C.-G. Duan, Phys. Rev. B 95, 014111 (2017).
- [14] S. Singh and M. N. Tripathi, J. Appl. Phys. 124, 065109 (2018).
- [15] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [16] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
- [17] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).

However, no net magnetic moment is found in our GGA calculation, even under pressure up to 40 GPa. Thus the R3c phase of LaMoN₃ is purely ferroelectric, not multiferroic.

Conclusion. In summary, the pressure-induced structural phase transition from the nonperovskite nonpolar C2/c phase to the polar perovskite R3c phase in LaMoN₃ has been studied using first-principles calculations. Such a transition occurs at a moderate pressure of less than 1.5 GPa, which is accessible in experiments. This polar structure remains at the ground state up to high pressures, and is probably metastable at the ambient condition. The ferroelectric properties of LaMoN₃ are prominent, and superior to LaWN₃. The partially covalent bond between the Mo and N ions is responsible for the ferroelectricity. Further experimental studies are encouraged to verify our prediction and find more functional nitrides.

Acknowledgments. This work was supported by the National Natural Science Foundation of China (Grants No. 11834002 and No. 11674055). We thank the Tianhe-II of the National Supercomputer Center in Guangzhou (NSCC-GZ) and the Big Data Center of Southeast University for providing the facility support on the numerical calculations.

- [18] R. Resta, Rev. Mod. Phys. 66, 899 (1994).
- [19] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).
- [20] J. Heyd and G. E. Scuseria, J. Chem. Phys. 121, 1187 (2004).
- [21] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 124, 219906 (2006).
- [22] X. Gonze and C. Lee, Phys. Rev. B 55, 10355 (1997).
- [23] A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).
- [24] S. Curtarolo, W. Setyawan, G. L. Hart, M. Jahnatek, R. V. Chepulskii, R. H. Taylor, S. Wang, J. Xue, K. Yang, O. Levy, M. J. Mehl, H. T. Stokes, D. O. Demchenko, and D. Morgan, Comput. Mater. Sci. 58, 218 (2012).
- [25] H. P. Su, S. F. Li, Y. Han, M. X. Wu, C. Gui, Y. Chang, M. Croft, S. Ehrlich, S. Khalid, U. Adem, S. Dong, Y. Sun, F. Huang, and M. R. Li, J. Mater. Chem. C 7, 12306 (2019).
- [26] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, APL Mater. 1, 011002 (2013).
- [27] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.102.180103 for more details of the structures and the phonon spectrum for C2/c at 0 GPa.
- [28] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA 30, 244 (1944).
- [29] J. Bonini, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B 102, 045141 (2020).
- [30] A. J. Hatt, N. A. Spaldin, and C. Ederer, Phys. Rev. B 81, 054109 (2010).
- [31] J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y. H. Chu, A. Rother, M. E. Hawkridge, P. Maksymovych, P. Yu, M. Gajek, N. Balke, S. V. Kalinin, S. Gemming, F. Wang, G. Catalan, J. F. Scott, N. A. Spaldin, J. Orenstein, and R. Ramesh, Nat. Mater. 8, 229 (2009).