Pressure-induced metal-insulator transition in oxygen-deficient LiNbO$_3$-type ferroelectrics

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Abstract

Hydrostatic pressure and oxygen vacancies usually have deleterious effects on ferroelectric materials because both tend to reduce their polarization. In this work we use first-principles calculations to study an important class of ferroelectric materials – LiNbO$_3$-type ferroelectrics (LiNbO$_3$ as the prototype), and find that in oxygen-deficient LiNbO$_{3-\delta}$, hydrostatic pressure induces an unexpected metal-insulator transition between 8 and 9 GPa. Our calculations also find that strong polar displacements persist in both metallic and insulating oxygen-deficient LiNbO$_{3-\delta}$ and the size of polar displacements is comparable to pristine LiNbO$_3$ under the same pressure. These properties are distinct from widely used perovskite ferroelectric oxide BaTiO$_3$, whose polarization is quickly suppressed by hydrostatic pressure and/or oxygen vacancies. The anomalous pressure-driven metal-insulator transition in oxygen-deficient LiNbO$_{3-\delta}$ arises from the change of an oxygen vacancy defect state. Hydrostatic pressure increases the polar displacements of oxygen-deficient LiNbO$_{3-\delta}$, which reduces the band width of the defect state and eventually turns it into an in-gap state. In the insulating phase, the in-gap state is further pushed away from the conduction band edge under hydrostatic pressure, which increases the fundamental gap. Our work shows that for LiNbO$_3$-type strong ferroelectrics, oxygen vacancies and hydrostatic pressure combined can lead to new phenomena and potential functions, in contrast to the harmful effects occurring to perovskite ferroelectric oxides such as BaTiO$_3$. 
I. INTRODUCTION

Ferroelectricity is one of the most important functional properties of transition metal oxides [1, 2]. Two classes of transition metal oxides: perovskite oxides (BaTiO$_3$ as the prototype) and small A-site LiNbO$_3$-type oxides (LiNbO$_3$ as the prototype) both exhibit robust ferroelectric polarization above room temperature [3–6], promising potential applications in ferroelectric-based electronic devices. The origin of ferroelectricity in BaTiO$_3$ arises from the hybridization between Ti-$d$ and O-$p$ states, which leads to a second-order Jahn-Teller distortion (SOJT) [7–9]. SOJT weakens the short-range repulsive forces that favor the non-polar structure and allows the long-range Coulombic forces to dominate, so that a polar structure is stabilized in BaTiO$_3$ [1, 10]. On the other hand, ferroelectricity in LiNbO$_3$ originates from a geometric mechanism rather than charge transfer or hybridization [11, 12]. The very small Li ion size (thus a tolerance factor $t < 1$) leads to a combined structural distortions of NbO$_6$ octahedral rotation and a Li polar displacement, which altogether optimize the Li-O bond length [13, 14]. For BaTiO$_3$, it is known that either hydrostatic (positive) pressure [15, 16] or (charge neutral) oxygen vacancies [17–21] can reduce its polarization, thereby limiting its applications under those unfavorable conditions [22–25]. Therefore it is interesting to explore how LiNbO$_3$ responds to oxygen vacancies and/or hydrostatic pressure. In our previous study, we carefully compare oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$ under ambient pressure [26]. We find that in BaTiO$_{3-\delta}$, the itinerant electrons doped by oxygen vacancies are uniformly distributed, but in LiNbO$_{3-\delta}$, the distribution of itinerant electrons is highly inhomogeneous.

In this work, we extend our study to hydrostatic pressure effects on oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$. We find a more striking distinction between these two representative ferroelectric materials. For BaTiO$_3$, since either charge neutral oxygen vacancies or hydrostatic pressure tends to suppress its ferroelectric property, when these two factors are combined, expectedly it yields a more unfavorable condition for sustaining its polarization. Our first-principles calculations find that in oxygen-deficient BaTiO$_{3-\delta}$, hydrostatic pressure can completely suppress its polarization and drive it into a paraelectric state. However, for LiNbO$_3$, in the presence of both charge neutral oxygen vacancies and external hydrostatic pressure, our calculations find an unexpected pressure-driven metal-insulator transition between 8 and 9 GPa, in a wide range of oxygen vacancy concentrations. The transition arises
from the change of an oxygen vacancy defect state in oxygen-deficient LiNbO$_{3-\delta}$, which is mainly composed of Nb-$d$ orbitals. Applying a hydrostatic pressure increases the Nb-O polar displacements in LiNbO$_{3-\delta}$, due to a cooperative coupling between octahedral rotations and polarity [27]. This in turn reduces the band width of the defect state. When the applied pressure makes the band width of oxygen vacancy defect state sufficiently narrow in oxygen-deficient LiNbO$_{3-\delta}$, the defect state splits off the conduction bands and becomes an in-gap state, and thus the itinerant electrons get trapped around the oxygen vacancy and a metal-insulator transition occurs. Our calculations also find that in both metallic and insulating oxygen-deficient LiNbO$_{3-\delta}$, their polar displacements are comparable in magnitude to pristine LiNbO$_3$ under the same pressure. These robust polar properties imply that LiNbO$_3$-based ferroelectric materials can have a wider range of applications, especially when they are under various conditions that are unfavorable to perovskite ferroelectrics such as BaTiO$_3$.

II. COMPUTATIONAL DETAILS

We perform density functional theory (DFT) calculations [28, 29], as implemented in Vienna Ab-initio Simulation Package (VASP) [30, 31]. We use an energy cutoff of 600 eV. Charge self-consistent calculations are converged to $10^{-5}$ eV. Both cell and internal coordinates are fully relaxed until each force component is smaller than 10 meV/Å and stress tensor is smaller than 1 kbar. For the exchange-correlation functional, we use local spin density approximation (LSDA) [32]. However, we do not find magnetization in either pristine BaTiO$_3$/LiNbO$_3$ or oxygen-deficient BaTiO$_{3-\delta}$/LiNbO$_{3-\delta}$ (see Appendix A). Therefore we sum over both spins in the calculation of density of states. For pristine bulk calculations, we use a tetragonal cell (5-atom) with a Monkhorst-Pack $k$-point sampling of $12 \times 12 \times 12$ to study BaTiO$_3$ and find that $a = 3.94$ Å and $c/a = 1.01$; we use a hexagonal cell (30-atom) with a Monkhorst-Pack $k$-point sampling of $10 \times 10 \times 10$ to study $R3c$ LiNbO$_3$ and find that $a = 5.09$ Å and $c = 13.80$ Å. Both of them are in good agreement with the previous studies [33]. Bulk polarization is calculated using Berry phase method [34, 36]. To study charge neutral oxygen vacancies, we use supercell calculations. For oxygen-deficient BaTiO$_{3-\delta}$, we start from the $P4mm$ structure of pristine BaTiO$_3$ and remove one charge neutral oxygen atom. There are two inequivalent Wyckoff positions for oxygen atoms in
the \( P4mm \) structure \[37\]. We find similar results when oxygen vacancy is induced in either position. For oxygen-deficient \( \text{LiNbO}_3 - \delta \), we start from the \( R3c \) structure of pristine \( \text{LiNbO}_3 \) and remove one charge neutral oxygen atom. There is only one Wyckoff position for oxygen atoms in the \( R3c \) \( \text{LiNbO}_3 \), i.e., all the oxygen atom positions are equivalent \[38\]. To simulate different oxygen vacancy concentrations, we use supercells of different sizes in which we remove one charge neutral oxygen vacancy. In the supercell calculations, we turn off all symmetries and fully relax the structure (both lattice constants and internal coordinates) to accommodate possible oxygen octahedral distortions and obtain the ground state property.

We use a Monkhorst-Pack \( k \)-point sampling of \( 8 \times 8 \times 8 \) in supercell calculations. For the main results, we use a 59-atom supercell for \( \text{BaTiO}_3 - \delta \) and \( \text{LiNbO}_3 - \delta \) to simulate an oxygen vacancy concentration of \( \delta = 8.3\% \). We also use a 79-atom, 119-atom and 179-atom supercell of \( \text{LiNbO}_3 - \delta \) to simulate a wide range of oxygen vacancy concentrations (\( \delta = 6.3\%, 4.2\% \) and \( 2.8\% \)) and test the robustness of our key results. We also use a higher energy cutoff (750 eV) and a denser \( k \)-point sampling to test the key results and we do not find any qualitative difference.

III. RESULTS

For completeness and benchmarking, we first study hydrostatic pressure effects on pristine \( \text{BaTiO}_3 \) and \( \text{LiNbO}_3 \). Then we compare oxygen-deficient \( \text{BaTiO}_3 - \delta \) and \( \text{LiNbO}_3 - \delta \) under hydrostatic pressure, and carefully study the pressure-driven metal-insulator transition in oxygen-deficient \( \text{LiNbO}_3 - \delta \).

A. Pressure effects on pristine \( \text{BaTiO}_3 \) and \( \text{LiNbO}_3 \)

We summarize the hydrostatic pressure effects on pristine \( \text{BaTiO}_3 \) and \( \text{LiNbO}_3 \) in Fig. 1. In both \( \text{BaTiO}_3 \) and \( \text{LiNbO}_3 \), the transition metal atoms (Ti and Nb) are in an oxygen octahedron and thus the crystal field splitting removes the \( d \) orbital degeneracy and separates the \( d \) orbitals into two energy groups \[39\]. The group with the lower (higher) energy is called \( t_{2g} \) (\( e_g \)) states. We focus on \( t_{2g} \) states for conciseness (we find similar results for \( e_g \) states). Panel a shows the band widths of \( \text{Ti-}t_{2g} \) and \( \text{Nb-}t_{2g} \) states as a function of applied hydrostatic pressure (the electronic band structures of pristine \( \text{BaTiO}_3 \) and \( \text{LiNbO}_3 \) under a
representative hydrostatic pressure are shown in Appendix B). Pressure naturally decreases the volumes of BaTiO$_3$ and LiNbO$_3$ (see panel b), which increases the hopping between Ti-$d$/Nb-$d$ orbitals and O-$p$ orbitals. As expected, the band width of both Ti-$t_{2g}$ and Nb-$t_{2g}$ states increases under hydrostatic pressure. However, as panel a shows, the band width of Nb-$t_{2g}$ states increases much more slowly than that of Ti-$t_{2g}$ states. To understand that, we compare the polar displacements (the definition of polar displacements in BaTiO$_3$ and LiNbO$_3$ can be found in Appendix C) and the polarization of BaTiO$_3$ and LiNbO$_3$ under hydrostatic pressure (panels c and d). Our calculations find that hydrostatic pressure reduces the polar displacements and polarization of BaTiO$_3$ and completely suppresses them above a critical value, due to the destabilization of short-range interaction at high pressure [15]. By contrast, our calculations find that hydrostatic pressure increases the polar displacements and polarization of LiNbO$_3$, due to a cooperative coupling between octahedral rotations and polarity [27]. Similar results have been obtained in ferroelectric ZnSnO$_3$ [27] and polar metal LiOsO$_3$ [40]. This means that in LiNbO$_3$, there are two competing forces: the overall volume reduction facilitates hopping, but the increased polar displacements make hopping more difficult; while in BaTiO$_3$, both volume reduction and weakened polar displacements help increase hopping. Since band width is proportional to hopping, this explains why the band width of Nb-$t_{2g}$ bands increases much more slowly than that of Ti-$t_{2g}$ bands under hydrostatic pressure.

**B. Pressure effects on oxygen-deficient BaTiO$_3$–δ and LiNbO$_3$–δ**

Next we study hydrostatic pressure effects on oxygen-deficient BaTiO$_3$–δ and oxygen-deficient LiNbO$_3$–δ and show that under pressure the electronic structure of these two materials behaves much more differently than pristine ones. Charge neutral oxygen vacancies are a common defect in complex oxides [41–45], which are electron donors and induce defect states that are close to conduction band edge [46–48]. If the band width of the defect states is large enough so that the Fermi level cuts through both defect bands and conduction bands, then the system is conducting and the doped electrons are itinerant.

Fig. 2 shows the density of states (DOS) of oxygen-deficient BaTiO$_3$–δ and LiNbO$_3$–δ (with δ = 8.3%) as a function of applied hydrostatic pressure. We find that under hydrostatic pressure, oxygen-deficient BaTiO$_3$–δ is conducting and its DOS almost does not change
FIG. 1. Hydrostatic pressure effects on pristine BaTiO$_3$ and LiNbO$_3$. As a function of hydrostatic pressure, a) the band width of Ti-$t_{2g}$ states of BaTiO$_3$ and Nb-$t_{2g}$ states of LiNbO$_3$; b) the volume of BaTiO$_3$ and LiNbO$_3$ per formula; c) Ba-O and Ti-O polar displacements of BaTiO$_3$ and Li-O and Nb-O polar displacements of LiNbO$_3$; d) the polarization of BaTiO$_3$ and LiNbO$_3$.

under increasing pressure (panels a, b, c). By contrast, our calculations find that LiNbO$_3$$_{3−δ}$ undergoes a metal-insulator transition. When the applied hydrostatic pressure is smaller than 8 GPa, LiNbO$_3$$_{3−δ}$ is conducting; and above 8 GPa, a small gap is opened in the electronic structure of LiNbO$_3$$_{3−δ}$ and the gap is further increased with pressure (see the insets of panels e and f). For pristine materials, this pressure-driven metal-insulator transition is rare, because pressure generically decreases volume and usually closes gap and makes materials more conducting.

To understand the origin of this pressure-driven metal-insulator transition, we study polar displacements (the definition of polar displacements in BaTiO$_3$$_{3−δ}$ and LiNbO$_3$$_{3−δ}$ is also found in Appendix C) and band structure of oxygen-deficient LiNbO$_3$$_{3−δ}$ and compare them to those of oxygen-deficient BaTiO$_3$$_{3−δ}$ (with $δ = 8.3\%$). Fig. 3a shows the site-resolved Ti-O polar
FIG. 2. Densities of states of oxygen-deficient BaTiO$_{3-\delta}$ (panels a, b, c) and oxygen-deficient LiNbO$_{3-\delta}$ (panels d, e, f) with $\delta = 8.3$% under a hydrostatic pressure of 0, 8 and 15 GPa, respectively. The black, red and blue are total, Ti-$d$ or Nb-$d$ and O-$p$ projected densities of states, respectively. The insets in e and f show the densities of states near the Fermi level.

Displacements in BaTiO$_{3-\delta}$ under hydrostatic pressure. Different from pristine BaTiO$_3$, each oxygen vacancy donates two mobile electrons, which already suppress the average Ti-O polar displacements under ambient pressure. Applying a hydrostatic pressure does not affect the Ti-O polar displacements. Fig. 3b shows the electronic band structure of oxygen-deficient BaTiO$_{3-\delta}$. The lowest band that crosses the Fermi level is an oxygen vacancy defect state. Applying a hydrostatic pressure only slightly increases the band width of the defect state and has little effect on the overall electronic structure. Fig. 3c and d show the site-resolved Li-O and Nb-O polar displacements in oxygen-deficient LiNbO$_{3-\delta}$ under hydrostatic pressure. The red (blue) squares in Fig. 3c and d refer to the polar displacements in the conducting (insulating) LiNbO$_{3-\delta}$. In the inset of panel d, we compare the average Li-O and Nb-O polar displacements between oxygen-deficient LiNbO$_{3-\delta}$ and pristine LiNbO$_3$ under hydrostatic pressure. We find that similar to pristine LiNbO$_3$ (see Fig. 1), hydrostatic pressure increases
FIG. 3. Panels a-b: oxygen-deficient BaTiO$_3$$_{\delta}$ (with $\delta = 8.3\%$) under a hydrostatic pressure of 0, 8 and 15 GPa. a: polar displacements of each Ti atom. b: electronic band structure close to the Fermi level. The high-symmetry k-path is $\Gamma(0,0,0)$-$X(0.5,0,0)$-$S(0.5,0.5,0)$-$Y(0,0.5,0)$-$\Gamma(0,0,0)$-$Z(0,0,0.5)$. Panels c-f: oxygen-deficient LiNbO$_3$$_{\delta}$ (with $\delta = 8.3\%$) under several hydrostatic pressures in the range of 0-15 GPa. c: polar displacements of each Li atom. d: polar displacements of each Nb atom. Red and blue squares represent conducting and insulating phases of oxygen-deficient LiNbO$_3$$_{\delta}$, respectively. The inset in d compares the average polar displacements of Li and Nb in oxygen-deficient LiNbO$_3$$_{\delta}$ (with $\delta = 8.3\%$) and pristine LiNbO$_3$. e: electronic band structure close to the Fermi level under a hydrostatic pressure of 0, 5 and 7 GPa, where LiNbO$_3$$_{\delta}$ is conducting. f: electronic band structure close to the Fermi level under a hydrostatic pressure of 8, 10 and 15 GPa, where LiNbO$_3$$_{\delta}$ is insulating. The high-symmetry k-point path is $X(0,-0.5,0)$-$\Gamma(0,0,0)$-$Y(0.5,0,0)$-$L(0.5,-0.5,0)$-$\Gamma(0,0,0)$-$Z(-0.5,0,0.5)$-$N(-0.5,-0.5,0.5)$-$\Gamma(0,0,0)$-$M(0,0,0.5)$-$R(0,-0.5,0.5)$-$\Gamma(0,0,0)$.
the polar displacements of oxygen-deficient LiNbO$_{3-\delta}$. In particular, the Nb atom and the Li atom that are closest to the oxygen vacancy have the most substantial increase in the polar displacement. However, different from pristine LiNbO$_3$, there is a sudden “jump” in the polar displacements between 7 and 8 GPa, which is evident in the inset of panel d. For a given hydrostatic pressure, the average polar displacements of conducting oxygen-deficient LiNbO$_{3-\delta}$ are slightly smaller than those of pristine LiNbO$_3$. This is because mobile electrons in conducting LiNbO$_{3-\delta}$ can screen internal electric fields and suppress the polar displacements [26]. However, in insulating LiNbO$_{3-\delta}$, the average polar displacements are almost the same as those of pristine LiNbO$_3$ because screening from mobile electrons is absent.

Accompanying this sudden “jump” in the polar displacements is a metal-insulator transition. Fig. 3e and f show the electronic band structures of conducting and insulating oxygen-deficient LiNbO$_{3-\delta}$, respectively. In conducting LiNbO$_{3-\delta}$, the band width of the defect state is reduced by hydrostatic pressure, which is in contrast to pristine LiNbO$_3$ and BaTiO$_3$ in which hydrostatic pressure always increases their band width. This anomalous pressure effect is because the defect state is closely related to Nb #6, which is the nearest neighbor of the oxygen vacancy. The substantially increased polar displacement of Nb #6 makes the electron hopping much more difficult, which overweighs the volume reduction from hydrostatic pressure. In insulating LiNbO$_{3-\delta}$, the defect state becomes an in-gap state. Similar to defects in semiconductors, hydrostatic pressure increases the repulsion between conduction band edge and in-gap states, which further increases the fundamental band gap of oxygen-deficient LiNbO$_{3-\delta}$ (i.e. the gap between the conduction band edge and the defect state) [49–53].

Next we study how hydrostatic pressure changes the spatial distribution of doped electrons in oxygen-deficient BaTiO$_{3-\delta}$ and oxygen-deficient LiNbO$_{3-\delta}$. Each oxygen vacancy donates two electrons and they occupy the defect state and conduction bands, which are mainly composed of Ti-$d$ or Nb-$d$ states. Fig. 4 shows the spatial distribution of doped electrons and the number of doped electrons on each Ti and Nb atoms in oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$ (with $\delta = 8.3\%$). Oxygen-deficient BaTiO$_{3-\delta}$ is always conducting and the doped electrons are almost homogeneously distributed, as is shown explicitly in Fig. 4a and b. Hydrostatic pressure makes the electron distribution even more homogeneous in BaTiO$_{3-\delta}$ (see Fig. 4c). However, in oxygen-deficient LiNbO$_{3-\delta}$, the distribution
FIG. 4. Panels a and b show the iso-value surfaces of doped electron distribution in oxygen-deficient BaTiO$_{3-\delta}$ with $\delta = 8.3\%$ under 0 and 15GPa, respectively. Panel c shows the doped electrons on each Ti atom in oxygen-deficient BaTiO$_{3-\delta}$ ($\delta = 8.3\%$) under a hydrostatic pressure of 0, 8 and 15 GPa. Panels d and e are the iso-value surfaces of doped electron distribution in oxygen-deficient LiNbO$_{3-\delta}$ with $\delta = 8.3\%$ under 7 and 8 GPa, respectively. Panel f shows the doped electrons on each Nb atom in oxygen-deficient LiNbO$_{3-\delta}$ ($\delta = 8.3\%$) under a hydrostatic pressure of 0, 7, 8 and 15 GPa. For both materials, the iso-surface corresponds to a charge density of $0.027e/\text{Å}^3$. The number of doped electrons on each Ti or Nb atom is obtained by integrating their $d$ states from the valence band edge to the Fermi level.

of doped electrons is highly inhomogeneous [26]. As we showed previously in Fig. 3 hydrostatic pressure increases the polar displacements of LiNbO$_{3-\delta}$ and narrows the band width of the defect state, which means the reduction of electron hopping. Correspondingly, the doped electrons tend to be localized in real space. From ambient pressure to 7 GPa, the doped electrons are distributed on all Nb sites (see Fig. 4d). However, under a hydrostatic pressure of 8 GPa that is just above the critical pressure, most doped electrons are concentrated in the void space between Nb #6 and Nb #12, which are the two nearest neighbors of the oxygen vacancy (see Fig. 4e). Such a localization effect can be more clearly seen from the two peaks in the Nb site-resolved electron distribution, shown in Fig. 4f. In oxygen-
FIG. 5. Densities of states of oxygen-deficient LiNbO$_{3-\delta}$ with different vacancy concentrations under 0 (panel a) and 9 GPa (panel b). The red, green and blue curves are for LiNbO$_{3-\delta}$ with $\delta = 6.3\%$, $\delta = 4.2\%$ and $\delta = 2.8\%$, respectively. The insets show the densities of states near the Fermi level.

deficient LiNbO$_{3-\delta}$, applying hydrostatic pressure localizes itinerant electrons and leads to a metal-insulator transition, in stark contrast to oxygen-deficient BaTiO$_{3-\delta}$. We note that the localized carriers in the insulating LiNbO$_{3-\delta}$ (Fig. 4e) correspond to two electrons that are donated by an oxygen vacancy. These two electrons completely fill the defect band (see Fig. 3f) and thus spin up and spin down channels have equal occupancy. Therefore, no local magnetic moment emerges from this charge localization. Our case is different from a recent work on doped BaTiO$_3$ under epitaxial strain [54] in which one electron half-fills a band and occupies a single spin channel. Correlation effects localize the lone electron and a magnetic polaron state is formed [55].

So far, we have only studied one concentration of oxygen vacancy $\delta = 8.3\%$. In Fig. 5 we study different oxygen vacancy concentrations in oxygen-deficient LiNbO$_{3-\delta}$. We find that the pressure-driven metal-insulator transition occurs in a wide range of vacancy concentrations. In addition to $\delta = 8.3\%$ (59-atom cell), we also calculate $\delta = 6.3\%$ (79-atom cell), $\delta = 4.2\%$ (119-atom) and 2.8\% (179-atom cell). In all three cases, under ambient pressure, LiNbO$_{3-\delta}$ is conducting (Fig. 5a) while under a hydrostatic pressure of 9 GPa, LiNbO$_{3-\delta}$ becomes insulating with the defect state turning into an in-gap state and lying below the conduction bands (Fig. 5b). The critical pressure weakly depends on vacancy concentration,
which ranges between 8 and 9 GPa for oxygen-deficient LiNbO$_3$$_{\delta}$.

Finally, we make two comments. One is that the pressure-driven metal-insulator transition in our study is fundamentally different from the pressure-driven insulator-to-metal transition in correlated materials [56–59]. In the former, high pressure stabilizes an insulating state in oxygen-deficient LiNbO$_3$$_{\delta}$; while in the latter, increasing pressure closes the Mott gap and leads to a metallic state. The pressure-driven insulator-to-metal transition in correlated materials is usually strongly first-order, accompanied by abrupt reduction in volume and/or collapse of local magnetic moment [60–62]. By contrast, the pressure-driven metal-insulator transition in our study is associated with a defect band, which is fully occupied when the fundamental gap is opened. As we mentioned above, since the defect band is fully occupied (in both spin up and spin down channels), no local magnetic moment is found in our calculations and correlation effects play a minor role. The second comment is the connection between our results and available experimental data. Oxygen vacancies have been widely found in important ferroelectric oxides, such as BaTiO$_3$ [63], PbTiO$_3$ [64], (Pb$_{1-x}$Ba$_x$)(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ [65, 66], KNbO$_3$ [67], LiNbO$_3$ [68], HfO$_2$ [69, 70], and amorphous Al$_2$O$_3$ [71]. The presence of oxygen vacancies can substantially change the structural, dielectric, and transport properties of ferroelectrics [22, 25], such as the reduction of polarization [72, 73] and the emergence of conduction [65, 67]. Sometimes combining oxygen vacancies and polar structure in ferroelectrics can also lead to new functions [71, 74, 75]. Most pertinent to the current study are oxygen-deficient BaTiO$_3$$_{\delta}$ and LiNbO$_3$$_{\delta}$. Oxygen vacancies in BaTiO$_3$ have been observed and studied in a few experiments [19–21]. The theoretical results in the current study are qualitatively consistent with the experiments in that 1) conduction appears in BaTiO$_3$$_{\delta}$ due to oxygen vacancies [19, 20]; 2) Ti-O polar displacements are reduced by itinerant electrons and are completely suppressed above a critical electron concentration of $1.9 \times 10^{21}$ cm$^{-3}$ [21]. For LiNbO$_3$, various types of defects such as Li-vacancies, O-vacancies, Li-Nb antisite defects, etc. are found in experiments [76, 79]. In particular, oxygen-deficient LiNbO$_3$$_{\delta}$ in nanocrystallites and single crystals have been reported in several experiments [80, 83], but high-pressure study has not been performed. We hope that our theoretical study may stimulate further experiments on oxygen-deficient LiNbO$_3$$_{\delta}$ under hydrostatic pressure.
IV. CONCLUSION

In summary, we compare the pressure effects on two important and representative ferroelectric oxides BaTiO$_3$ and LiNbO$_3$ in the pristine form and in a defective form with oxygen vacancies. In pristine BaTiO$_3$, hydrostatic pressure reduces the polar displacements and increases the band width of Ti-$d$ states. In oxygen-deficient BaTiO$_{3-\delta}$, pressure makes the doped electrons more homogeneously distributed. Both phenomena are within expectation. By contrast, in both pristine LiNbO$_3$ and oxygen-deficient LiNbO$_{3-\delta}$, pressure increases their polar displacements. More strikingly, in oxygen-deficient LiNbO$_{3-\delta}$, we find an unexpected pressure-driven metal-insulator transition. The anomalous transition arises from the fact that the substantially increased polar displacements in oxygen-deficient LiNbO$_{3-\delta}$ under hydrostatic pressure reduce the overlap between Nb-$d$ and O-$p$ orbitals and thus decrease the band width of the defect state. When the band width of the defect state is sufficiently narrow, it turns into an in-gap state and the system becomes insulating with itinerant electrons trapped around the oxygen vacancy. This pressure-driven metal-insulator transition occurs to oxygen-deficient LiNbO$_{3-\delta}$ in a wide range of oxygen vacancy concentrations.

Our work shows that LiNbO$_3$-type ferroelectric materials have more robust polar properties against oxygen vacancies and hydrostatic pressure than BaTiO$_3$. Furthermore, the intriguing pressure-driven metal-insulator transition in oxygen-deficient LiNbO$_{3-\delta}$ is not found in widely used ferroelectric materials BaTiO$_3$ or BaTiO$_{3-\delta}$. This implies that LiNbO$_3$-based ferroelectric devices may have a wider range of applications, in particular when they are under conditions that are unfavorable to perovskite ferroelectrics such as BaTiO$_3$.

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Appendix A: LSDA calculations for possible magnetization

In this section, we show the LSDA calculations of pristine BaTiO$_3$ and LiNbO$_3$, as well as oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$. We find that while we intentionally break the spin symmetry, the resulting density of states do not exhibit any magnetization in our calculations.

Fig. 6 shows the density of states of pristine BaTiO$_3$ and LiNbO$_3$ under a hydrostatic pressure of 0, 8 and 15 GPa. Fig. 7 shows the density of states of oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$ under a hydrostatic pressure of 0, 8 and 15 GPa.

FIG. 6. Densities of states of pristine BaTiO$_3$ (panels a, b, c) and pristine LiNbO$_3$ (panels d, e, f) under a hydrostatic pressure of 0, 8 and 15 GPa. The black and red lines are total and Ti-d/Nb-d projected densities of states, respectively. $m$ shown in each sub-plot is the average magnetization per Ti or per Nb. The green solid line is the Fermi level.
FIG. 7. Densities of states of oxygen-deficient BaTiO$_{3-\delta}$ (panels a, b, c) and oxygen-deficient LiNbO$_{3-\delta}$ (panels d, e, f) with $\delta = 8.3$ % under a hydrostatic pressure of 0, 8 and 15 GPa. The black and red lines are total and Ti-d/Nb-d projected densities of states, respectively. $m$ shown in each sub-plot is the average magnetization per Ti or per Nb. The green solid line is the Fermi level.
Appendix B: Electronic band structure of pristine BaTiO$_3$ and LiNbO$_3$ under a hydrostatic pressure

Fig. 8 shows densities of states and electronic band structure of pristine BaTiO$_3$ (panels a and c) and pristine LiNbO$_3$ (panels b and d) under a representative hydrostatic pressure of 8 GPa. Both pristine BaTiO$_3$ and LiNbO$_3$ are wide gap insulators under ambient pressure and they remain insulating under a hydrostatic pressure of 8 GPa. In the calculations, we find that the overall electronic structures of BaTiO$_3$ and LiNbO$_3$ do not change substantially with pressure but the band width of Ti-$d$ and Nb-$d$ states increase under pressure. Since we are interested in the band width of Ti-$d$ and Nb-$d$ states, we only show the electronic band structure above the conduction band minimum (CBM). Due to the crystal field splitting in BaTiO$_3$ and LiNbO$_3$, both Ti-$d$ and Nb-$d$ orbitals are split into $t_{2g}$ and $e_g$ states. The Ti-$t_{2g}$ and Nb-$t_{2g}$ states are highlighted in red in panels c and d of Fig. 8. Our calculations find that the band width of both $t_{2g}$ and $e_g$ states increase under pressure. For conciseness, we only show the pressure dependence of Ti-$t_{2g}$ and Nb-$t_{2g}$ band width in Fig. 1 in the main text.
FIG. 8. Densities of states and electronic band structure of pristine BaTiO$_3$ (panels a and c) and pristine LiNbO$_3$ (panels b and d) under a hydrostatic pressure of 8 GPa. The black, red, and blue lines in a and b are total, Ti-$d$ or Nb-$d$, and O-$p$ projected densities of states, respectively. Only those energy bands that are above the conduction band minimum (CBM) are shown in c and d. Ti-$t_{2g}$ and Nb-$t_{2g}$ states are highlighted in red. The high-symmetry $\mathbf{k}$-path of BaTiO$_3$ is $\Gamma(0,0,0)$-$X(0.5,0,0)$-$M(0.5,0.5,0)$-$\Gamma(0,0,0)$-$Z(0,0,0.5)$-$R(0,0.5,0.5)$-$A(0.5,0.5,0.5)$-$Z(0,0,0.5)$. The high-symmetry $\mathbf{k}$-path of LiNbO$_3$ is $\Gamma(0,0,0)$-$L(0.5,0,0)$-$B(0.5,0.236,-0.236)$-$Z(0.5,0.5,0.5)$-$\Gamma(0,0,0)$-$X(0.368,0,-0.368)$. 
Appendix C: Definition of polar displacements

The advantage of using polar displacements to characterize ferroelectric-like distortions is that they are well defined in both insulating and conducting systems, while polarization is ill-defined in metals [22, 84, 85].

Pristine BaTiO$_3$ and LiNbO$_3$ are both insulators. However, oxygen vacancies donate itinerant electrons and make oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$ conducting under ambient pressure. We follow the previous definition of polar displacements when we study BaTiO$_3$ and LiNbO$_3$ under ambient pressure [26] and now extend the definition to the case in which both materials are under hydrostatic pressure. For self-containedness, we outline the definition of polar displacement $\delta z$ briefly below.

Fig. 9a and b show the crystal structure of pristine BaTiO$_3$ and oxygen-deficient BaTiO$_{3-\delta}$ with $\delta = 8.3\%$. In the $ab$ plane, each Ti atom is surrounded by four O atoms in TiO$_2$ layer and Ti atoms move along the $c$ axis, therefore Ti-O displacement $\delta z_{Ti-O}$ is defined as:

$$\delta z_{Ti-O} = z_{Ti} - \frac{1}{4} \sum_{i=1}^{4} z_{O_i} \quad (C1)$$

where $z_{Ti}$ is the $c$ position of Ti and $z_{O_i}$ is the $c$ position of the four nearest O atoms. $\delta z_{Ba-O}$ is defined in a similar way as $\delta z_{Ti-O}$. We note that in oxygen-deficient BaTiO$_{3-\delta}$, the two Ti atoms that are closest to the oxygen vacancy only have three nearest O atoms in TiO$_2$ layer in $ab$ plane, therefore the Ti-O displacement $\delta z_{Ti-O}$ for these two Ti atoms is defined as:

$$\delta z_{Ti-O} = z_{Ti} - \frac{1}{3} \sum_{i=1}^{3} z_{O_i} \quad (C2)$$

where $z_{O_i}$ is the $c$ position of the three nearest O atoms around the Ti atom in $ab$ plane.

Fig. 9c and d show the crystal structure of pristine LiNbO$_3$ and oxygen-deficient LiNbO$_{3-\delta}$ with $\delta = 8.3\%$. $\delta z_{Li-O}$ and $\delta z_{Nb-O}$ are defined in slightly different ways. Each Li atom is surrounded by three O atoms and Li atoms move along the $c$ axis. Li-O displacement $\delta z_{Li-O}$ is defined as:

$$\delta z_{Li-O} = z_{Li} - \frac{1}{3} \sum_{i=1}^{3} z_{O_i} \quad (C3)$$

where $z_{Li}$ is the $c$ position of Li and $z_{O_i}$ is the $c$ position of the three nearest O atoms. Each Nb atom is surrounded by six O atoms and Nb atoms move along the $c$ axis. Nb-O
FIG. 9. Crystal structures of pristine BaTiO$_3$ (panel a), oxygen-deficient BaTiO$_{3-\delta}$ with $\delta = 8.3\%$ (panel b), pristine LiNbO$_3$ (panel c) and oxygen-deficient LiNbO$_{3-\delta}$ with $\delta = 8.3\%$ (panel d). Green, blue and red balls in panels a and b are Ba, Ti and O atoms, respectively. Brown, green and red balls in panels c and d are Li, Nb and O atoms, respectively. The oxygen vacancy in oxygen-deficient BaTiO$_{3-\delta}$ and LiNbO$_{3-\delta}$ is highlighted by the orange open circle.

The displacement $\delta z_{\text{Nb-O}}$ is defined as:

$$\delta z_{\text{Nb-O}} = z_{\text{Nb}} - \frac{1}{6} \sum_{i=1}^{6} z_{O_i}$$

(C4)

where $z_{\text{Nb}}$ is the $c$ position of Nb and $z_{O_i}$ is the $c$ position of the six nearest O atoms. We note that in oxygen-deficient LiNbO$_{3-\delta}$, the Li atom that is closest to the oxygen vacancy only has two nearest O atoms, and the two Nb atoms that are closest to the oxygen vacancy only have five nearest O atoms. Therefore, the Li-O displacement for this Li atom and the
Nb-O displacement for these two Nb atoms are defined as:

\[
\delta z_{\text{Li-O}} = z_{\text{Li}} - \frac{1}{2} \sum_{i=1}^{2} z_{O_i} \tag{C5}
\]

where \( z_{O_i} \) is the position of the two nearest O atoms for the Li atom and

\[
\delta z_{\text{Nb-O}} = z_{\text{Nb}} - \frac{1}{5} \sum_{i=1}^{5} z_{O_i} \tag{C6}
\]

where \( z_{O_i} \) is the position of the five nearest O atoms around the Nb atom.
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