

## PAPER

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2979Second-order Jahn–Teller effect induced high-  
temperature ferroelectricity in two-dimensional  
NbO<sub>2</sub>X (X = I, Br)<sup>†</sup>Huasheng Sun, Kaiming Deng, Erjun Kan <sup>\*</sup> and Yongping Du <sup>\*</sup>

Based on the first-principles calculations, we investigated the ferroelectric properties of two-dimensional (2D) materials NbO<sub>2</sub>X (X = I, Br). Our cleavage energy analysis shows that exfoliating one NbO<sub>2</sub>I monolayer from its existing bulk counterpart is feasible. The phonon spectrum and molecular dynamics simulations confirm the dynamic and thermal stability of the monolayer structures for both NbO<sub>2</sub>I and NbO<sub>2</sub>Br. Total energy calculations show that the ferroelectric phase is the ground state for both materials, with the calculated in-plane ferroelectric polarizations being 384.5 pC m<sup>−1</sup> and 375.2 pC m<sup>−1</sup> for monolayers NbO<sub>2</sub>I and NbO<sub>2</sub>Br, respectively. Moreover, the intrinsic Curie temperature *T<sub>C</sub>* of monolayer NbO<sub>2</sub>I (NbO<sub>2</sub>Br) is as high as 1700 K (1500 K) from Monte Carlo simulation. Furthermore, with the orbital selective external potential method, the origin of ferroelectricity in NbO<sub>2</sub>X is revealed as the second-order Jahn–Teller effect. Our findings suggest that monolayers NbO<sub>2</sub>I and NbO<sub>2</sub>Br are promising candidate materials for practical ferroelectric applications.

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## Introduction

Ferroelectric (FE) materials, which exhibit spontaneous polarization that can be switched by an external electric field, have attracted tremendous research interest over the past decades due to their wide applications in capacitors, sensors, and non-volatile memories.<sup>1–4</sup> In the literature, many efforts have been made to develop perovskite-type oxides, such as BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, PbZr<sub>1–x</sub>Ti<sub>x</sub>O<sub>3</sub>, and La<sub>1/3</sub>NbO<sub>3</sub> in which the cations have an electron configuration of d<sup>0</sup> (Ti<sup>4+</sup>, Zr<sup>4+</sup>, Nb<sup>5+</sup>).<sup>5–8</sup> Moreover, the spontaneous polarization of these compounds is usually induced by off-centering of cations which originates from the second-order Jahn–Teller (SOJT) effect.<sup>9,10</sup> SOJT-active cations have been shown to induce structural distortion, which would break the inversion symmetry, by anisotropic covalent bonding with ligands. Interestingly, the Curie temperature *T<sub>C</sub>* of these compounds is far above room temperature (*i.e.*, the *T<sub>C</sub>* of BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, PbZr<sub>1–x</sub>Ti<sub>x</sub>O<sub>3</sub>, and La<sub>1/3</sub>NbO<sub>3</sub> is 393, 763, 659, and 473 K respectively).<sup>11–14</sup> This inspires us to search for high-temperature ferroelectric materials with SOJT-activated cations.

On the other hand, the urgent requirement for the miniaturization of electronic devices stimulates researchers to devote significant effort to reducing the thickness of thin-film

ferroelectrics.<sup>15,16</sup> However, the depolarization field will destroy ferroelectricity at critical thicknesses for conventional ferroelectric compounds.<sup>17</sup> Recently, the discovery of ferroelectricity in monolayer or few-layer van der Waals (vdW) materials provides new opportunities for reducing the size of ferroelectric devices to atomic thickness.<sup>18–22</sup> In addition, the weak interlayer interaction and the dangling bond-free surface of two-dimensional (2D) vdW materials make it easy to integrate them with other materials in applications.

Thanks to the development of high-throughput calculations and machine learning methods, plenty of calculations have been proposed to predict promising 2D ferroelectric materials. However, only a few dozens of them have been confirmed by experiments.<sup>13,14</sup> The most intuitive strategy for designing new 2D ferroelectric materials is to use the structure of existing 2D ferroelectric materials in the databases as a prototype and then test different combinations of chemical elements. To date, only tens of prototypes, like CuInP<sub>2</sub>S<sub>6</sub> type,<sup>15,16</sup> SnTe type,<sup>17,18</sup> α-In<sub>2</sub>Se<sub>3</sub> type,<sup>19,20</sup> 1T′-MoTe<sub>2</sub> type,<sup>21,22</sup> sliding ferroelectrics and so on, are proposed theoretically and experimentally. Another strategy is to design new prototypes of 2D ferroelectric structures. Investigating the cation off-centring induced by the SOJT effect may provide insight into the design of new 2D ferroelectric structure prototypes.

In this work, we propose a new 2D ferroelectric structure prototype whose structural distortion is induced by the SOJT effect. Using first-principles calculations, we comprehensively investigate the ferroelectric properties of monolayer NbO<sub>2</sub>I cleaved from its existing bulk counterpart. Total energy calculations show that the ferroelectric phase is the ground state with

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an in-plane ferroelectric polarization of  $384.5 \text{ pC m}^{-1}$ , and the intrinsic Curie temperature  $T_c$  as high as 1700 K. Moreover, with the orbital selective external potential (OSEP) method,<sup>23</sup> we reveal that the SOJT effect originates ferroelectricity in  $\text{NbO}_2\text{I}$ . The finite indirect band gap is about 0.95 eV, which indicates that monolayer  $\text{NbO}_2\text{I}$  is a semiconductor. The carrier mobilities of electrons and holes along the two directions are different due to the crystal anisotropy. We also systematically studied the electronic and ferroelectric properties of monolayer  $\text{NbO}_2\text{Br}$ , which has the same structure as  $\text{NbO}_2\text{I}$  with the replacement of I atoms by Br atoms. Our numerical results show that the properties of  $\text{NbO}_2\text{Br}$  are very similar to the ones of  $\text{NbO}_2\text{I}$ .

## Calculation methods

All calculations in this work were based on density functional theory (DFT) implemented in the Vienna *Ab initio* simulation package (VASP).<sup>24</sup> The generalized gradient approximation (GGA) with the form proposed by Perdew, Burke, and Ernzerhof (PBE)<sup>25</sup> was chosen as the exchange–correlation functional. The Projector Augmented Wave (PAW) method<sup>26</sup> was used to describe electron–ion interactions. The vacuum distance was set larger than  $30 \text{ \AA}$  in order to avoid spurious periodic interactions. The kinetic energy cutoff was set to 550 eV, and the first Brillouin zone was sampled with a grid of  $17 \times 15 \times 1$   $k$  points according to the Monkhorst–Pack scheme.<sup>27</sup> The convergence criteria for electronic and ionic relaxations are  $10^{-6}$  eV per atom and  $10^{-3} \text{ eV \AA}^{-1}$ , respectively. van der Waals (vdW) correction was included using the D2 method.<sup>28</sup> The electronic contribution to polarization was calculated using the Berry phase method.<sup>29,30</sup> The nudged elastic band (NEB) approach<sup>31,32</sup> was used to simulate the minimum energy path (MEP) and associated energy barriers.

## Results and discussion

The bulk  $\text{NbO}_2\text{I}$  material was successfully synthesized experimentally in 2007.<sup>33</sup> The crystal structure of  $\text{NbO}_2\text{I}$  possesses a centrosymmetric space group  $Pnma$  with a 7-coordinated  $\text{Nb}^{5+}$  cation and is shown as an example in Fig. 1. Interestingly, 7 ligands of  $\text{Nb}^{5+}$  form a pentagonal bipyramid that is connected *via* the apical  $\text{O}_1$  atoms to chains and *via* three  $\text{O}_2$  atoms to the double-layer structure (Fig. 1(b)). Between these double layers there are only weak van der Waals interactions of I atoms. Two I atoms and three  $\text{O}_2$  atoms are on the pentagonal base plane. At the same time, the axial sites are occupied by the  $\text{O}_1$  atom with very different Nb– $\text{O}_1$  distances of 1.78 and  $2.20 \text{ \AA}$ , which indicate the shift of  $\text{Nb}^{5+}$  and form the structural distortion which could cause the polarization denoted in Fig. 1(c). However, the other  $\text{Nb}^{5+}$  ion in the double layer shifts to the opposite direction (Fig. 1(a)), and thus the bulk  $\text{NbO}_2\text{I}$  does not exhibit macroscopic polarization. As a comparison, the compound  $\text{UO}_2\text{Br}$  has a crystal structure very similar to  $\text{NbO}_2\text{I}$  except for equal U– $\text{O}_1$  distances and no displacement of the U atom (for details see Fig. S1†).<sup>34</sup> Thus, the space group of  $\text{UO}_2\text{Br}$  is  $Cmcm$  with inversion symmetry and has only the paraelectric (PE) phase without spontaneous polarization.

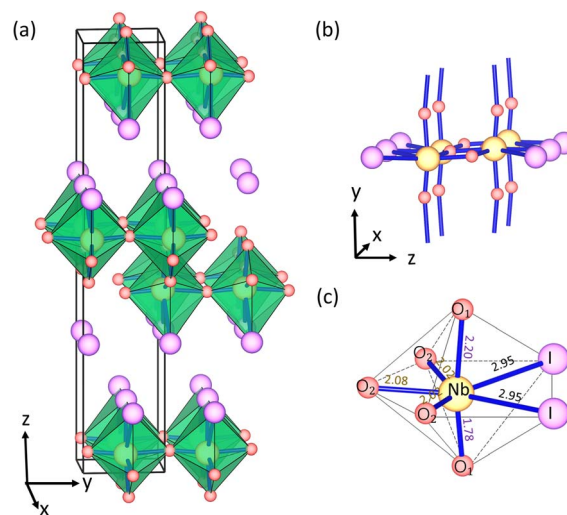


Fig. 1 (a) The layered bulk crystal structure of  $\text{NbO}_2\text{I}$ . (b) The connectivity of the polyhedral in  $\text{NbO}_2\text{I}$ . (c) Coordination polyhedron and bond length of  $\text{Nb}^{5+}$  in  $\text{NbO}_2\text{I}$ .

Because the bulk  $\text{NbO}_2\text{I}$  has a layered structure, it is of much interest to investigate the  $\text{NbO}_2\text{I}$  monolayer for promising ferroelectricity and other valuable properties. We first calculate the cleavage energy to check the accessibility of exfoliation and show the results in Fig. 2(a). The cleavage energy for  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  is  $0.28$  and  $0.21 \text{ J m}^{-2}$ , respectively. They are smaller than the one of graphite.<sup>35</sup> The smaller cleavage energy means that the exfoliation of  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  is feasible. Thus, one layer  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  can be exfoliated from their bulk counterparts, as shown in the inset of Fig. 2.

The crystal structure dynamics and thermal stability can be explored by calculating the phonon spectra and molecular dynamics (MD) simulations. The phonon spectra of  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  along the high-symmetry lines are plotted in Fig. 4(a) and (b). It is observed that there is no imaginary phonon frequency in the entire Brillouin zone, confirming that  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  are dynamically stable. Considering the probability of successful experimental fabrication, the MD simulation of a 5

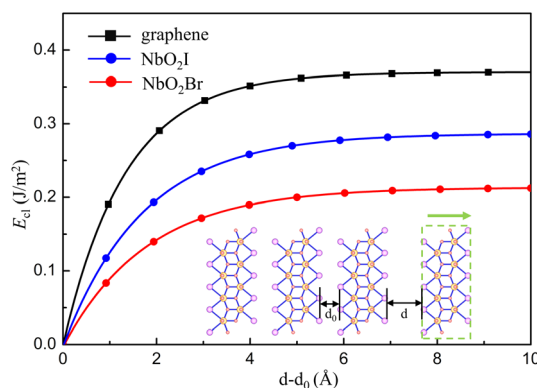


Fig. 2 Cleavage energy  $E_{cl}$  versus the separation distance  $d-d_0$  in the process of exfoliating one  $\text{NbO}_2\text{X}$  ( $X = \text{I}, \text{Br}$ ) layer from their bulk counterparts illustrated by the inset.



× 5 supercell at 500 K with 5 ps time is carried out. The results are presented in Fig. 4(c) and (d) for NbO<sub>2</sub>I and NbO<sub>2</sub>Br, respectively. The MD simulation suggests the thermal stability of the two monolayers. For monolayer NbO<sub>2</sub>Br, we systematically search all possible 2D structures with the Nb:O:Br composition equal to 1:2:1 using the particle swarm optimization (PSO)<sup>36</sup> structure search algorithm and first-principles calculations. After comprehensive calculation, we found that there are six most energetically stable structures, as listed in Fig. S2.† However, the most stable structure is still our NbO<sub>2</sub>I

prototype structure, which again confirms that our NbO<sub>2</sub>I monolayer prototype is stable.

Now we start to explore the ferroelectric properties of monolayers NbO<sub>2</sub>I and NbO<sub>2</sub>Br. As we analyzed before, Nb<sup>5+</sup> has a displacement from the centre of pentagonal bipyramids, causing the spontaneous polarization. To find the ground state, we set three configurations of Nb<sup>5+</sup> in the monolayer, namely ferroelectric (FE), paraelectric (PE), and antiferroelectric (AFE), as shown by the schematics in Fig. 3(b). The total energies of the three configurations are illustrated in Fig. 3(a), in which we use the energy of FE as a reference energy and set it to zero. We can easily see that the FE state is the ground state, which is totally different from bulk NbO<sub>2</sub>I with two Nb<sup>5+</sup> ions in one layer shifting in opposite directions.

The fully relaxed monolayer structure reveals that the Nb<sup>5+</sup> ion shifts from the centre of pentagonal bipyramids with an unequal bond length with two apical O<sub>1</sub> atoms. The polarization is therefore in the in-plane direction. By using the Berry phase method, the polarization *P*<sub>s</sub> was estimated, with values equal to 384.5 and 375.2 pC m<sup>-1</sup> for NbO<sub>2</sub>I and NbO<sub>2</sub>Br, respectively. The reversal of polarization is realized through a phase transition between two symmetry-equivalent ferroelectric states with opposite *P*<sub>s</sub>. We constructed two potential switching paths and computed the energy evolution using the NEB approach as shown in Fig. 5(a) and (b) in order to explore the polarization switching and the pertinent energy barrier of 2D NbO<sub>2</sub>I and NbO<sub>2</sub>Br. The PE phase is the intermediate state of the first path,

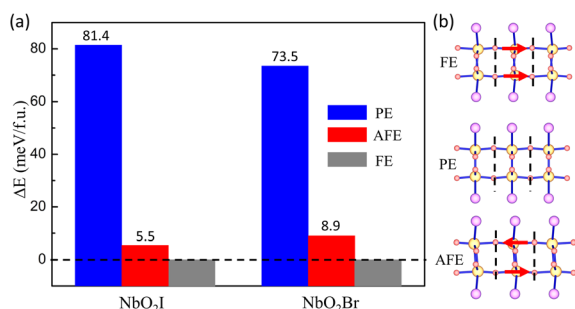


Fig. 3 (a) Relative energy per unit cell (in meV) of monolayer NbO<sub>2</sub>X (X = I and Br) at different polarization directions and takes the energy of FE as reference. (b) Schematic diagram of different polarization directions, where the direction of the arrow indicates the displacement direction of the Nb atom.

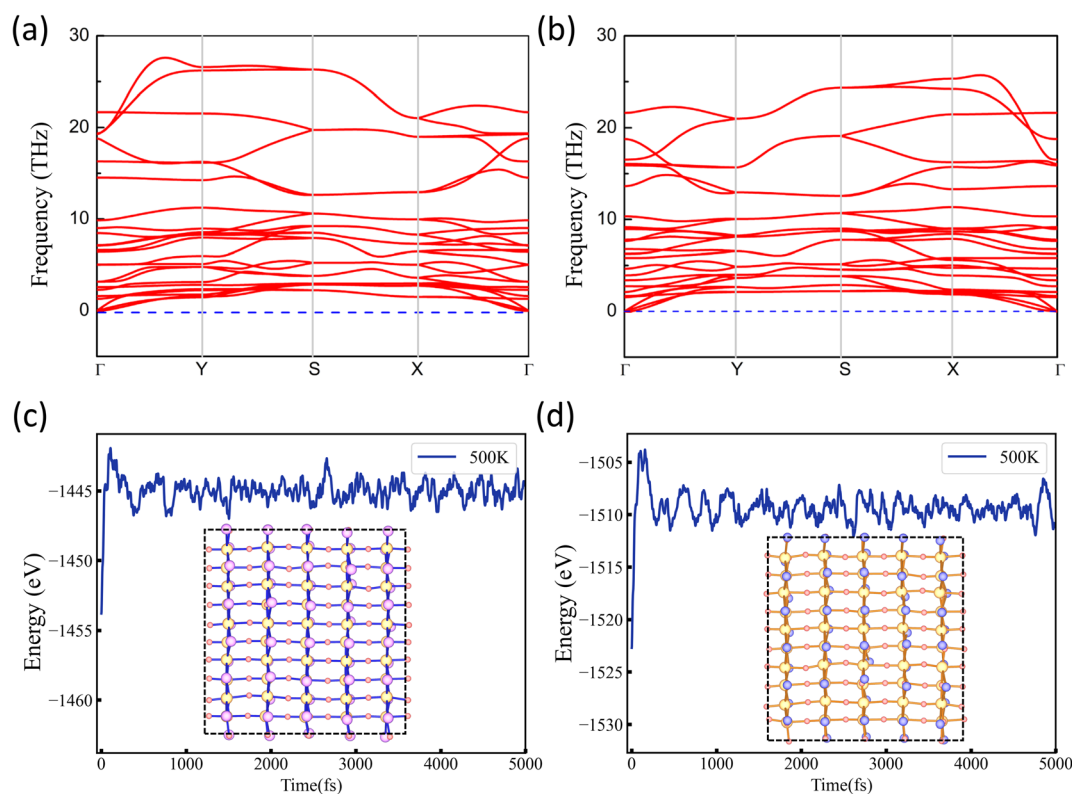


Fig. 4 (a) and (b) Phonon dispersions of the NbO<sub>2</sub>X (X = I and Br) monolayer. (c) and (d) Evolution of total energy for the NbO<sub>2</sub>I and NbO<sub>2</sub>Br monolayers at 500 K from molecular dynamics simulation. Insets present the snapshots at the end of simulations.



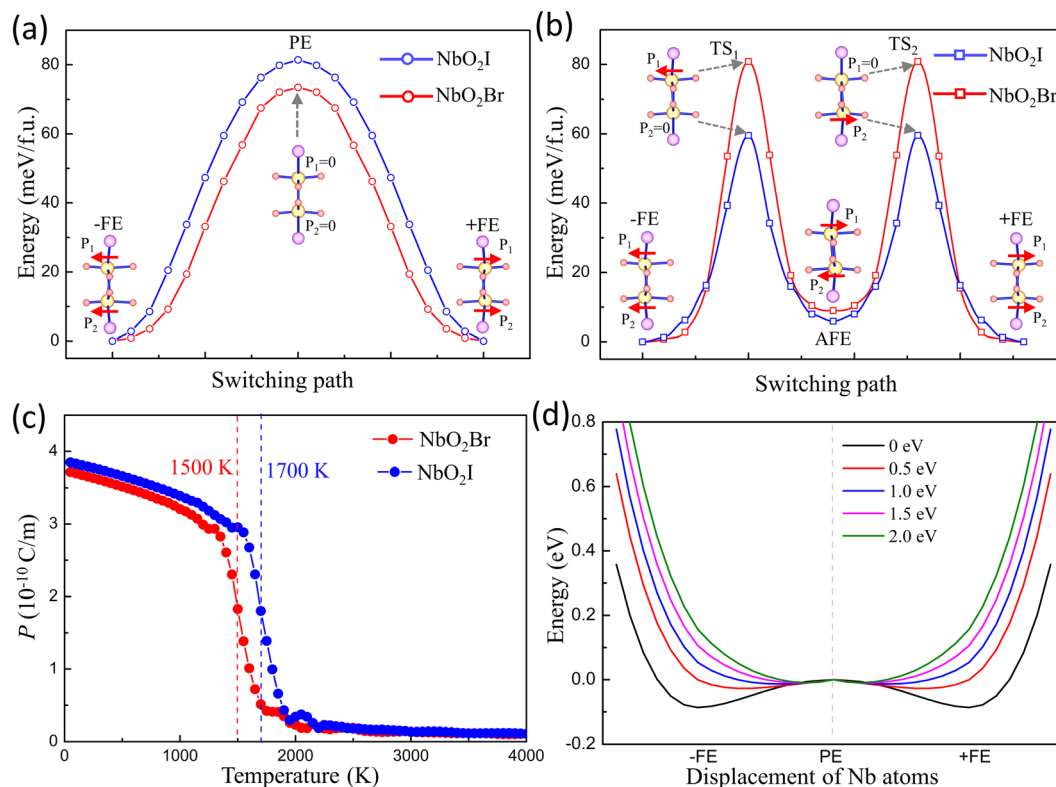


Fig. 5 The energy evolution of two polarization switching paths of the FE  $\text{NbO}_2\text{X}$  monolayer in two cases: (a) the transition proceeds through an intermediate PE phase; (b) the intermediate phase during the switching path is the AFE configuration. The inset views display the structures of initial, transition (TS), and final states, where the direction of the red arrow indicates the displacement direction of the Nb atom. (c) Curie temperatures of  $\text{NbO}_2\text{X}$  monolayers using Monte Carlo (MC) simulations. (d) The double-well evolution as the external potential applied on Nb  $4d_{xy}$  and  $4d_{xz}$  orbitals.

and the AFE phase is the intermediate state of the second path. We discovered that the first path's energy barrier, which uses the PE phase as an intermediate state, is around 80 meV, whereas the second path's energy barrier is 60 meV. As a result, we came to the conclusion that the FE-AFE-FE transformation is possible during the  $\text{NbO}_2\text{I}$  monolayer's ferroelectric switching. However, in the case of the  $\text{NbO}_2\text{Br}$  monolayer, there is a slight difference (7 meV) of the energy barrier between the first and second paths. This indicates a potential transformation path of FE-PE-FE for the  $\text{NbO}_2\text{Br}$  monolayer that differs from the behaviour of the  $\text{NbO}_2\text{I}$  monolayer.

Ferroelectricity is further emphasized by the Curie temperature above which the macroscopic spontaneous polarization disappears. The effective Hamiltonian of  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  supercells is carried out by applying the Landau-Ginzburg phase transition theory (for more details see ESI†). After fitting the parameters of effective Hamiltonian we perform the Monte Carlo simulation to investigate the  $T_c$  of 2D  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$ . The numerical results are shown in Fig. 5(c), and the  $T_c$  of the  $\text{NbO}_2\text{I}$  ( $\text{NbO}_2\text{Br}$ ) monolayer is as high as 1500 K (1700 K) that again proves that  $\text{NbO}_2\text{X}$  is a stable and robust 2D ferroelectric material.

It is well known that in the local coordinate of a pentagonal bipyramid, the d orbitals will be split into three groups by the crystal field. The  $d_{xz}$  and  $d_{yz}$  orbitals possess the lowest energy.

When we transfer to the global coordinate of  $\text{NbO}_2\text{I}$ , the local  $d_{xz}$  and  $d_{yz}$  of  $\text{Nb}^{5+}$  in the pentagonal bipyramid will transfer to  $d_{xy}$  and  $d_{xz}$ . In the following parts, we will discuss the results in the global coordinate. The critical mechanism and feature of the SOJT effect are the hybridization between the empty cation's d orbitals (*i.e.*,  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ ) and occupied anion's p orbitals (*i.e.*,  $\text{O}^{2-}$ ,  $\text{I}^{1-}$ ).<sup>37</sup> Moreover, Wheeler and Hoffman *et al.*<sup>38</sup> and Kunz and Brown<sup>39</sup> pointed out that the magnitude of the distortion of the cation surrounded by its ligands (*i.e.*,  $\text{TiO}_6^{2-}$ ,  $\text{NbO}_5\text{I}_2$  pentagonal bipyramid in this work) attributable to the SOJT effect depends on the strength of hybridization between the empty cation's d orbitals and occupied anion's 2p orbitals.

The density of states of  $\text{NbO}_2\text{I}$  is plotted in Fig. 6(c). The partial density of states (PDOS) clearly shows that both apical  $\text{O}_1$ -2p and planar  $\text{O}_2$ -2p orbitals are mainly located between  $-8$  and  $-1$  eV, indicating that the 2p orbitals of apical  $\text{O}_1$  and planar  $\text{O}_2$  are fully occupied. The I-5p orbitals are mainly distributed from  $-5$  eV to Fermi energy with a narrower bandwidth. The Nb-4d orbitals are located above the Fermi energy with the  $4d^0$  configuration. However, there are finite states of  $2p_y$  and  $2p_z$  of apical  $\text{O}_1$  distributing between 0.5 and 3 eV, where there are also major contributions from Nb  $4d_{xy}$  and  $4d_{xz}$ , which means that there are strong hybridizations between unoccupied Nb  $4d_{xy}$  and  $4d_{xz}$  orbitals and occupied apical  $\text{O}_1$   $2p_y$  and  $2p_z$ , indicating the SOJT effect in  $\text{NbO}_2\text{I}$ . The electronic





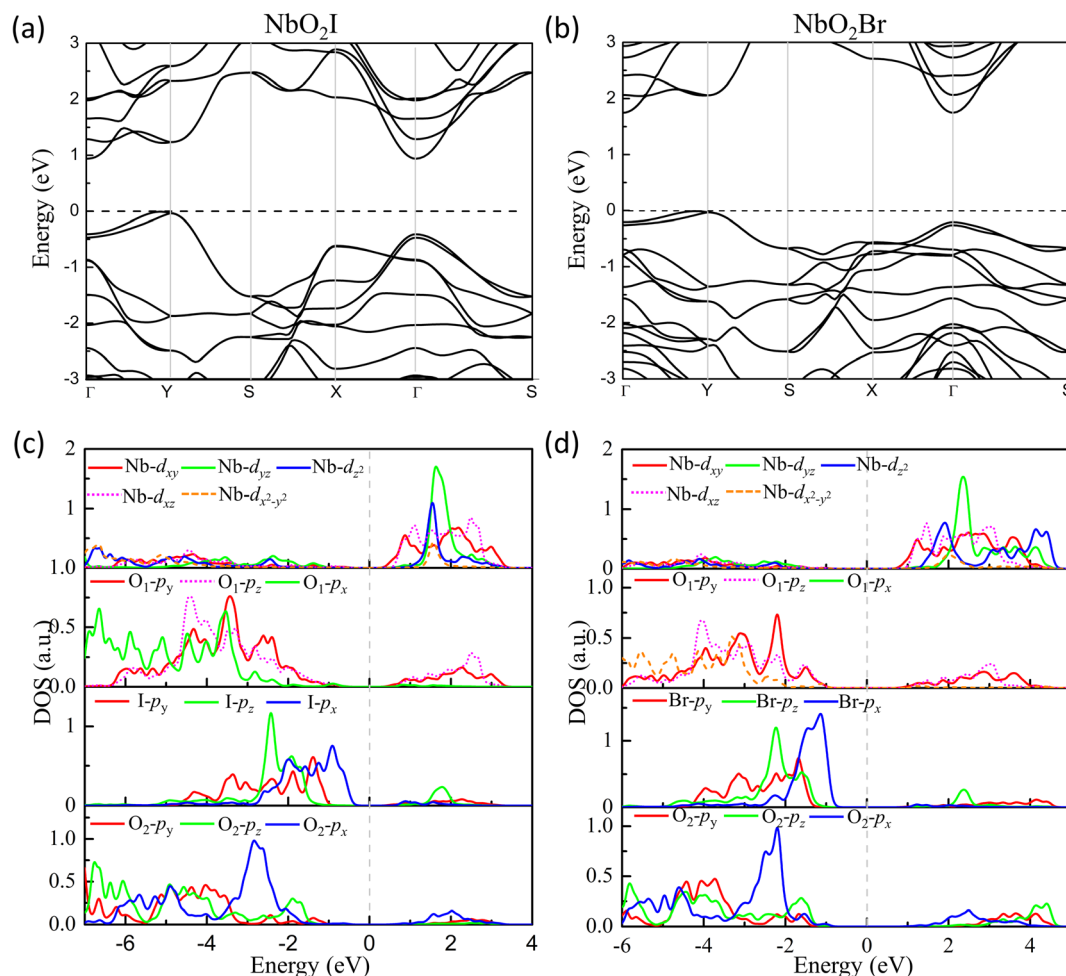


Fig. 6 Energy band structures (a) and (b) for FE  $\text{NbO}_2\text{X}$  monolayers. Projected density of states (PDOS) for monolayers (c)  $\text{NbO}_2\text{I}$  and (d)  $\text{NbO}_2\text{Br}$ .

structure of  $\text{NbO}_2\text{Br}$  shown in Fig. 6(d) is very similar to that of  $\text{NbO}_2\text{I}$ . As a result, we will not give a detailed discussion about  $\text{NbO}_2\text{Br}$ .

According to our discussion above, if we tune the strength of the hybridization, we can adjust the SOJT effect and further investigate the FE phase transition. Here, we apply the OSEP method by adding an external potential to raise the energy of  $\text{Nb-}4d_{xy}$  and  $4d_{xz}$  orbitals by different values to increase the energy difference between them and  $\text{O}_1$   $2p_y$  and  $2p_z$ . The OSEP approach can introduce an exceptional external potential that only can be felled by certain appointed orbitals.<sup>23</sup> We take the 2 eV potential on  $\text{Nb-}4d_{xy}$  and  $4d_{xz}$  as an example shown in Fig. S7.† The DOS of  $\text{Nb-}4d_{xy}$  and  $4d_{xz}$  is indeed shifted-up by almost 2 eV, which indicates that the OSEP approach can effectively shift the energy of certain selective orbitals. More interestingly, due to a larger energy difference between  $\text{Nb-}4d_{xy}/4d_{xz}$  and  $\text{O}_1$   $2p_y/2p_z$ , the strength of hybridization between them is decreased. One can expect that the SOJT effect induced distortion will disappear and result in a PE ground state instead of FE when hybridization between them vanishes.

Thus, we apply different external potentials on  $\text{Nb-}4d_{xy}$  and  $4d_{xz}$  to study the FE phase transition in  $\text{NbO}_2\text{I}$ . Fig. 5(d) illustrates the results. When the external potential on  $\text{Nb-}4d_{xy}$  and

$4d_{xz}$  rises, the characteristic double well of monolayer  $\text{NbO}_2\text{I}$  becomes shallower and eventually disappears, suggesting that the ground state becomes the PE phase. The same calculation is also carried out for  $\text{NbO}_2\text{Br}$ , and the same behaviour of double well evolution is obtained (shown in Fig. S6†). These results demonstrate that the SOJT effect is the reason for the ferroelectric phase transition.

Regarding the ferroelectricity, the band structure of  $\text{NbO}_2\text{X}$  monolayers is also calculated. Our numerical results demonstrate that both monolayers  $\text{NbO}_2\text{I}$  and  $\text{NbO}_2\text{Br}$  are Indirect bandgap semiconductors with  $E_g = 0.95$  eV and 1.75 eV, respectively. As illustrated in Fig. 4, their valence band maximum (VBM) is near the Y point, while their conduction band minimum (CBM) is at the  $\Gamma$  point. The effective mass at the VBM for  $\text{NbO}_2\text{I}$  is  $0.48 m_0$  along the x axis and  $1.37 m_0$  along the y axis, and the effective mass at the CBM is  $0.44 m_0$  along the x axis and  $1.18 m_0$  along the y axis, where  $m_0$  is the electron mass (for more details see ESI†). Different effective mass values along the two axes show band structure anisotropy, which is caused by crystal structure anisotropy. Interestingly, the carrier mobility of holes is an order of magnitude greater than that of electrons, implying that  $\text{NbO}_2\text{I}$  is an excellent P-type semiconductor.



## Conclusions

In summary, we explored the crystal structure, ferroelectric, and electronic properties of monolayers NbO<sub>2</sub>I and NbO<sub>2</sub>Br using first-principles calculation. We clarified that the FE phase is the energetically stable phase. The origin of polarization comes from the displacement of Nb<sup>5+</sup> cations driven by the SOJT effect. The monolayers NbO<sub>2</sub>I and NbO<sub>2</sub>Br are indirect semiconductors with the calculated band gap of 0.95 eV and 1.75 eV respectively. In addition, the carrier mobility shows anisotropy along two directions. Our findings add a new member to the family of 2D ferroelectric prototypes, providing a microscopic mechanism of the FE phase transition that will help the discovery and design of new FE materials.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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