Topological insulators in the NaCaBi family with large spin-orbit coupling gaps

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By means of first-principles calculations and crystal structure searching techniques, we predict that a different NaCaBi family crystallized into the ZrBeSi-type structure (i.e., $P6_3/mmc$) are strong topological insulators (STIs). Taking $P6_3/mmc$ NaCaBi as an example, the calculated band structure indicates that there is a band inversion between two opposite-parity bands at the Γ point. In contrast to the well-known Bi_2Se_3 family, the band inversion in the NaCaBi family has already occurred even without spin-orbit coupling (SOC), giving rise to a nodal ring surrounding Γ in the $k_z = 0$ plane (protected by M_z symmetry). With time-reversal symmetry ($\mathcal{T}$) and inversion symmetry ($\mathcal{I}$), the spinless nodal-line metallic phase protected by $[\mathcal{TI}]^2 = 1$ is the weak-SOC limit of the spinful topological insulating phase. Upon including SOC, the nodal ring is gapped, driving the system into a STI. Besides inversion symmetry, the nontrivial topology of NaCaBi can also be indicated by $\tilde{\delta}$ symmetry. More surprisingly, the SOC-induced band gap in NaCaBi is about 0.34 eV, which is larger than the energy scale of room temperature. Four other compounds (KBaBi, KSrBi, RbBaBi, and RbSrBi) in the family are stable at ambient pressure, both in thermodynamics and lattice dynamics, even though their gaps are smaller than that of NaCaBi. Thus, they provide good platforms to study topological states both in theory and experiments.

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I. INTRODUCTION

Topological insulators (TIs) have been studied broadly and deeply in both theory and experiments since the two-dimensional quantum spin Hall effect (2D TI) was proposed in 2005 [1]. By generalizing the concept of TIs, the three-dimensional (3D) TIs were predicted in the Bi_2Se_3 family [2], which were later verified in the experiments [3–5]. TIs embody a new quantum state characterized by a topological invariant rather than a spontaneously broken symmetry. The nontrivial topology of TIs is well defined by the wave functions of occupied bands, as long as there is a continuous energy gap between the conduction bands and valence bands in the whole Brillouin zone (BZ). Then, the $\mathcal{T}$ -invariant TIs are generalized to topological crystalline insulators (TCIs) [6–10], in which the lattice symmetries play important roles. Generally, symmetry eigenvalues and irreducible representations (irreps) can indicate topological property. For example, the well-known Fu-Kane parity indices are widely used for

centrosymmetric TIs [11], and the recently established symmetry indicators and topological quantum chemistry are very efficient to diagnose the nontrivial topology of TIs and TCIs [12–22]. Although many candidates for TIs and TCIs have been proposed, the TIs protected by sixfold rotoinversion symmetry [i.e., the sixfold rotoinversion $\tilde{\delta}$ ($\equiv \mathcal{IC}_6$) is a sixfold rotation (C_6) followed by inversion ($\mathcal{I}$)] are rarely reported.

The 3D TIs have attracted tremendous attention because their surface states possess odd spin-momentum locked Dirac cones, and thus the backscattering channels of the surface states are suppressed, leading to dissipationless electronic transport [2,3,23,24]. In proximity to an s -wave superconductor (SC), the topological surface states can acquire an effective p -wave superconducting pairing, resulting in a 2D topological SC [25]. In addition, the TIs can be tuned into many interesting topological states. For instance, the quantum anomalous Hall (QAH) insulator is found in the Cr-doped Bi_2Te_3 [26,27]. Furthermore, the compound MnBi_2Te_4 is predicted to be an antiferromagnetic TI at zero magnetic field and a Weyl semimetal under the out-of-plane magnetic field [28]. Recently, the QAH effect has been observed in few-layer thin films [29]. Moreover, the unconventional SC has been proposed and some experimental evidence was revealed in Cu-doped Bi_2Se_3 [30,31]. The strong evidence of a Majorana zero-energy mode within a vortex in the TI-SC heterostructure— $\text{Bi}_2\text{Te}_3/\text{NbSe}_2$ —has been proposed recently [32]. Therefore, the TI candidates are of great interest, especially those with relatively large band gaps, which not only

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FIG. 1. (a) Calculated enthalpy relative to that of the $P6_3/mmc$ phase vs pressure. (b) Phonon dispersions for the $P6_3/mmc$ phase at the ambient pressure, which justify the lattice dynamical stability of this phase. (c) Five crystal structures crystallized into the $P6_3/mmc$, $P3m1$, $Pnma$, $F43m$, and $P42m$ phases of stoichiometric NaCaBi near the convex hull from the formation enthalpies.

benefit the future applications of spintronics and quantum computation from the dissipationless surface states, but also provide good platforms to study the interplay between the topological phase and symmetry-breaking phases. Though many TI candidates and corresponding interesting properties have been proposed [2,23,24,33,34], TIs with relatively large band gaps and clear 2D Dirac-cone surface states as the Bi_2Se_3 family are rare.

In this work, using crystal structure searching techniques and first-principles calculations, we predict that NaCaBi can be stable in the space group (SG) of $P6_3/mmc$ at pressures up to 10 GPa from both the thermal dynamics and the lattice dynamics. Calculations of the band structures indicate that without spin-orbit coupling (SOC), $P6_3/mmc$ NaCaBi is a topological semimetal with a nodal ring surrounding the Γ point in the $k_z = 0$ plane. Upon including SOC, the crossing

points of the nodal line are all gapped and the system becomes a strong topological insulator (STI). We find that the nontrivial topology can be indicated not only by inversion symmetry, but also by the $\bar{6}$ symmetry. Moreover, it is exciting that the topologically nontrivial band gap is about 0.34 eV due to strong SOC, which is even larger than the energy scale of room temperature. At last, four other dynamically stable XYBi compounds with similar electronic structures and STI natures are proposed (See details in the Appendix).

II. CALCULATIONS AND RESULTS

A. The crystal structures of stoichiometric NaCaBi

We used crystal structure prediction techniques integrated in USPEX [35–37] and the machine-learning accelerated crystal structure search method [38] to find the best candidates of NaCaBi under pressure. From the phase diagrams based on convex hull analysis of formation enthalpies for the Na-Ca-Bi ternary system at 0 and 10 GPa, shown in Fig. 5, we find that stoichiometric NaCaBi crystallizes in the $Pnma$ phase at 0 GPa and $P6_3/mmc$ phase at 10 GPa, respectively. We extract several structures of stoichiometric NaCaBi near the two stable phases from the formation enthalpy, which are in SGs of $P6_3/mmc$, $P3m1$, $Pnma$, $F43m$, and $P42m$, respectively. The detailed structural information can be seen in Appendix B. The enthalpy-pressure ($\Delta H - P$) curves between these phases plotted in Fig. 1(a) exhibit the best ones from our structural predictions at pressures up to 10 GPa. At ambient pressure, the most stable structure of NaCaBi is found to be the $Pnma$ phase, and the enthalpy of the $P6_3/mmc$ phase is just 0.17 eV/f.u. higher than that of the $Pnma$ phase. Our calculations reveal that the $P6_3/mmc$ phase becomes preferred at pressures higher than 1 GPa.

As shown in Fig. 1(b) and Appendix D, there is no phonon mode with negative frequency in the phonon spectra of $P6_3/mmc$ NaCaBi under pressures from 0 to 10 GPa, which indicates that the metastable $P6_3/mmc$ phase could be quenched to ambient pressure if they can be synthesized at high pressure. These results are in accordance with the earlier work [39,40]. As shown in Fig. 7(c), calculations of the *ab initio* molecular dynamics (AIMD) simulations at ambient pressure and $T = 600$ K indicate that there is no structural collapse after 10 ps (10 000 steps). In addition, motivated

FIG. 2. (a) Orbital-resolved band structures of $P6_3/mmc$ NaCaBi at 0 GPa without SOC. (b) The BZ of $P6_3/mmc$ NaCaBi, where the high-symmetry $\vec{k}$ points are marked out. (c) Band structures of $P6_3/mmc$ NaCaBi at 0 GPa with SOC. The red line corresponds to the 0.06 hole-doping case (i.e., $E_H - E_F = -0.25$ eV). (d) The constant-energy contour surface at E_H is a torus.

TABLE I. Band gaps of the NaCaBi family at 0 GPa.

XYBi	NaCaBi	KBaBi	KSrBi	RbBaBi	RbSrBi
Gaps (eV)	0.34	0.22	0.26	0.20	0.25

by earlier works [41,42], how the parameters evolve under pressure, strain potential, and the possible substrates are also discussed in Appendix H. In Appendix H, we also list many other XYBi compounds in the $P6_3/mmc$ phase which are dynamically stable at low pressures. Besides NaCaBi, four other XYBi compounds (i.e., KBaBi, KSrBi, RbBaBi, and RbSrBi) have similar band structures, and thus the same STI nature with NaCaBi (see Appendix D). Different from NaCaBi, the $P6_3/mmc$ phase of KBaBi, KSrBi, RbBaBi, and RbSrBi is always energetically preferred from 0 to 10 GPa, as depicted in Appendix B. Moreover, the NaCaBi system possesses the largest inverted band gap, as shown in Table I. In the following, we will focus on NaCaBi with the $P6_3/mmc$ phase.

B. The band structures of $P6_3/mmc$ NaCaBi

From the band structures of $P6_3/mmc$ NaCaBi without SOC, shown in Fig. 2(a), we can find two band crossings along $K-\Gamma$ and $\Gamma-M$ at E_F . The orbital-resolved band structures in Fig. 2(a) indicate that the valence-band maximum is contributed by the Bi- p states, while the conduction-band minimum is from the Ca- s states (which also hybridize with the Bi- s , Na- s , and Ca- d states). Calculations of the irreps [43] indicate that the two bands belong to $GM1+$ and $GM2-$ irreps, respectively [Fig. 2(a)], in the convention of the Bilbao Crystallographic Server notations at Γ (GM). The parities of the occupied bands at eight time-reversal invariant momenta (TRIMs) are given in Table II. Thus, we conclude that the band inversion appears between opposite-parity bands around Γ without SOC, which guarantees the existence of nodal line(s) in the spinless systems with $\mathcal{T}$ and $\mathcal{I}$. Furthermore, this nodal ring surrounding Γ lies in the $k_z = 0$ plane due to the presence of M_z symmetry (i.e., the two inverted bands have different M_z eigenvalues).

The spinful topological insulating phase can be considered as a (strong-)SOC limit of the spinless nodal-line metallic phase protected by $[\mathcal{TI}]^2 = 1$ [12]. As shown in Fig. 2(c), we can find that SOC induces a visible band gap between the two inverted bands around Γ , but it does not change the ordering of energy bands at Γ . The nodal ring is fully gapped, and thus the NaCaBi becomes a STI. More surprisingly, the SOC-induced band gap is as large as 0.34 eV, which is comparable with the thermal energy of room temperature. The $P6_3/mmc$ phase of NaCaBi family compounds provides good platforms to study topological states both in theory and experiments. Considering the possible underestimation of the band gap by

 TABLE II. The product of the parities for all the occupied bands at the eight TRIMs for the $P6_3/mmc$ phase of NaCaBi.

TRIM	Γ	$3M$	A	$3L$	Product
Parity	+	-	-	-	-

FIG. 3. Surface states of NaCaBi terminated in the (a) (010) surface and (b) (001) surface. Both (010) and (001) surfaces exhibit a 2D Dirac cone.

the Perdew-Burke-Ernzerhof (PBE) method [44], the band inversion can be further confirmed by the calculations using the hybrid Heyd-Scuseria-Ernzerhof (HSE) functional [45]. The results, shown in Appendix E, indicate that the SOC-induced band gap is almost unchanged, although the inverted gap at Γ (i.e., $E_g \equiv |E_{GM1+} - E_{GM2-}|$) becomes smaller.

Symmetry eigenvalues (or irreps) play key roles in identifying TIs and TCIs in solids [14–16]. As we know, SG 194 belongs to a $\mathbb{Z}_{12}$ classification. Using IRVSP [43] and CHECKTOPMAT [20], all symmetry indicators are calculated to be $z_{2w,i=1,2,3} = 0$, $z_4 = 3$, $z_{6m,0} = 5$, $z'_{12} = 11$. By performing the symmetry analysis, we find that there are two essential symmetries indicating the nontrivial topology in this system. One is the inversion symmetry, while the other is the $\bar{6}$ symmetry. In other words, even though the inversion is broken when the SG is reduced to SG 174 ($P\bar{6}$), the nontrivial topology can still be indicated by $z_{3m,0} = 1$ and $z_{3m,\pi} = 0$. With $M_z \equiv [\bar{6}]^3$, these indicate that the mirror Chern numbers of the $k_z = 0$ and $k_z = \pi$ planes are 1 and 0, respectively. Thus, this system has to be a 3D STI.

C. The surface states of $P6_3/mmc$ NaCaBi

Exotic topological surface states serve as significant fingerprints to identify various topological phases. Based on the tight-binding model constructed with the maximally localized Wannier functions and surface Green's function methods [46–48], we have calculated the corresponding surface states of this system with SOC to identify its topological properties (see Appendix F). As shown in Figs. 3(a) and 3(b), the 2D Dirac cone is obtained on (010) and (001) surfaces. Thus, the calculated surface states agree well with the analysis of the symmetry indicators, which confirm the STI nature of NaCaBi.

D. Low-energy effective model

We find that the topologically nontrivial nature is determined by the low-energy dispersions near E_F around Γ , which motivates us to build the effective $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian to get further insights into this system. In the presence of SOC, the irreps for the lower-energy bands at Γ are Γ_7^+ and Γ_7^- , respectively (labeled in the double point group of D_{6h}).

Thus, we can construct the 4×4 Hamiltonian under the bases of the two irreps (i.e., $|+, \uparrow\rangle; |+, \downarrow\rangle; |-, \uparrow\rangle$ and $|-, \downarrow\rangle$) with the theory of invariants [49]. Here, the $\pm$ denote the

FIG. 4. Electron-phonon coupling calculations of $P6_3/mmc$ NaCaBi. (a) Phonon spectra, phonon density of states (PDOS), and Eliashberg spectral functions $\alpha^2 F(\omega)$, together with the electron-phonon integral $\lambda(\omega)$ in the left, middle, and right panels, respectively. (b) The B_{2g} vibrational mode.

parities of the eigenstates and $\uparrow$ ($\downarrow$) denotes $j_z = +\frac{1}{2}$ ($-\frac{1}{2}$). Taking time-reversal symmetry and the symmetries of double group D_{6h} into consideration (see details in Appendix G), we derive the following $\mathbf{k} \cdot \mathbf{p}$ invariant Hamiltonian in the vicinity of Γ (up to the second order of $\vec{k}$):

$$H_0(\vec{k}) = \epsilon_0(\vec{k})\mathbb{I}_4 + \begin{pmatrix} M(\vec{k}) & 0 & A_1 k_z & A_2 k_- \\ 0 & M(\vec{k}) & A_2 k_+ & -A_1 k_z \\ A_1 k_z & A_2 k_- & -M(\vec{k}) & 0 \\ A_2 k_+ & -A_1 k_z & 0 & -M(\vec{k}) \end{pmatrix}, \quad (1)$$

where $k_{\pm} = k_x \pm ik_y$, $\epsilon_0(\vec{k}) = C + D_1 k_z^2 + D_2 k_{\perp}^2$, and $M(\vec{k}) = M - B_1 k_z^2 - B_2 k_{\perp}^2$, with $k_{\perp}^2 = k_x^2 + k_y^2$. This is simply the well-known 3D TI Hamiltonian in the Bi_2Se_3 family [2] in the case of $MB_{1,2} > 0$, where the band inversion happens between the two different-parity bands. By fitting the energy dispersions, we obtain the following parameters: $M = -0.4554$ eV, $A_1 = 4.0$ eVÅ, $A_2 = 1.3$ eVÅ, $B_1 = -16.7$ eVÅ², $B_2 = 18.6$ eVÅ², $C = -0.0689$ eV, $D_1 = -6.4$ eVÅ², $D_2 = 8.5$ eVÅ².

As mentioned earlier, the nontrivial topology of this system can be also protected or indicated by $\bar{\delta}$ symmetry. If we introduce the additional δ_1 (δ_2) term as shown in Eq. (2), C_{2x} (C_{2y}) and M_y (M_x) will be broken. Therefore, by simply adding the two additional terms (both of which break C_{6z} and $\mathcal{T}$), the

$\bar{\delta}$ -invariant Hamiltonian is obtained,

$$H(\vec{k}) = H_0(\vec{k}) + H_1(\delta_1 + i\delta_2, \vec{k}),$$

$$H_1(z, \vec{k}) = \begin{pmatrix} 0 & 0 & 0 & -z^* k_+^2 \\ 0 & 0 & z k_-^2 & 0 \\ 0 & z^* k_+^2 & 0 & 0 \\ -z k_-^2 & 0 & 0 & 0 \end{pmatrix}. \quad (2)$$

In the presence of $\bar{\delta}$ symmetry, the C_{3z} and M_z symmetries are still preserved. Thus, one can check that in the case of $MB_{1,2} > 0$, the mirror Chern number of the $k_z = 0$ plane is 1. On the other hand, one can also compute the symmetry indicators of SG 174 ($P\bar{6}$), which are found to be $z_{3m,0} = 1$. This implies that the $\mathbb{Z}_2$ invariant for the $k_z = 0$ plane is 1. Combined with the trivial $\mathbb{Z}_2$ invariant for the $k_z = \pi$ plane, one can conclude that $z_{3m,0} = 1$ and $z_{3m,\pi} = 0$ yield the STI nature of $P6_3/mmc$ NaCaBi. Suppose that we move the two Na atoms at $2a$ Wyckoff positions reversely along the z axis a little (e.g., two percent of the third lattice vector along the z axis); this distortion preserves $\bar{\delta}$ symmetry, but breaks inversion symmetry and C_{6z} symmetry. In this disturbed structure, the δ_1 and δ_2 are fitted to be 0.4 and 0 eVÅ². The STI phase is indicated by the symmetry indicators, $z_{3m,0} = 1$ and $z_{3m,\pi} = 0$, since there is no band crossing occurring in this process.

TABLE III. Crystal structures of NaCaBi after structure optimization. The SG column denotes the space group that NaCaBi crystallizes into. $\{\alpha, \beta, \gamma\}$ and $\{a, b, c\}$ denote the lattice parameters of the conventional cell (while not primitive cell) in each phase. The “Wyckoff positions” column gives the Wyckoff positions of Na, Ca, and Bi in each phase. $1a \oplus 1c$, $1b \oplus 1c$, and $1a \oplus 1b$ in the $P3m1$ phase indicate that there exist two nonequivalent Na/Ca/Bi atoms occupying the $(1a$ and $1c)$ / $(1b$ and $1c)$ / $(1a$ and $1b)$ Wyckoff positions in this phase, respectively.

SG	$\{\alpha, \beta, \gamma\}$	$\{a, b, c\}$	Wyckoff positions
$P6_3/mmc$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$\{a = b = 5.566 \text{ \AA}, c = 6.804 \text{ \AA}\}$	$\{2a, 2c, 2d\}$
$P3m1$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$\{a = b = 5.3431 \text{ \AA}, c = 7.41 \text{ \AA}\}$	$\{1a \oplus 1c, 1b \oplus 1c, 1a \oplus 1b\}$
$Pnma$	$\alpha = \beta = \gamma = 90^\circ$	$\{a = 8.088 \text{ \AA}, b = 4.784 \text{ \AA}, c = 9.681 \text{ \AA}\}$	$\{4c, 4c, 4c\}$
$F\bar{4}3m$	$\alpha = \beta = \gamma = 90^\circ$	$\{a = b = c = 7.530 \text{ \AA}\}$	$\{4a, 4b, 4c\}$
$P\bar{4}2m$	$\alpha = \beta = \gamma = 90^\circ$	$\{a = b = 7.5706 \text{ \AA}, c = 7.5032 \text{ \AA}\}$	$\{1a \oplus 1b \oplus 2f, 1c \oplus 1d \oplus 2e, 4n\}$

FIG. 5. Phase diagram based on convex hull analysis of formation enthalpies for the Na-Ca-Bi ternary system at (a) 0 GPa and (b) 10 GPa. The solid red circles in the figures denote the stable structures, while the hollow red circles denote the corresponding structures lying above the convex hull, which indicates that these structures are metastable candidates. The solid red circle in the center of the equilateral triangle denotes the (a) $Pnma$ phase at 0 GPa and (b) $P6_3/mmc$ phase at 10 GPa.

III. DISCUSSION

In carrier-doped TIs, odd-parity pairing and nematic pairing have been theoretically proposed to realize topological superconductivity [50,51]. Some supporting evidence in Cu-doped Bi_2Se_3 is revealed in experiments, but the pairing symmetry is still under active debate [52–56]. Analogous to Bi_2Se_3 , superconductivity and topological pairing states may be achieved with hole doping in NaCaBi. One prominent feature of $P6_3/mmc$ NaCaBi is that the band inversion is kept with SOC and is significantly large, resulting in a double-peak valence band around Γ , as shown in Fig. 2(c). Within a relatively large hole-doping region, the Fermi surface is a torus around the Γ point rather than spheres in other TIs, as shown in Fig. 2(d). As the topology of the Fermi surface is distinct from the electron-doped case, the pairing state can also be different and may be unconventional. For example, for the intraorbital spin-singlet pairing $c_{+\uparrow}c_{+\downarrow} - c_{-\uparrow}c_{-\downarrow}$, which belongs to a trivial irrep, two nodal lines of gap functions in band space are expected on the torus. We leave the question of determining possible pairing states by solving effective models to future work. Nevertheless, we investigate the superconducting properties by electron-phonon coupling calculations and the Allen-Dynes modified McMillan equation [57]. Considering 0.06 hole doping in the NaCaBi system at ambient pressure, T_c is estimated to be about 1.5 K with a commonly used screened Coulomb potential $\mu^* = 0.10$. Most of the contributions to the electron-phonon coupling constant arise from the B_{2g} vibrational mode, i.e., vibrations of Ca atoms and Bi atoms along the z axis, as shown in Fig. 4(b).

In summary, we propose a NaCaBi family which are STIs with large SOC-induced band gaps, among which KBaBi, KSrBi, RbBaBi, and RbSrBi are stable at ambient pressure, both in thermodynamics and lattice dynamics. In terms of the NaCaBi system, the corresponding symmetry analysis indicates that there exists a clear band inversion between two opposite-parity bands near E_F . Without SOC, the band inversion gives rise to a nodal ring around Γ in the $k_z = 0$ plane. Upon including SOC, it becomes a STI with a SOC-induced band gap of 0.34 eV, which is larger than the energy scale of room temperature. The calculated symmetry indicators of SG 194 indicate that the nontrivial topology of NaCaBi can be revealed by not only the inversion symmetry, but also $\bar{6}$ symmetry. As expected, 2D Dirac cones are obtained in the (010)-surface and (001)-surface spectra. Due to the large SOC-induced band gap in the STI phase, it is promising to expect clear experimental evidence of the topological surface states from angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy in the future. With hole doping, the contour surface of the valence band near E_F is a torus, which may bring unconventional superconducting pairing.

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TABLE IV. Crystal structures of the Na-Ca-Bi ternary system near the convex hull at ambient condition. ΔH column is in units of meV.

SG	$\{\alpha, \beta, \gamma\}$	$\{a, b, c\}$	Wyckoff positions	ΔH
$Pnma$ -NaCaBi	$\alpha = \beta = \gamma = 90^\circ$	$\{a = 8.088 \text{ \AA}, b = 4.784 \text{ \AA}, c = 9.681 \text{ \AA}\}$	$\{4c, 4c, 4c\}$	0
$P4/mmm$ -NaCaBi ₂	$\alpha = \beta = \gamma = 90^\circ$	$\{a = b = 5.2019 \text{ \AA}, c = 9.6268 \text{ \AA}\}$	$\{1c, 1a, 2e\}$	16
$Cmmm$ -NaCa ₂ Bi ₃	$\alpha = \beta = \gamma = 90^\circ$	$\{a = 15.2393 \text{ \AA}, b = 5.1890 \text{ \AA}, c = 4.5445 \text{ \AA}\}$	$\{2a, 4g, 4h \oplus 2c\}$	13.3
$R3m$ -Na ₄ CaBi ₂	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$\{a = b = 5.4382 \text{ \AA}, c = 26.6190 \text{ \AA}\}$	$\{3a \oplus 3a \oplus 3a \oplus 3a, 3a, 3a \oplus 3a\}$	19.7

FIG. 6. Calculated enthalpy between the *Pnma* phase and the *P6₃/mmc* phase vs pressure for NaCaBi, NaSrBi, KBaBi, KSrBi, RbBaBi, and RbSrBi, respectively.

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APPENDIX A: CALCULATION METHODS

Ab initio calculations. We performed first-principles calculations based on the density functional theory (DFT) using the projector augmented wave (PAW) method implemented in the Vienna *ab initio* simulation package (VASP) [58] for

the calculations of the structure optimization and electronic structures. The generalized gradient approximation (GGA), as implemented in the Perdew-Burke-Ernzerhof (PBE) functional [44], was adopted. The cutoff parameter for the wave functions was 850 eV. The BZ was sampled by the Monkhorst-Pack method [59] with a k spacing of $0.025 \times 2\pi \text{ \AA}^{-1}$ for the 3D periodic boundary conditions. The phonon calculations were performed by the finite displacement method implemented in the PHONOPY code [60], with a $2 \times 2 \times 2$ supercell. A k mesh of $20 \times 20 \times 16$ was used to calculate the Fermi surface of the valence band near the Fermi level. Electron-phonon coupling calculations are performed in the framework of density functional perturbation theory, as implemented in the QUANTUM ESPRESSO code [61].

APPENDIX B: CRYSTAL STRUCTURE SEARCHING

We perform a variable composition calculation to get the phase diagrams of the Na-Ca-Bi ternary system at ambient condition (0 GPa) and 10 GPa. We have extracted five structures of stoichiometric NaCaBi near the two stable phases from the formation enthalpy, which are in SGs of *P6₃/mmc*,

TABLE V. Crystal structures of the Na-Ca-Bi ternary system near the convex hull at 10 GPa.

SG	$\{\alpha, \beta, \gamma\}$	$\{a, b, c\}$	Wyckoff positions	ΔH
<i>P6₃/mmc</i> -NaCaBi	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$\{a = b = 5.1857 \text{ \AA}, c = 6.2652 \text{ \AA}\}$	$\{2a, 2c, 2d\}$	0
<i>Cmmm</i> -NaCa ₂ Bi ₂	$\alpha = \beta = \gamma = 90^\circ$	$\{a = 14.6714 \text{ \AA}, b = 4.7828 \text{ \AA}, c = 4.3440 \text{ \AA}\}$	$\{2a, 4g, 4h \oplus 2c\}$	0
<i>Cmmm</i> -NaCaBi ₂	$\alpha = \beta = \gamma = 90^\circ$	$\{a = 6.7302 \text{ \AA}, b = 8.7712 \text{ \AA}, c = 3.3638 \text{ \AA}\}$	$\{2c, 2d, 4e\}$	1.2
<i>P4/mmm</i> -NaCa ₂ Bi	$\alpha = \beta = \gamma = 90^\circ$	$\{a = b = 4.7903 \text{ \AA}, c = 4.3642 \text{ \AA}\}$	$\{2c, 2d, 4e\}$	9.5

FIG. 7. After a 10 ps AIMD simulation, the side view (a) along the (001) direction and (b) along the (110) direction of the $3 \times 3 \times 2$ supercell of NaCaBi at 600 K. (c) The NVT-molecular dynamics (MD) simulations of the NaCaBi at static pressure and $T = 600$ K.

$P3m1$, $Pnma$, $F\bar{4}3m$ and $P4_2m$, respectively. The detailed structural information can be seen in Table III. At ambient condition, we find that $Pnma$ NaCaBi is the unique ternary phase lying in the convex hull (denoted by the solid red circle in the center of the equilateral triangle), as shown in Fig. 5(a).

Meanwhile, there exist three other metastable ternary candidates, i.e., $P4/mmm$ NaCaBi₂, $Cmmm$ NaCa₂Bi₃, and $R3m$ Na₄CaBi₂, above the convex hull (denoted by the hollow red circles in the the equilateral triangle). The corresponding enthalpies of these metastable ternary candidates above

FIG. 8. (Continued.)

FIG. 8. (Continued.)

FIG. 8. Band structures and phonon spectra of $P6_3/mmc$ RbHgSb and XYBi when they are dynamically stable under 0, 5, and 10 GPa, respectively. Our calculations reproduce the Dirac point in the $P6_3/mmc$ RbMgBi system [64].

the convex hull (denoted by ΔH) of $P4/mmm$ NaCaBi₂, $Cmmm$ NaCa₂Bi₃ and $R3m$ Na₄CaBi₂ are 16.0, 13.3, and 19.7 meV/atom, respectively. We have listed the structure parameters of these ternary structures in Table IV.

At 10 GPa, we find $P6_3/mmc$ NaCaBi and $Cmmm$ NaCa₂Bi₃ (denoted by two solid red circles lying inside the equilateral triangle) are two stable ternary structures lying in the convex hull, as shown in Fig. 5(b). In addition, the convex

hull analysis indicates that there are three other structures ($C2/m$ Ca₃Bi₂, $Cmmm$ NaCaBi₂, and $P4/mmm$ NaCa₂Bi) lying above the convex hull, which indicates that they are metastable candidates. The corresponding structure parameters are listed in Table V. It should be noted that $C2/m$ Ca₃Bi₂ and $Cmmm$ NaCaBi₂ are metastable candidates with only 0.64 and 1.2 meV/atom above the convex hull. We also remind the reader that the binary Na-Bi and binary Ca-Bi phases in

TABLE VI. Dynamically stable RbHgSb and XYBi systems at 0, 5, and 10 GPa, respectively. Structures with * denote those possessing similar band structures with $P6_3/mmc$ NaCaBi.

Pressure (GPa)	RbHgSb and XYBi systems
0 GPa	NaCaBi*, KBaBi*, KSrBi*, KZnBi, RbBaBi*, RbCdBi, RbHgSb, RbMgBi, RbSrBi*, RbZnBi
5 GPa	NaCaBi*, NaSrBi*, NaZnBi, KBaBi, KSrBi, RbBaBi, RbCaBi, RbSrBi, RbZnBi
10 GPa	NaCaBi*, NaCdBi, NaSrBi*, NaZnBi, KBaBi, KSrBi, RbBaBi, RbCaBi, RbHgSb, RbSrBi

the convex hull are almost in accordance with earlier works [62,63].

We do not perform ternary structural searching for the other four XYBi candidates because it will be time consuming. But, similar to NaCaBi, the thermal stability between the $P6_3/mmc$ phase and the $Pnma$ phase is discussed. As shown in Fig. 6, the $Pnma$ phase of NaSrBi is always preferred under pressures from 0 to 10 GPa, while for the cases of KBaBi, KSrBi, RbBaBi, and RbSrBi, the $P6_3/mmc$ phase is always preferred. It means that the STI phase can be obtained in the KBaBi, KSrBi, RbBaBi, and RbSrBi systems without any quenched progress.

APPENDIX C: MOLECULAR DYNAMICS

To check the thermal stability of $P6_3/mmc$ NaCaBi, we have performed *ab initio* molecular dynamics (AIMD) simulations with a $3 \times 3 \times 2$ supercell at ambient pressure and $T = 600$ K. As shown in Fig. 7(c), no structural collapse was observed after 10 ps (10 000 steps), which indicates the thermal stability of NaCaBi at ambient pressure.

APPENDIX D: PHONON SPECTRA AND BAND STRUCTURES OF XYBi COMPOUNDS WITH $P6_3/mmc$ STRUCTURE UNDER LOW PRESSURES

According to the online Materials Project [65] database, the Inorganic Crystal Structure Database [66], and the earlier work [39], RbHgSb and several XYBi systems with $X = \{\text{Na, K, Rb}\}$ and $Y = \{\text{Mg, Ca, Sr, Ba, Zn, Cd, Hg}\}$ can crystallize into the ZrBeSi-type structure of $P6_3/mmc$. We performed calculations in terms of the lattice dynamical stability for them at 0, 5, and 10 GPa, respectively. Among

these, only the dynamically stable ones are listed in Table VI. Their phonon spectra and band structures are giving in Fig. 8. From Fig. 8, we can find that they are mainly classified into three classes: the KHgSb-type TCI phase [9] (i.e., KZnBi, RbCdBi, RbHgSb, and RbZnBi), the Na_3Bi -type Dirac phase [67] (i.e., NaZnBi, NaCdBi, and RbMgBi), and the STI phase. Since we are focused on the STI phase, several of these dynamically stable compounds of the STI phase, having the similar band structures with $P6_3/mmc$ NaCaBi in the main text, are denoted by * symbols.

APPENDIX E: HSE CALCULATIONS

It is known that the PBE functional tends to underestimate the band gap; therefore, we recalculated the band structures of the $P6_3/mmc$ NaCaBi system with the HSE06 functional [45], as shown in Fig. 9. We find that the energy dispersions for low-energy bands using the HSE06 functional are similar to that using the PBE functional, which indicates that the topological nature is solid.

APPENDIX F: WANNIER-BASED TIGHT-BINDING MODEL AND SURFACE STATES

The surface state plays an important role in justifying and characterizing TIs from the bulk-boundary correspondence. Here we choose Ca-*s*, Ca-*d*, and Bi-*p* as the projected orbits to build the Wannier-based tight-binding model; it reproduces the DFT band structures well, as shown in Fig. 10. Then, we calculated the surface states based on this Wannier-based tight-binding model of NaCaBi on the (010) and (001) surfaces, as presented in Fig. 3 in the main text.

FIG. 9. HSE band structures in comparison with DFT band structures.

FIG. 10. DFT vs Wannier bands.

APPENDIX G: MATRIX PRESENTATIONS OF SYMMETRY OPERATORS

Under the basis of Γ_7^+ and Γ_7^- , the symmetry operators (e.g., $\mathcal{T}$, $\mathcal{I}$, C_{6z} , C_{2x} , C_{2y}) are represented as

$$\begin{aligned} \mathcal{T} &= \tau_0 \otimes (-i)\sigma_y \mathcal{K}; \quad \mathcal{I} = \tau_z \otimes \sigma_0; \quad C_{6z} = \tau_0 \otimes e^{-i\frac{\pi}{3}\sigma_z}; \\ C_{2x} &= \tau_0 \otimes (-i)\sigma_x; \quad C_{2y} = \tau_0 \otimes (-i)\sigma_y, \end{aligned} \quad (\text{A1})$$

where $\mathcal{K}$ denotes the complex conjugation, and $\tau_{x,y,z}$ ($\sigma_{x,y,z}$) are Pauli matrices in the orbital (spin) space. Their ($\mathcal{O} = P, Q, R, \mathcal{T}$) representations in momentum space are given by $\mathcal{O}[k_x, k_y, k_z]^T = g_{\mathcal{O}}[k_x, k_y, k_z]^T$,

$$\begin{aligned} g_{\mathcal{T}} = g_{\mathcal{I}} &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad g_{C_{6z}} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ g_{C_{2x}} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad g_{C_{2y}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \end{aligned} \quad (\text{A2})$$

The low-energy effective $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian satisfies the condition placed by the symmetry $\mathcal{O}$:

$$\mathcal{O}\mathcal{H}(\delta\mathbf{k})\mathcal{O}^{-1} = \mathcal{H}(g_{\mathcal{O}}\delta\mathbf{k}). \quad (\text{A3})$$

After considering all symmetry restrictions of D_{6h} , the low-energy effective model is derived as given in the main text.

APPENDIX H: PRESSURE, STRAIN, AND SUBSTRATE CANDIDATES

From the electronic properties of $P6_3/mmc$ NaCaBi at 0, 5, and 10 GPa shown in Fig. 8, we find that there is an electron pocket of the conduction band around K dropping to the Fermi level quickly under pressure. And when the applied pressure is as large as 10 GPa, this pocket goes across the Fermi level, which leads $P6_3/mmc$ NaCaBi to be a metal. As shown in Fig. 11(a), we can find that the lattice parameters $a(=b)$ and c decrease under pressure. Moreover, the lattice parameters a/c decrease about 1%/1.3% at 1 GPa, from which the $P6_3/mmc$ phase of NaCaBi becomes preferred. It should also be noted that though the $P6_3/mmc$ NaCaBi changes from an insulator to a metal from 0 to 10 GPa, the inverted direct gap is always kept. Thus, the STI nature with topological surface states is kept up to 10 GPa.

Looking along the c axis, the $P6_3/mmc$ NaCaBi is a layered hexagonal structure with its layer lying in the xy plane. Thus, we can introduce substrates perpendicular to the layer plane. As shown in Table VII, we have introduced 31 substrates with the lattice mismatch less than 1% along the x and y axes to assist growth teams attempting to synthesize the $P6_3/mmc$ phase of NaCaBi. Some commonly used crystals such as KTiO_3 and BaNiO_3 only have lattice mismatch with NaCaBi of about -0.1% and 0.3% , which are very small and can be good substrate candidates. However, it should be noted that as theoreticians, our proposal is very rough and more complicated experimental details should be considered before real experiments.

Similar with applying pressure, imposing various strains is also considered as a convenient method to tune the electronic properties in the condensed systems. Here we focus on applying biaxial linear strain along the a and b axes, which keeps the symmetries of this system unchanged. From Fig. 11(b), we find that the strain energy of this kind of biaxial linear strain increases parabolically with $-5\% \leq \varepsilon \leq 5\%$, which indicates that this kind of strain can be seen as elastic strain in a very large range. Thus, it offers the experimental team a large degree of freedom to choose potential substrates candidates.

 FIG. 11. (a) Lattice parameters $a(=b)$ and c vs pressure. (b) Strain energy vs the linear biaxial strain along the x and y axes.

TABLE VII. 31 substrate candidates with the lattice mismatch less than 1% with the $P6_3/mmc$ phase of NaCaBi. No-MP column denotes the materials ID recorded in the Materials Project, while No-ICSD column denotes the materials ID recorded in the ICSD. $\epsilon > 0$ denotes that the lattice parameter a of the substrate candidate is larger than that of $P6_3/mmc$ NaCaBi, while $\epsilon < 0$ denotes that the lattice parameter a of the substrate candidate is smaller than that of $P6_3/mmc$ NaCaBi.

Formula	No-MP	No-ICSD	Band gap (eV)	a (Å)	Mismatch (ϵ)
KAl(MoO ₄) ₂	mp-19352	28018	3.890	5.545	−0.4%
AlTi(MoO ₄) ₂	mp-18733	250339	3.871	5.544	−0.4%
CsAl(MoO ₄) ₂	mp-505784	280947	3.879	5.551	−0.3%
RbFe(MoO ₄) ₂	mp-563010	245666	2.572	5.596	0.5%
HfPd ₃	mp-11453	638769, 104254	0	5.595	0.5%
KTiO ₃	mp-1180658	94775	0	5.560	−0.1%
KAg ₂	mp-12735	150142	0	5.589	0.4%
Na ₂ LiAu ₃	mp-12815	152090	0	5.530	−0.6%
BaNiO ₃	mp-19138	175, 30661	1.542	5.580	0.3%
Ce ₂ In	mp-19733	621365, 621356, 102186	0	5.557	−0.2%
Sm ₂ In	mp-19816	59527, 59526, 640547, 640544	0	5.549	−0.3%
Pr ₂ In	mp-19854	640268, 108555	0	5.558	−0.1%
Nd ₂ In	mp-21295	59423, 59422, 59421, 640067	0	5.589	0.4%
CaAl ₁₂ O ₁₉	mp-28234	34394	4.320	5.564	≈0%
Rb ₂ Te	mp-383	55157, 55152, 55160, 55154,...	1.372	5.574	0.1%
In ₂ Pt ₃	mp-510439	640295, 59498, 640287	0	5.575	0.2%
SmOs ₂	mp-570007	150521	0	5.574	0.1%
TaPd ₃	mp-582360	648968	0	5.520	−0.8%
PF ₅	mp-8511	62554	7.109	5.563	≈0%
Ba ₃ BPO ₃	mp-9712	402017	1.471	5.502	−1.1%
Ba ₃ BAO ₃	mp-9793	402682	1.529	5.528	−0.7%
LaAl ₂ Ag ₃	mp-16766	57329	0	5.565	≈0%
Na ₃ OsO ₅	mp-555476	416999	0.113	5.553	−0.2%
Li ₂ Ta ₂ (OF ₂) ₃	mp-561011	405777	3.835	5.581	0.3%
Sr ₂ MgH ₆	mp-644225	88205	2.758	5.546	−0.4%
LaBPt ₂	mp-31052	98425	0	5.522	−0.8%
LaB ₂ Ir ₃	mp-10112	44422	0	5.543	−0.4%
BaPd ₅	mp-2606	58672, 616030	0	5.540	−0.5%
NaBPt ₃	mp-28614	68092	0	5.547	−0.3%
CaB ₂ Rh ₃	mp-28705	66767	0	5.551	−0.3%
SrZn ₅	mp-638	106114, 418615	0	5.541	−0.4%

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