Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Design Dirac semimetals with honeycomb Na_3Bi-lattice *via* isovalent cation substitution

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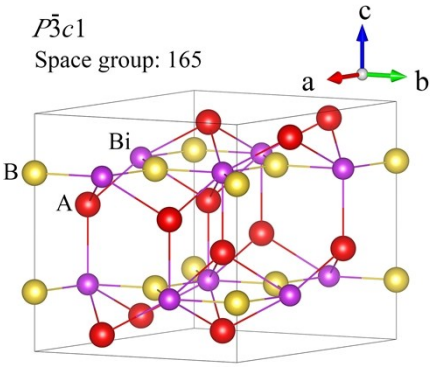

Fig. S1 Structure representation of Na_3Bi with $P\bar{3}c1$ symmetry that can be approximated as a supercell ($\sqrt{3}\times\sqrt{3}\times1$) of the $P6_3/mmc$ phase (A and B denote the cation sites surrounded by Bi_4 tetrahedron and Bi_3 triangle, respectively).

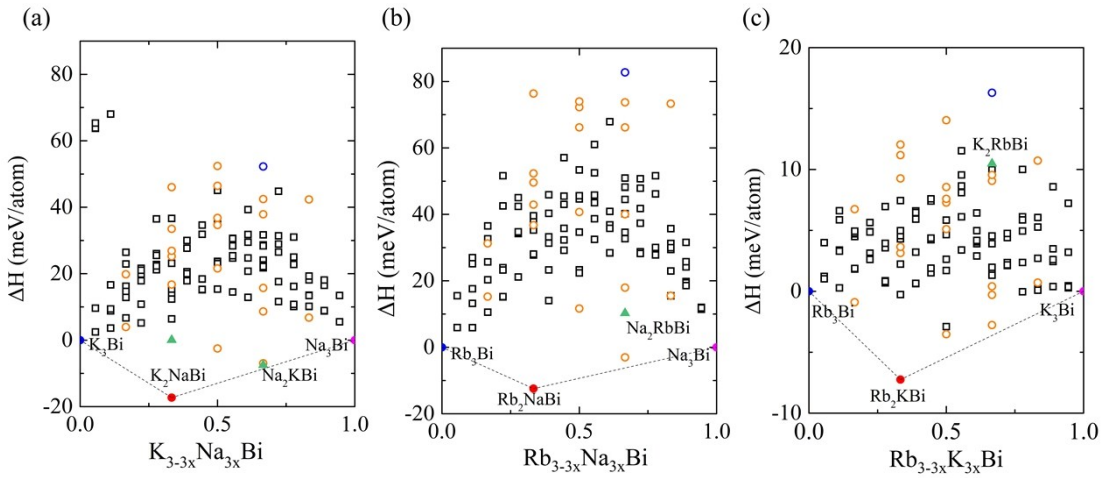

Fig. S2 Formation enthalpies of the alloy structures (a) $K_{3-3x}Na_{3x}Bi$, (b) $Rb_{3-3x}Na_{3x}Bi$ and (c) $Rb_{3-3x}K_{3x}Bi$ *w.r.t.* their binary constituents from PBE. Each of the circles (squares) represents an individual alloy structure constructed by randomly placing two types of alkali atoms on the cation sites in the unit cell ($\sqrt{3}\times\sqrt{3}\times1$ supercell) of the

honeycomb structure. The blue circles represent the unstable compounds (plus signs) which are introduced in the Fig. 1(b). The compounds on the convex hulls are shown by solid circles. The green solid triangles in (a) represent the experimentally known compound Na_2KBi (space group No. 225)[1] and other compounds (K_2NaBi, Na_2RbBi, K_2RbBi) in the experimental Na_2KBi phase. Meanwhile, two of them (Rb_2NaBi, Rb_2KBi) in the experimental phase are even out of the range in the figure which are above the convex hulls.

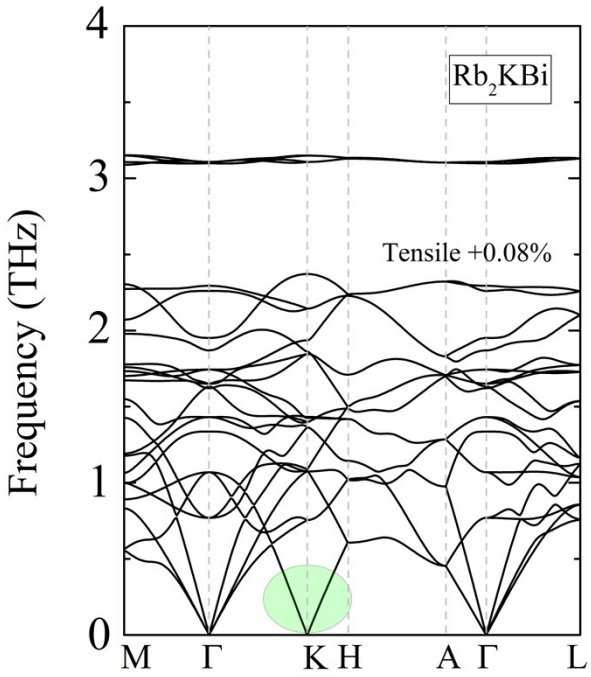

Fig. S3 Phonon spectrum of Rb_2KBi under biaxial tensile strain (+0.08%).

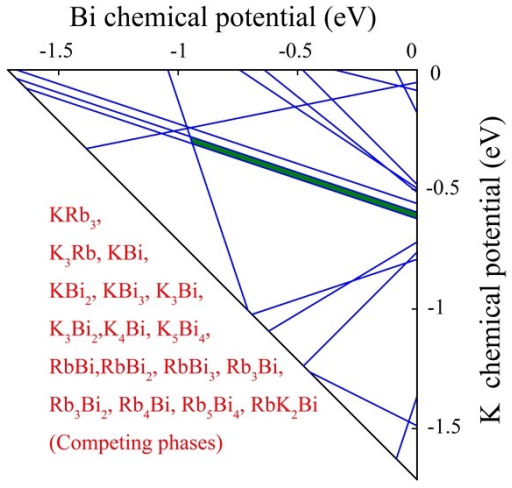

Fig. S4 Thermodynamic stability analysis of Rb_2KBi under biaxial tensile strain (+0.08%) in the element chemical potential space with stability region shown by green zone. Each of the blue lines represents a binary or ternary competing phase.

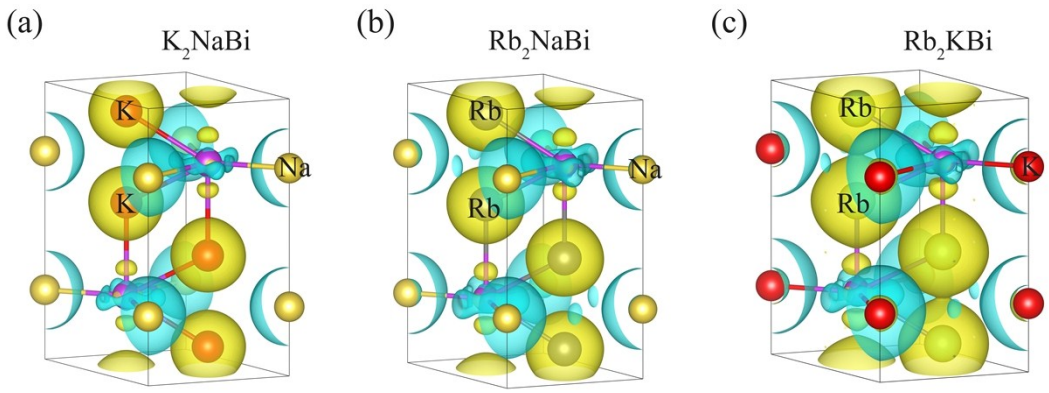

Fig. S5 The differential charge densities of (a) K_2NaBi ($\rho = 9.2 \times 10^4$ eÅ^{-3}), (b) Rb_2NaBi ($\rho = 9.2 \times 10^4$ eÅ^{-3}) and (c) Rb_2KBi ($\rho = 2.0 \times 10^4$ eÅ^{-3}), as evaluated by subtracting from the charge density of the ternary (*e.g.* K_2NaBi), the charge densities of binaries (*e.g.* K_3Bi and Na_3Bi) with the same structure as the ternary but only one cation identity. Blue: charge dissipation. Yellow: charge accumulation.

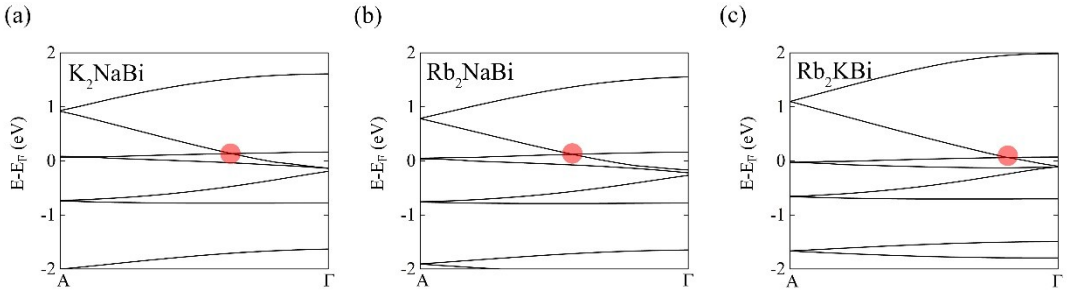

Fig. S6 Electronic structures of (a) K_2NaBi, (b) Rb_2NaBi and (c) Rb_2KBi from HSE06+SOC. The red circles indicate the positions of Dirac cones.

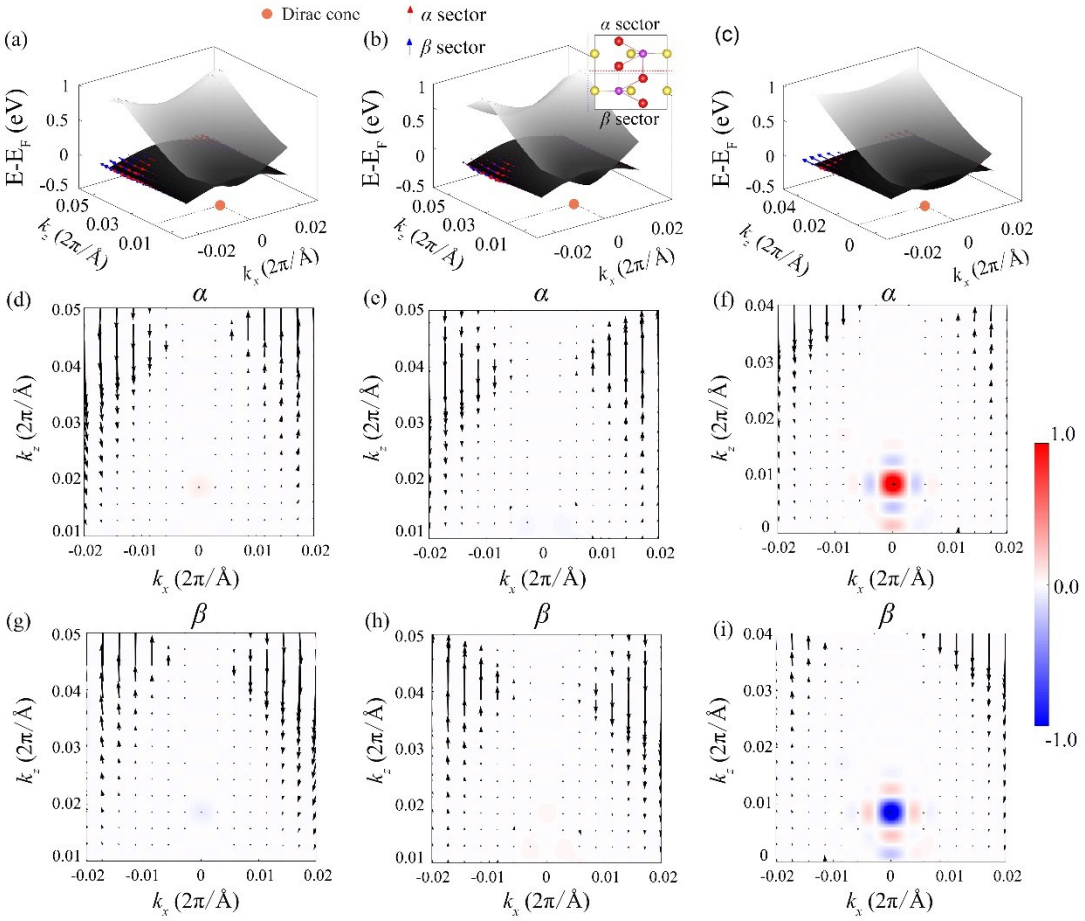

Fig. S7 Hidden spin polarizations of the electronic states near the Dirac cone at Fermi level for (a, d, g) K_2NaBi, (b, e, h) Rb_2NaBi and (c, f, i) Rb_2KBi. Inset: α and β sectors as inversion partners in the honeycomb structure. (a, b, c) Three-dimensional plots with red (blue) arrows indicating the local spin polarizations on the α (β) sectors, demonstrating the strong (vanishing) spin polarizations on the lower (upper) part of the Dirac cone. (d, e, f) and (g, h, i) Corresponding two-dimensional diagrams of spin polarizations of the lower cone on α and β sectors, respectively. The arrows indicate the in-plane spin direction and the color scheme indicates the out-of-plane components.

Table S1 Total energies (E_{tot}'s) of K_2NaBi, Rb_2NaBi and Rb_2KBi in crystal structures with chemical formula AB_2X relative to the honeycomb structure. The $P\bar{3}c1$ structure as shown in Fig. S1 relaxes into $P6_3/mmc$ honeycomb structure for the three ternaries (K_2NaBi, Rb_2NaBi and Rb_2KBi). The other possible structures have much higher total energy than the $P6_3/mmc$ phase and the five structures with the lowest energies for each compound are shown here. The remaining structures are listed below (with space group in parentheses): V_2FeGe (40), As_2LaAu (42), Ti_2CoNi (44), Li_2HN (57), Ni_2GeP (61), As_2SmAu (64), Ti_2ZrO (65), C_2NCl (72), H_2BN (96), In_2SnPb (99), Pd_2CePt (123), B_2LuC (127), B_2TbC (135), Si_2LiB (137), H_2LiN (138), H_2CO (161), Bi_2PdPt (164), and Er_2MgOs (225).

Compound	Space group No.	E_{tot} of K_2NaBi (eV/atom)	E_{tot} of Rb_2NaBi (eV/atom)	E_{tot} of Rb_2KBi (eV/atom)
Na_2NaBi (Na_3Bi-type)	194	0	0	0
Al_2CuIr	67	0.027	0.034	0.027
Li_2MgSi	215	0.030	0.039	0.028
Sr_2BaNp	216	0.037	0.051	0.030
Si_2MnNi	4	0.037	0.051	0.030
I_2YbO	62	0.037	0.043	0.029

Reference:

[1] I. Y. Sklyadneva, I. P. Rusinov, R. Heid, K.-P. Bohnen, P. M. Echenique, E. V. Chulkov. *Sci. Rep.*, 2016, **6**, 24137.