A new class of three-dimensional topological insulator, ternary rare earth chalcogenides, is theoretically investigated with ab initio calculations. Based on both bulk band structure analysis and the direct calculation of topological surface states, we demonstrate that LaBiTe\(_3\) is a topological insulator. La can be substituted by other rare earth elements, which provide candidates for novel topological states such as quantum anomalous Hall insulator, axionic insulator and topological Kondo insulator. Moreover, YBiTe\(_3\) and YSbTe\(_3\) are found to be normal insulators. They can be used as protecting barrier materials for both LaBiTe\(_3\) and Bi\(_2\)Te\(_3\) families of topological insulators for their well matched lattice constants and chemical composition.

PACS numbers: 71.20.-b, 73.43.-f, 73.20.-r
have been synthesized in experiments\textsuperscript{28}. In this work we focus on these four compounds based on \textit{ab initio} calculations, among which we find that LaBiTe\textsubscript{3} is a strong topological insulator. Moreover, La and Y can be replaced by other rare earth elements which have magnetic moments due to the localized $f$ electrons. These systems could provide realizations of the topological Mott insulator state\textsuperscript{29}. The versatility of rare earth elements will bring us new possibilities beyond Bi\textsubscript{2}Te\textsubscript{3} family.

\textbf{Method and crystal structure} - The electronic structures of LaBiTe\textsubscript{3}, YBiTe\textsubscript{3}, LaSbTe\textsubscript{3} and YSbTe\textsubscript{3} are calculated in the framework of the density functional theory with Perdew-burke-Ernzerhof type generalized gradient approximation (GGA)\textsuperscript{30}. For our calculations, both the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{31,32} with the projected augmented wave method and the BSTATE package with plane-wave pseudo-potential method are employed. We adopt the $12 \times 12 \times 12$ k-point grid for self-consistent calculations. The kinetic energy cutoff for the plane wave basis in BSTATE package is fixed to 340 eV. SOC is included in all of our calculation, except in the calculations for the ionic optimization which is confirmed to be insensitive to SOC.

LaBiTe\textsubscript{3}, YBiTe\textsubscript{3}, LaSbTe\textsubscript{3} and YSbTe\textsubscript{3} share the same rhombohedral crystal structure with the space group $D_3^3$ (R$3m$) (see Ref.28 and references therein). Here we take LaBiTe\textsubscript{3} as an example. Similar to Bi\textsubscript{2}Te\textsubscript{3}, the crystal consists of triangular layers stacking along [111] direction with A-B-C· · · order. Five atomic layers form a quintuple layer (QL) with the order of Te-X-Te-X$'$-Te, where X and X$'$ denote La or Bi organized in certain pattern, as discussed below. Though the lattice parameters have been measured by experiments, up to our knowledge, the relative position between M and M$'$ has not been fully resolved experimentally. Thus we compare the total energy obtained in \textit{ab initio} calculation for different configurations to search for the most stable structure. Our result indicates that the structures with La and Bi separated in different atomic layers are more stable than those with La and Bi mixed in the same atomic layer. There are two structures which have lowest energy. Because the energy difference between the two configurations are very small, in the following we will study both of them separately. (i) Type-I structure consists of stacking quintuple layers along [111] direction, each of which is ordered as Te-La-Te-Bi-Te, as shown in Fig. 1(a). This structure is inversion asymmetric. (ii) Type-II structure consists of stacking pairs of quintuple layers along [111] direction, ordered as Te-La-Te-La-Te and Te-Bi-Te$'$-Bi-Te. This structure is inversion symmetric. The experimental lattice constants and optimized atomic coordinates for the two structures are listed in Table I.

\textbf{Type-I structure}. We start by computing the band structures for LaBiTe\textsubscript{3}, YBiTe\textsubscript{3}, LaSbTe\textsubscript{3} and YSbTe\textsubscript{3} in the type-I crystal structure. As examples, Fig.2 shows

![FIG. 2: Band structures for(a) LaBiTe\textsubscript{3} and (b) YBiTe\textsubscript{3} of type-I structures and (c) LaBiTe\textsubscript{3} and (d) YBiTe\textsubscript{3} of type-II structures. The strengths of spin-orbit coupling(SOC) are tuned to be 50\% (dashed purple lines), 89\% (thin red lines) and 100\% (thick black lines) respectively, in (a) and (b). The Fermi energy is set to zero. The energy gap decreases to zero and re-opens as SOC increases from zero to 100\% for LaBiTe\textsubscript{3}, showing a clear band anti-crossing feature. The Dirac type level crossing at 89\% SOC is highlighted in the inset. (e) Brillouin zone for this class of materials. The four inequivalent time-reversal-invariant points are $\Gamma(0;0;0)$, $L(\pi;0;0)$, $F(\pi;\pi;0)$ and $T(\pi;\pi;\pi)$. The surface Brillouin zone is projected from the 3D bulk Brillouin zone into the plane of the atomic layer.]

![FIG. 3: The band dispersion for an semi-infinite surface of (a) LaBiTe\textsubscript{3}, (b) YBiTe\textsubscript{3}, (c) LaSbTe\textsubscript{3} and YSbTe\textsubscript{3} of type-I structures. The inset of (a) highlights the surface states near the Dirac cone.]

\begin{figure}
\centering
\includegraphics[width=\linewidth]{Fig2.png}
\caption{Band structures for (a) LaBiTe\textsubscript{3} and (b) YBiTe\textsubscript{3} of type-I structures and (c) LaBiTe\textsubscript{3} and (d) YBiTe\textsubscript{3} of type-II structures. The strengths of spin-orbit coupling(SOC) are tuned to be 50\% (dashed purple lines), 89\% (thin red lines) and 100\% (thick black lines) respectively, in (a) and (b). The Fermi energy is set to zero. The energy gap decreases to zero and re-opens as SOC increases from zero to 100\% for LaBiTe\textsubscript{3}, showing a clear band anti-crossing feature. The Dirac type level crossing at 89\% SOC is highlighted in the inset. (e) Brillouin zone for this class of materials. The four inequivalent time-reversal-invariant points are $\Gamma(0;0;0)$, $L(\pi;0;0)$, $F(\pi;\pi;0)$ and $T(\pi;\pi;\pi)$. The surface Brillouin zone is projected from the 3D bulk Brillouin zone into the plane of the atomic layer.}
\end{figure}
|    | LaBiTe₃ | YBiTe₃ | LaSbTe₃ | YSbTe₃ |
|----|---------|--------|---------|--------|
| a  | 4.39    | 4.46   | 4.24    | 4.47   |
| c  | 30.20   | 31.65  | 30.40   | 30.32  |
| Te(²Te/²Te') | 0.20876 | 0.22243 | 0.20426 | 0.21850 |
| Te  | -0.20893 | -0.21228 | -0.21136 | -0.21306 |
| Bi(Sb) | 0.40274 | 0.40161 | 0.40102 | 0.40156 |
| La(Y) | -0.39938 | -0.39416 | -0.40111 | -0.39582 |
| E₉ | 0.12    | 0.12   | 0.15    | 0.28   |

TABLE I: The experimental lattice parameters of hexagonal lattice in unit of angstrom, the theoretically optimized atomic positions and band gaps. Type-II structure has twice the length of type-I along c axis (see Fig.1) and therefor has double atoms. The atomic coordinate is (0,0,z₋₋₋) in the rhombohedral primitive unitcell. We listed z₋₋₋ values for all atoms. These Te atoms as inversion centers of type-II are marked as TeⅠ and TeⅡ. The energy gap(E₀) is in unit of eV.

The results for LaBiTe₃ and YBiTe₃. Both of them have similar band gap 0.12 eV around the T point. The band gap of YBiTe₃ is close to the previous experimental value of 0.18 ~ 0.23 eV. As mentioned above, due to the lack of inversion symmetry, the parity criteria for topological insulators does not apply. Alternatively, we study the evolution of conduction and valence bands by tuning the SOC strength artificially. Without SOC, any insulator must be topologically trivial, so that a topological insulator phase can be identified by studying the topological phase transition at some critical SOC strength. A Dirac type level crossing between valence and conduction bands separate the topologically trivial and nontrivial phases. The continuous tuning of SOC is obtained by changing the speed of light c in the VASP package. As shown in Fig.2, upon the increase of SOC strength, the band gap of LaBiTe₃ decreases and vanishes on a ring in Brillouin zone (BZ) near T at 89% SOC and opens again, which indicates a topological phase transition and suggests that LaBiTe₃ is a topologically non-trivial insulator with full SOC strength. In contrast, the band gap remains finite upon turning on SOC for YBiTe₃, which is thus a topologically trivial insulator. We perform the same calculations for LaSbTe₃ and YSbTe₃, and find both of them are topologically trivial insulators.

The existence of topological surface states is one of the most important physical consequence of the TIs. To further confirm the topological nature of the proposed materials and study the detailed features of the surface states, we obtain the dispersion of surface states based on ab initio method. We construct Tight-binding(TB) Hamiltonian of the semi-infinite system with Maximally localized Wannier functions (MLWF) basis for LaBiTe₃ family materials, and then apply the standard Green function iteration method to obtain the surface density of states. The detail of this method can be found in Ref. In Fig.3 we can see clearly that the topological surface states form a single-Dirac-cone at the T point in 2D BZ within the bulk gap for LaBiTe₃, while no such surface states are observed for YBiTe₃, LaSbTe₃ and YSbTe₃. This result determines the topologically non-trivial nature of LaBiTe₃ without any doubt. From this calculation, we can further obtain the Fermi velocity for LaBiTe₃ to be 4.0 × 10⁵ m/s, similar to that of Bi₂Se₃.[12]

Type-II structure. The band structures for LaBiTe₃ and YBiTe₃ of type-II are shown in Figs 2(c) and 2(d). Their band gaps are 0.07 eV near the Γ point, smaller than those of type-I structures. Due to inversion symmetry, we can follow the parity criteria proposed by Fu and Kane to calculate Z₂ topological index. The product of the parities of the Bloch wave functions are determined for the occupied bands at all time-reversal-invariant momenta Γ(0, 0, 0), L(π, 0, 0), F(π, π, 0), T(π, π, π) in BZ. For LaBiTe₃, we find that the product of parities at Γ is “+” and those at L, F, T are all “-”. Thus LaBiTe₃ is topologically non-trivial with Z₂ index (1:000). For YBiTe₃ and YSbTe₃, we find that the products of parities at Γ, L, F, T are all “-”, so that both of them are topologically trivial with Z₂ index (0:000). In addition, LaSbTe₃ is found to be a semimetal. For both type-I and -II structures, it is noted that the states near Fermi energy are partially composed by La/Y−5d₋₋₋ as well as Bi/Sb-6p₋₋₋ and Te-5p₋₋₋ orbitals.

Discussion- In summary, our ab initio calculation has verified that LaBiTe₃ is a strong topological insulator. The substitution of La in LaBiTe₃ with other rare earth elements will open a wide platform to study various topological non-trivial behaviors. It is found that many isostructural stoichiometric compounds similar to LaBiTe₃ also exist in the family of ternary rare earth chalcogenides, such as LnBiTe₃ (with Ln standing for La, Ce, Pr, ......Lu or Y) and LnSbTe₃, many of which have intrinsic magnetic moments due to the localized f electrons (e.g. Pr, Sm or Gd). Since the strong correlation effect induced by f electrons can not be properly taken into account in the current GGA calculations, we will leave the detailed study of these materials for the future work but discuss the possible states induced by
strong electron correlation. First, if the coupling between magnetic moments is ferromagnetic, quantum anomalous Hall effect may emerge in thin films or heterostructures of LuBiTe$_3$ when the band structure is normal for one spin while inverted for the other, similar to the proposals in Hg$_{1-x}$Mn$_x$Te$_2$[42] and Bi$_{2-x}$Fe$_x$Se$_3$[27]. Second, if the magnetic coupling is ferromagnetic within one atomic layer but anti-ferromagnetic between two neighboring atomic layers, the dynamical axion field may be realized, which is proposed as a novel optical modulators device[6]. The recently proposed topological Kondo insulator[43] may also exist in this class of materials due to the existence of $f$ electrons. Besides the topological insulators the newly proposed materials have another important potential application. As we have shown, some materials in this family are trivial insulators such as YBiTe$_3$ and YSbTe$_3$. Due to their similarity with the Bi$_2$Te$_3$ family, the trivial insulators in this new family are natural candidates of barrier materials for thin films or quantum wells of the TIs in the Bi$_2$Te$_3$ family and the new LaBiTe$_3$ family. Especially, YBiTe$_3$ (a=4.46 Å) - LaBiTe$_3$ (a=4.39 Å) and YBiTe$_3$ - Bi$_2$Te$_3$ (a=4.3835 Å)[43] pairs have the best-matched lattice constants. Such a barrier material may help protecting a clean surface of TI and greatly improve the surface condition in transport experiments, which is a main difficulty in the current experiments.

We would like to thank I. R. Fisher for the helpful discussion. This work is supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE-AC02-76SF00515. C.X.L. and B.Y. acknowledge financial support by the Alexander von Humboldt Foundation of Germany. B.Y. thanks the support by the Supercomputer Center of Northern Germany (HLRN Grant No. hbp00002).

---

[1] X. Qi and S. Zhang, Physics Today 63, 33 (2010).
[2] J. Moore, Nature 464, 194 (2010).
[3] M. Hasan and C. Kane, arXiv:1002.3895v1 (2010).
[4] X.-L. Qi, T. L. Hughes, and S.-C. Zhang, Phys. Rev. B 78, 195424 (2008).
[5] X. Qi, R. Li, J. Zang, and S. Zhang, Science 323, 1184 (2009).
[6] R. Li, J. Wang, X.-L. Qi, and S.-C. Zhang, Nature Physics 6, 284 (2010).
[7] L. Fu and C. L. Kane, Phys. Rev. Lett. 100, 096407 (2008).
[8] B. A. Bernevig, T. L. Hughes, and S.C. Zhang, Science 314, 1757 (2006).
[9] M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. Molenkamp, X.-L. Qi, and S.-C. Zhang, Science 318, 766 (2007).
[10] L. Fu and C. L. Kane, Phys. Rev. B 76, 045302 (2007).
[11] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature 452, 970 (2008).
[12] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Physics 5, 438 (2009).
[13] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, et al., Nature Physics 5, 398 (2009).
[14] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, et al., Science 325, 178 (2009).
[15] B. Yan, C.-X. Liu, H.-J. Zhang, C.-Y. Yam, X.-L. Qi, T. Frauenheim, and S.-C. Zhang, Europhysics Letters 90, 37002 (2010).
[16] Y. Chen, Z. Liu, J. Analytis, J. Chu, H. Zhang, S. Mo, R. Moore, D. Lu, I. Fisher, S. Zhang, et al., arXiv:1006.3843v1 (2010).
[17] T. Sato, K. Segawa, H. Guo, K. Sugawara, S. Souma, T. Takahashi, Y. Ando, W. Cai, D. Chen, Y. Ren, et al., arXiv:1006.2437 (2010).
[18] S. Chadov, X. L. Qi, J. Kübler, G. H. Fecher, C. Felser, and S. C. Zhang, Nature Mater. 9, 541 (2010).
[19] H. Lin, L. A. Wray, Y. Xia, S. Xu, S. Jia, R. J. Cava, A. Bansil, and M. Z. Hasan, Nature Mater. 9, 546 (2010).
[20] H. Lin, R. S. Markiewicz, L. A. Wray, L. Fu, M. Z. Hasan, and A. Bansil, arXiv:1003.2015 (2010).
[21] S.-Y. Xu, L. A. Wray, Y. Xia, R. Shankar, A. Petersen, A. Fedorov, H. Lin, A. Bansil, Y. S. Hor, D. Grauer, et al., arXiv:1007.5111 (2010).
[22] M. Klintenberg, arXiv:1007.4538 (2010).
[23] W. Feng, J. Ding, D. Xiao, and Y. Yao, arXiv:1008.0056 (2010).
[24] H. Jin, J. Song, A. Freeman, M. Kanatzidis, P. Coussot, G. Ovarlez, C. Cen, D. Bogorin, J. Levy, J. Eckmann, et al., arXiv:1007.5480v1 (2010).
[25] Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, and S.-C. Zhang, Phys. Rev. Lett. 102, 156603 (2009).
[26] Y. S. Hor, P. Roushan, H. Beidenkopf, J. Seo, D. Qi, J. G. Checkelsky, L. A. Wray, D. Hsieh, Y. Xia, S.-Y. Xu, et al., Phys. Rev. B 81, 195203 (2010).
[27] R. Yu, W. Zhang, H. Zhang, S. Zhang, X. Dai, and Z. Fang, Science 329, 61 (2010).
[28] O. Madelung, U. Rössler, and M. Schulz, Ternary Compounds, Organic Semiconductors, in Landolt-Börnstein, Condensed Matter, Subvolume III/41E, Springer, Berlin, 2000, pp.471-477.
[29] S. Raghu, X. Qi, C. Honerkamp, and S. Zhang, Physical review letters 100, 156401 (2008).
[30] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[31] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[32] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[33] G. Kresse and D. Joubert, Phys. Rev. Lett. 86, 3483 (1996).
[34] Z. Fang and K. Terakura, Journal of Physics: Condensed Matter 14, 3001 (2002).
[35] P. Rustamov, F. Sadrygin, Z. Melikova, M. Alidzhanov, and M. Ali-Zade, Inorg. Mater. 15, 607 (1979).
[36] H.-J. Zhang, C.-X. Liu, X.-L. Qi, X.-Y. Deng, X. Dai, S.-C. Zhang, and Z. Fang, Phys. Rev. B 80, 085307 (2009).
[37] S. Murakami, New Journal of Physics 9, 356 (2007).
[38] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
[39] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).
[40] M. P. L. Sancho, J. M. L. Sancho, and J. Rubio, Journal of Physics F: Metal Physics 14, 1205 (1984).
[41] M. P. L. Sancho, J. M. L. Sancho, J. M. L. Sancho, and J. Rubio, Journal of Physics F: Metal Physics 15, 851 (1985).
[42] C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Phys. Rev. Lett. 101, 146802 (2008).
[43] M. Dzero, K. Sun, V. Galitski, and P. Coleman, Phys. Rev. Lett. 104, 106408 (2010).
[44] O. Madelung, U. Rössler, and M. Schulz, Bismuth telluride (Bi$_2$Te$_3$) crystal structure, chemical bond, lattice parameters (including data for related compounds), in SpringerMaterials - The Landolt-Böntstein Database.