DOI: 10.11858/gywlxb.20230765

Prediction of Superconducting RbBSi Compounds under Pressure

LIU Jinyu[1], CUI Xiangyue[2], LIU Ailing[1], CHENG Xiaoran[1], WANG Xingyu[1], WANG Yujia[1], ZHANG Miao[1]

(1. *Department of Physics*, *School of Sciences*, *Beihua University*, *Jilin* 132013, *Jilin*, *China*;
2. *Joint Key Laboratory of the Ministry of Education*, *Institute of Applied Physics and Materials Engineering*, *University of Macau*, *Taipa* 999078, *Macau*, *China*)

Abstract: In this work, we have performed extensive swarm-intelligence structures searching simulations on the RbBSi compounds within the pressure range from 0 to 100 GPa. We have proposed three different phases of RbBSi, of which the stability, the electronic structure and the potential superconductivity were calculated by first-principles calculations. All predicted phases are thermodynamically and dynamically stable within the studied pressure range. The bands of the three phases crossing the Fermi level indicate the structures are all metallic. In addition, *P*4/*nmm*-RbBSi is a superconductor with T_c of 14.4 K at ambient pressure. This work extends the understanding and potential application of alkali metal boron-silicide compounds in the field of superconductor.

Keywords: first-principles calculations; high-pressure; alkali-metal boron-silicide; crystal structure prediction

CLC number: O521 **Document code:** A

The development of superconductors at high temperatures or even ambient temperature has been a long-standing goal in the scientific community since 1911[1]. Superconductors have great applications in various fields, such as power transmission, magnetic resonance imaging, and quantum computing[2−4]. In recent years, there has been a major breakthrough in the field of new phonon-mediated superconductor, specifically in the study of clathrate hydrides. Clathrate hydrides attract attention due to their unique crystal structure and high superconducting critical temperatures above 200 K under high pressure[5−8]. One noteworthy discovery is CaH_6, and this hydride exhibits a superconducting critical temperature (T_c) of 215 K at 172 GPa[9−10]. This is followed by the discovery of LaH_{10}, and it has T_c of 260 K at about 170 GPa[11−13]. While these high-T_c hydrides show promising superconducting properties, they require comparable high pressures to synthesize and are typically

* **Received date:** 2023-10-24; **Revised date:** 2024-01-22

Foundation item: Jilin Provincial Science and Technology Development Joint Fund Project (YDZJ202201ZYTS581); Scientific and Technological Research Project of Jilin Province Education Department (Grant No. JJKH20240077KJ)

Biography: Liu Jinyu (2000—), female, postgraduate, mainly focuses on the materials science at extreme condition. E-mail: liujinyu2577@163.com
Cui Xiangyue (1995—), female, doctoral student, mainly focuses on the materials science at extreme condition. E-mail: nacy_cuixiangyue@126.com

Corresponding author: Zhang Miao (1981—), female, professor, mainly focuses on the computational design of novel functional materials and materials science at extreme condition. E-mail: zhangmiaolmc@126.com

unrecoverable at ambient pressure, limiting their practical applications. Researchers continue to explore novel materials and mechanisms that can exhibit superconductivity at more accessible conditions. Such advancements would greatly enhance the feasibility and utilization of superconductors in various technological applications.

Encouragingly, some non-hydrogen clathrates, in particular the sp^3 bonded ones with light elements, have been suggested to be superconducting at moderate or even ambient pressure. Many doped albite structures, such as XC_6[14–15], $X(BN)_6$[16], XB_3C_3[17], and XB_3Si_3[18], where X represents different doping elements, as well as FC_{34}[19], has been predicted to be good superconductors at ambient pressure. For example, T_c calculated for NaC_6 is 116–127 K at ambient pressure. It is noteworthy that with the guiding from particle-swarm structure prediction method, Zhu *et al.*[17] successfully synthesized a thermodynamically stable carbon-boron sp^3 bonded clathrate at high pressures near 50 GPa, namely SrB_3C_3. The calculations further suggested that SrB_3C_3 is a superconductor, with the superconducting transition temperature of 40 K[20–22]. Carbon and silicon are elements of group-14 in the periodic table of elements[23]. They have four valence electrons, allowing them to form covalent bonds with other elements by sharing electrons. Moreover, they have certain similarities in atomic structure and chemical properties[24–25]. In the silicon analogues, RbB_3Si_3 is theoretically proposed to be thermodynamically stable between 7 and 35 GPa, and to be metastable at 1 atmospheric pressure, with T_c estimated to be 14 K[18]. Therefore, it is of great interest to explore whether the RbBSi compounds have the potential for superconductivity under ambient pressures.

In this work, we employed CALYPSO (crystal structure analysis by particle swarm optimization) method to predict the stable structure of RbBSi within the pressure range from zero to 100 GPa, and studied their physical properties by first-principles calculations.

1 Methods

We explored the properties of RbBSi in the pressure range of 0−100 GPa using CALYPSO code[26–29], which has been developed specifically to explore the potential energy surfaces of chemical systems and find the global minima. The structural relaxations and electronic properties were calculated using density functional theory with the Perdew-Burke-Ernzerhof generalized gradient approximation as implemented in the VASP code[30–31]. We used projector augmented wave (PAW) potentials[32] in which the valence electrons for the Rb, B and Si atoms were represented as $4s^24p^65s^1$, $2s^22p^1$, and $3s^23p^2$. In order to ensure the enthalpy convergence, the cutoff energy was adopted 500 eV. The Monkhorst-Pack *k*-point meshes are 8×8×2 for $P6_3/mmc$-RbBSi, 3×8×2 for $C2/m$-RbBSi, and 8×8×3 for $P4/nmm$-RbBSi, respectively. The phonon dispersion curves were used to verify the dynamic stability of RbBSi via a supercell approach as implemented in PHONOPY package[33]. The electron-phonon coupling constant was obtained from first-principles density-functional perturbation theory as implemented in QUANTUM ESPRESSO package[34].

2 Results and Discussion

The RbBSi crystal structure prediction was successfully conducted in the pressure range of 0—100 GPa, and three phases ($P6_3/mmc$, $C2/m$ and $P4/nmm$) were discovered. As shown in Fig. 1(a), $P6_3/mmc$-RbBSi at standard atmospheric pressure has a layered hexagonal structure that consists of alternate B-Si honeycomb layers separated by a layer of interstitial Rb atoms. The bond length between boron and silicon is 2.049 Å, forming a stable hexagonal structure. In the pressure range of 17 GPa to 33 GPa, the $C2/m$ phase was found to be more stable (see Fig. 1(b)). In the $C2/m$-RbBSi structure, there are six membered rings and four membered rings composed of folded B-Si layers. The layers in these structures are separated by Rb atoms in the gap between the two layers. The lengthes of the boron-silicon bond in the four-membered ring and in the six-membered ring are 2.095 and 2.115 Å, respectively, and the length of the boron-boron bond is 1.678 Å. As the pressure increases, the $P4/nmm$-

RbBSi phase becomes more stable above 33 GPa (see Fig. 1(c)). Different from *C*2/*m*-RbBSi, the space group of *P*4/*nmm*-RbBSi changes from monoclinic to tetragonal, and the folded B-Si layer for *P*4/*nmm*-RbBSi is only composed of four-membered rings. The bond length of the boron-silicon bond is 2.098 Å. The detailed lattice parameters and atomic positions of the structures are given in Table 1.

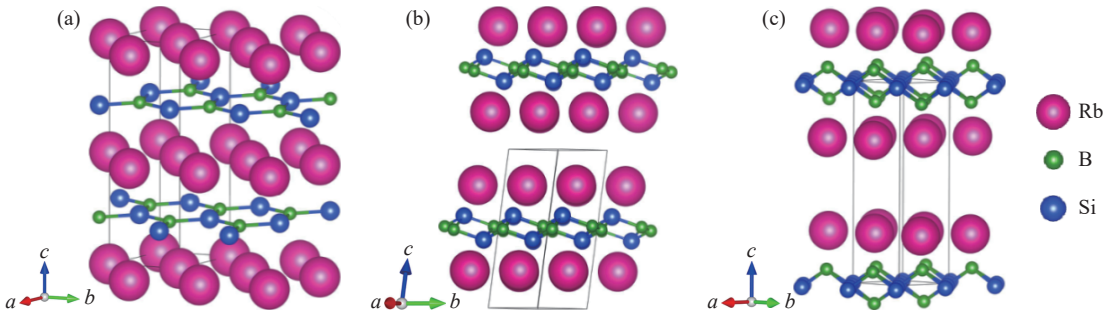


Fig. 1　The predicted crystal structures of the RbBSi: (a) $P6_3/mmc$, (b) $C2/m$, and (c) $P4/nmm$

Table 1　Detailed structure information of the predicted RbBSi compounds at standard atmospheric pressure

Space group	Lattice parameters	Atomic positions
$P6_3/mmc$	$a = b = 3.549$ Å, $c = 11.365$ Å $\alpha = \beta = 90°$, $\gamma = 120°$	Rb 2a (0, 0, 0) B 2d (0.667, 0.333, 0.250) Si 2c (0.667, 0.333, 0.750)
$C2/m$	$a = 9.004$ Å, $b = 3.518$ Å, $c = 11.226$ Å $\alpha = \gamma = 90°$, $\beta = 109.364\,2°$	Rb 4i (0.532, 0, 0.770) B 4i (0.903, 0, 0.489) Si 4i (0.770, 0.500, 0.424)
$P4/nmm$	$a = b = 3.752$ Å, $c = 11.170$ Å $\alpha = \beta = \gamma = 90°$	Rb 8j (0, 0.500, 0.736) B 8j (0, 0.500, 0.084) Si 4d (0.500, 0.500, 0)

We also calculated the formation enthalpy (see Fig. 2), and systematically studied the stability of the three phases of RbBSi compounds. The formation enthalpy for RbBSi were defined as: $\Delta H = H(\text{RbBSi}) - H(\text{Rb}) - H(\text{B}) - H(\text{Si})$. For Rb, we used the enthalpy from bcc → fcc → $I4_1/amd$ → $Cmca$ structure transitions, with the phase transitions occurring at 8.2, 15.1 and 41.0 GPa, respectively[35]. For B, we used the enthalpy from $R\bar{3}m$ → $Pnnm$ (γ-B) → $Cmca$ (α-Ga) structure transitions, with the phase transitions occurring at 17.7 and 91.3 GPa, respectively[36]. For Si, we used the enthalpies from $Fd\bar{3}m$ (dia-Si) → $Imma$ → $P6_3/mmc$ (hcp) → $Fm\bar{3}m$ structure transitions, with the phase transitions occurring at 8.9, 40.0 and 83.9 GPa, respectively[37]. It can be seen from Fig. 2 that as the pressure increases, the crystal structure phase changes from the $P6_3/mmc$ phase to the $C2/m$ phase at 17 GPa . Once the pressure reaches 33 GPa, the crystal structure phase with the lowest energy is the $P4/nmm$ phase.

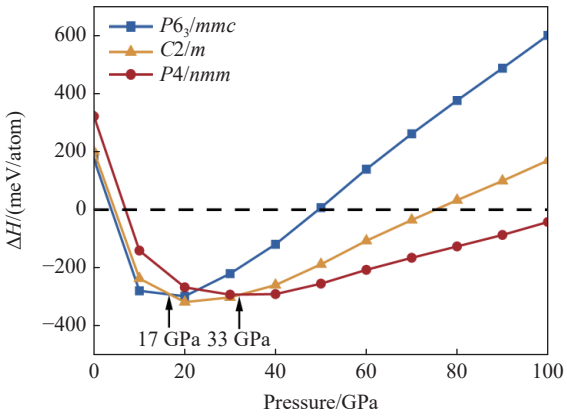


Fig. 2　Calculated formation enthalpies of RbBSi compounds with the $P6_3mmc$, $C2/m$, and $P4/nmm$ structures

The phonon calculation is a reliable measure to confirm the dynamic stability of studied materials. Therefore, we calculated phonon dispersion curves for $P6_3/mmc$ at 0 and 10 GPa, for $C2/m$ at 0 and 20 GPa, and for $P4/nmm$

at 0 and 40 GPa, as shown in Fig. 3. Our phonon calculations showed that all the three phases are dynamically stable because of the absence of any imaginary frequency vibrations in the whole Brillouin zone.

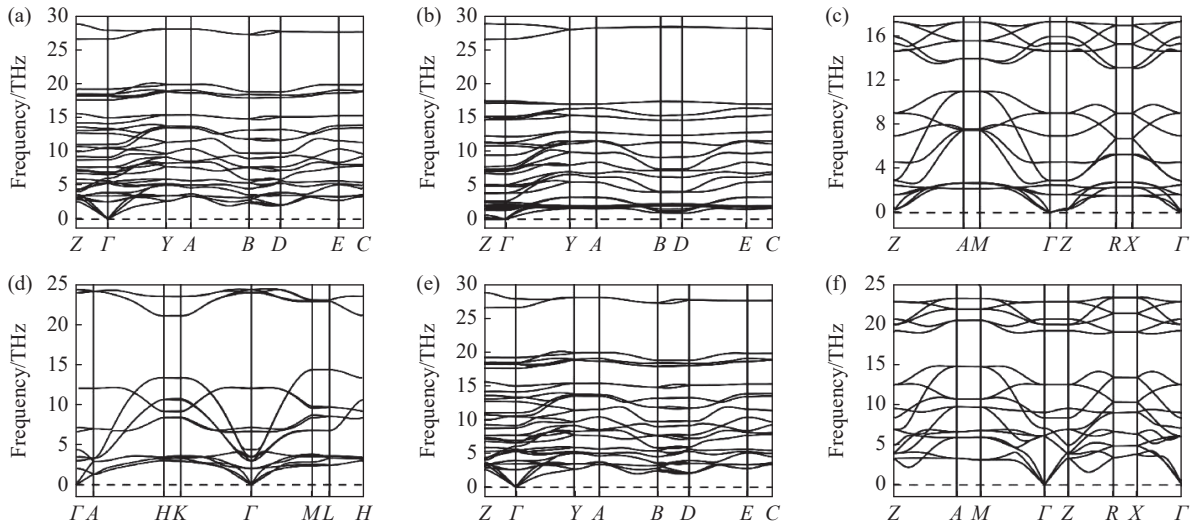


Fig. 3　Phonon dispersion curves of the three structre of RbBSi under different pressures: (a) $P6_3/mmc$ at 0 GPa, (b) $C2/m$ at 0 GPa, (c) $P4/nmm$ at 0 GPa, (d) $P6_3/mmc$ at 10 GPa, (e) $C2/m$ at 20 GPa, (f) $P4/nmm$ at 40 GPa

We next explored the electronic properties of the predicted RbBSi compounds via electronic band structures and densities of electronic states (DOS). As shown in Fig. 4, it can be observed that there is a significant consistency between the band structures and DOS. As shown in Fig. 4(a)−Fig.4(c), the bands cross over the Fermi level, indicating that these phases are metallic, which agrees well with the results of DOS (see Fig. 4(d)−Fig. 4(f)). In addition, the major contribution of metallicity comes from the B-*p* state and the Si-*p* state.

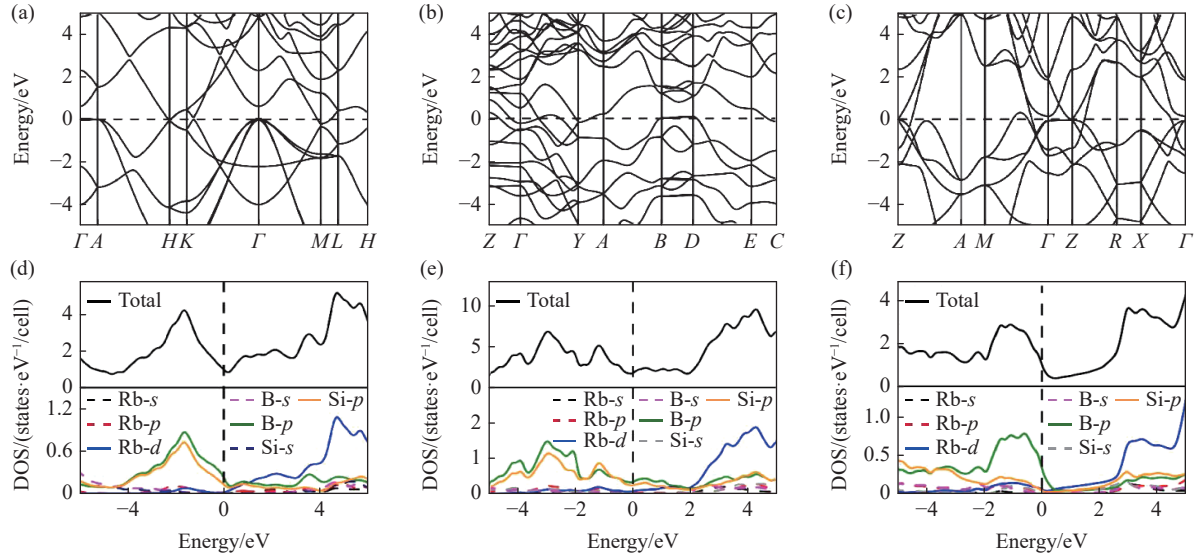


Fig. 4　Calculated band and densities of electronic states of RbBSi: (a) and (d) $P6_3/mmc$ at 10 GPa, (b) and (e) $C2/m$ at 20 GPa, (c) and (f) $P4/nmm$ at 40 GPa

Turning to the phonon and electron-phonon coupling in $P4/nmm$-RbBSi, the calculated phonon dispersion results are shown in Fig. 5. No imaginary phonon modes are present in the entire Brillouin zone, indicating the dynamic stability of this crystal structure. We then computed the Eliashberg spectral function $\alpha^2F(\omega)$, where α represents the electron-phonon interaction strength and ω represents the frequency. The overall isotropic electron-

phonon coupling parameter λ can be obtained via a simple integration in the frequency domain. λ is 0.84, which is quite large for phonon-mediated superconductors. These calculations suggest that $P4/nmm$-RbBSi is a superconductor with T_c of 14.4 K at standard atmospheric pressures. The superconducting transition temperature is reduced to 0 K at 40 GPa.

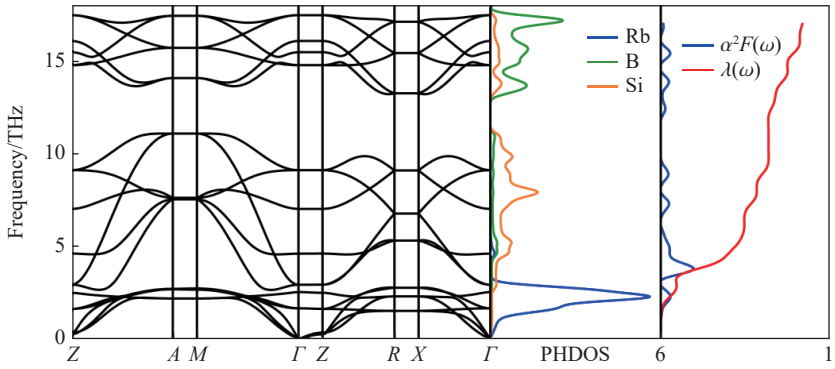


Fig. 5　Calculated phonon dispersions, projected phonon density of states and Eliashberg spectral function $\alpha^2F(\omega)$ of the $P4/nmm$-RbBSi at standard atmospheric pressure

In addition, it was found that $P6_3/mmc$-RbBSi also exhibits superconducting properties, and the superconducting transition temperature under standard atmospheric pressure is 5.2 K. Its λ is 0.50. However, its superconducting transition temperature is reduced to 3.3 K at 10 GPa, and the corresponding λ is 0.44.

3　Conclusions

In summary, we have extensively explored the RbBSi within the pressure range of 0−100 GPa using CALYPSO method. It is found that RbBSi has three thermodynamically stable phases, denoted as $P6_3/mmc$-, $C2/m$-, $P4/nmm$-RbBSi. All the phases studied are dynamically stable in the pressure ranges of 0−10 GPa, 0−20 GPa and 0−40 GPa, respectively. Based on our calculations of formation enthalpy and density of electronic states, it is shown that these structures exhibit metallic properties. Electron-phonon calculations predicted that $P4/nmm$-RbBSi would be a superconductor with T_c of 14.4 K at standard atmospheric pressures. Our current findings predict a superconductor with synthetic potential, which provides a driving force for further research and development of superconducting materials.

References:

[1] LARBALESTIER D, CANFIELD P C. Superconductivity at 100—where we've been and where we're going [J]. MRS Bulletin, 2011, 36(8): 590–593.

[2] ANLAGE S M. The physics and applications of superconducting metamaterials [J]. Journal of Optics, 2011, 13(2): 024001.

[3] HASSENZAHL W V, HAZELTON D W, JOHNSON B K, et al. Electric power applications of superconductivity [J]. Proceedings of the IEEE, 2004, 92(10): 1655–1674.

[4] GREENBERG Y S. Application of superconducting quantum interference devices to nuclear magnetic resonance [J]. Reviews of Modern Physics, 1998, 70(1): 175–222.

[5] MA L, WANG K, XIE Y, et al. High-temperature superconducting phase in clathrate calcium hydride CaH_6 up to 215 K at a pressure of 172 GPa [J]. Physical Review Letters, 2022, 128(16): 167001.

[6] JEON H, WANG C Z, LIU S Y, et al. Electron-phonon coupling and superconductivity in an alkaline earth hydride CaH_6 at high pressures [J]. New Journal of Physics, 2022, 24(8): 083048.

[7] QIAN S F, SHENG X W, YAN X Z, et al. Theoretical study of stability and superconductivity of ScH_n (n=4–8) at high pressure [J].

Physical Review B, 2017, 96(9): 094513.

[8] TROYAN I A, SEMENOK D V, KVASHNIN A G, et al. Anomalous high-temperature superconductivity in YH_6 [J]. Advanced Materials, 2021, 33(15): 2006832.

[9] MA L, WANG K, XIE Y, et al. High-T_c superconductivity in clathrate calcium hydride CaH_6 [EB/OL]. arXiv: 2103.16282, (2021-11-04)[2023-10-24]. https://arxiv.org/abs/2103.16282.

[10] WANG H, TSE J S, TANAKA K, et al. Superconductive sodalite-like clathrate calcium hydride at high pressures [J]. Proceedings of the National Academy of Sciences of the United States of America, 2012, 109(17): 6463–6466.

[11] DROZDOV A P, KONG P P, MINKOV V S, et al. Superconductivity at 250 K in lanthanum hydride under high pressures [J]. Nature, 2019, 569(7757): 528–531.

[12] SOMAYAZULU M, AHART M, MISHRA A K, et al. Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressures [J]. Physical Review Letters, 2019, 122(2): 027001.

[13] LIU H Y, NAUMOV I I, GEBALLE Z M, et al. Dynamics and superconductivity in compressed lanthanum superhydride [J]. Physical Review B, 2018, 98(10): 100102.

[14] LU S Y, LIU H Y, NAUMOV I I, et al. Superconductivity in dense carbon-based materials [J]. Physical Review B, 2016, 93(10): 104509.

[15] SANO K, MASUDA Y, ITO H. Superconductivity of carbon compounds with sodalite structure [J]. Journal of the Physical Society of Japan, 2022, 91(8): 083703.

[16] LI X, YONG X, WU M, et al. Hard BN clathrate superconductors [J]. The Journal of Physical Chemistry Letters, 2019, 10(10): 2554–2560.

[17] ZHU L, STROBEL T A, COHEN R E. Prediction of an extended ferroelectric clathrate [J]. Physical Review Letters, 2020, 125(12): 127601.

[18] CUI X Y, HILLEKE K P, WANG X Y, et al. RbB_3Si_3: an alkali metal borosilicide that is metastable and superconducting at 1 atm [J]. The Journal of Physical Chemistry C, 2020, 124(27): 14826–14831.

[19] ZIPOLI F, BERNASCONI M, BENEDEK G. Electron-phonon coupling in halogen-doped carbon clathrates from first principles [J]. Physical Review B, 2006, 74(20): 205408.

[20] ZHU L, BORSTAD G M, LIU H Y, et al. Carbon-boron clathrates as a new class of sp^3-bonded framework materials [J]. Science Advances, 2020, 6(2): eaay8361.

[21] ZHANG P Y, LI X, YANG X, et al. Path to high-T_c superconductivity via Rb substitution of guest metal atoms in the SrB_3C_3 clathrate [J]. Physical Review B, 2022, 105(9): 094503.

[22] WANG J N, YAN X W, GAO M. High-temperature superconductivity in SrB_3C_3 and BaB_3C_3 predicted from first-principles anisotropic Migdal-Eliashberg theory [J]. Physical Review B, 2021, 103(14): 144515.

[23] KIEFER F, KARTTUNEN A J, DOBLINGER M, et al. Bulk synthesis and structure of a microcrystalline allotrope of germanium (*m-allo*-Ge) [J]. Chemistry of Materials, 2011, 23(20): 4578–4586.

[24] ZHANG H J, REN J D, WU L L, et al. Predicted semiconductor to metal transition from $LiBSi_2$ to $RbBSi_2$ by first-principles calculations [J]. Computational Materials Science, 2016, 124: 267–272.

[25] KARTTUNEN A J, FÄSSLER T F, LINNOLAHTI M, et al. Structural principles of semiconducting group 14 clathrate frameworks [J]. Inorganic Chemistry, 2011, 50(5): 1733–1742.

[26] YAN H Y, CHEN L, WEI Z T, et al. Superhard high-pressure structures of beryllium diborocarbides [J]. Vacuum, 2020, 180: 109617.

[27] LAZICKI A, YOO C S, CYNN H, et al. Search for superconductivity in LiBC at high pressure: diamond anvil cell experiments and first-principles calculations [J]. Physical Review B, 2007, 75(5): 054507.

[28] WANG Y C, LV J, ZHU L, et al. Crystal structure prediction via particle-swarm optimization [J]. Physical Review B, 2010, 82(9): 094116.

[29] WANG Y C, LV J, ZHU L, et al. CALYPSO: a method for crystal structure prediction [J]. Computer Physics Communications, 2012, 183(10): 2063–2070.

[30] KRESSE G, FURTHMÜLLER J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set [J]. Physical Review B, 1996, 54(16): 11169–11186.

[31] PERDEW J P, CHEVARY J A, VOSKO S H, et al. Atoms, molecules, solids, and surfaces: applications of the generalized

gradient approximation for exchange and correlation [J]. Physical Review B, 1992, 46(11): 6671–6687.

[32] KRESSE G, JOUBERT D. From ultrasoft pseudopotentials to the projector augmented-wave method [J]. Physical Review B, 1999, 59(3): 1758–1775.

[33] TOGO A, OBA F, TANAKA I. First-principles calculations of the ferroelastic transition between rutile-type and $CaCl_2$-type SiO_2 at high pressures [J]. Physical Review B, 2008, 78(13): 134106.

[34] GIANNOZZI P, BARONI S, BONINI N, et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials [J]. Journal of Physics:Condensed Matter, 2009, 21(39): 395502.

[35] DEGTYAREVA O. Crystal structure of simple metals at high pressures [J]. High Pressure Research, 2010, 30(3): 343–371.

[36] OGANOV A R, SOLOZHENKO V L, GATTI C, et al. The high-pressure phase of boron, γ-B_{28}: disputes and conclusions of 5 years after discovery [J]. Journal of Superhard Materials, 2011, 33(6): 363–379.

[37] CUI X Y, ZHANG M, GAO L L. Exploration of AB_3Si_3 (A=Na/K/Rb/Cs) compounds under moderate pressure [J]. Physical Chemistry Chemical Physics, 2023, 25(35): 23847–23854.

压力下超导 RbBSi 化合物的预测

刘金禹[1], 崔湘粤[2], 刘爱玲[1], 程潇冉[1], 王星宇[1], 王雨佳[1], 张　淼[1]

（1. 北华大学理学院物理系, 吉林 吉林　132013；
2. 澳门大学应用物理与材料工程学院教育部联合重点实验室, 澳门 氹仔岛　999078）

摘要：对 RbBSi 化合物在 0～100 GPa 压力范围内进行了广泛的群体智能结构搜索。提出了 RbBSi 的 3 种不同相，并通过第一性原理计算了其稳定性、电子结构和潜在的超导电性。在所研究的压力范围内，所有预测相在热力学和动力学上都是稳定的。3 个相的能带都穿过费米能级，表明结构具备金属性。此外，*P*4/*nmm*-RbBSi 在常压下的超导转变温度为 14.4 K。这项工作加深了人们对碱金属硼硅化合物在超导体领域的理解，有望拓宽碱金属硼硅化合物在超导体领域的应用。

关键词：第一性原理计算；高压；碱金属硼硅化物；晶体结构预测

中图分类号：O521　　**文献标志码：**A