Rich stoichiometries of stable Ca-Bi system: Structure prediction and superconductivity

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Using a variable-composition ab initio evolutionary algorithm implemented in the USPEX code, we have performed a systematic search for stable compounds in the Ca-Bi system at different pressures. In addition to the well-known tI12-Ca2Bi and oS12-CaBi2, a few more structures were found by our calculations, among which phase transitions were also predicted in Ca2Bi (tI12 → oI12 → hP6), Ca3Bi2 (hP5 → mC20 → aP5) and CaBi (tI2 → tI8), as well as a new phase (Ca3Bi) with a cF4 structure. All the newly predicted structures can be both dynamically and thermodynamically stable with increasing pressure. The superconductive properties of cF4-CaBi3, tI2-CaBi and cF4-Ca3Bi were studied and the superconducting critical temperature $T_c$ can be as high as 5.16, 2.27 and 5.25 K, respectively. Different superconductivity behaviors with pressure increasing have been observed by further investigations.

Superconductivity has been deeply studied and developed very quickly since its discovery in 1911, but its origin remains enigmatic. The copper oxide family is of enduring interest for initiating energetic activities of high-temperature superconductivity1,2 and has been applied in a variety of fields. The discovery of the iron-based superconductors3, which is unconventional, has attracted great attention and aroused extensive research with the intention of finding new superconductors. Iron-based superconductors have been extended to various material groups, such as the so called 11114,5,12,25,11 116,117 compounds, etc. Moreover, it is observed that compounds in which iron is completely substituted by other 3d, 4d, or 5d transition metals8,9, exhibit superconductivity. Since a large variety of phosphide, arsenide and antimonide superconductors have been found, attention is now focusing on bismuthides and related pnictide systems. So bismuth has been a part of various superconducting compounds, such as NiBi310, Bi2O2S11,12, CsBi2Te613 and LaO1-xFxBiS214. Recently, Sturza et al. reported a new complex alkaline earth intermetallic compound superconductor Ca111Bi10.8 with $T_c \sim 2.2$ K, which stimulates our interests to find new superconductors in the Ca-Bi system.

A large number of BCS superconductors have been theoretically proposed16-18 as the development of computational crystal structure prediction tools19,20 and methods. In this paper, we perform a systematic search for thermodynamically stable calcium bismuth at ambient and high pressure by using the variable-composition ab initio evolutionary algorithm21-23 and density functional theory (DFT). Here we predict several new structures at different pressures that were never reported, and discuss their structures, electronic structures and superconductivity properties of the selected structures.

Results

Crystal structure and structural properties of calcium bismuthides. Some reported experimental crystal structures in the Ca-Bi system are summarized by H. Kim et. al.24 and other similar Sr-Bi compounds have also been studied by first-principles calculations25. In this paper, we use the variable-composition evolutionary algorithm, which is very effective, to predict stable compositions and their structures. We have performed structure searches with up to 16 atoms in the unit cell at different pressures for the Ca-Bi system of all possible compositions.

Fig. 1 shows the enthalpies of formation of the predicted structures. At ambient pressure, it can be clearly seen that there are three stable structures on the convex hull, i.e., tI12-Ca2Bi (Fig. 2a), hP5-Ca3Bi2 (Fig. 2b) and oS12-CaBi2 (Fig. 2c). The previously reported oP32-Ca2Bi326 and tI84-Ca11Bi1027, although not found by our prediction possibly limited by the computational resources, are also on the convex hull, suggesting that they are thermo-
dynamically stable. However, these two structures lie above the convex hull curve at 0 GPa, which implies that they will become meta-stable phases under high-pressure conditions.

The Ca$_3$Bi$_2$ phase has been reported in the literature without structural information. Our prediction indicates that it has a hexagonal structure of the La$_2$O$_3$ type, and belongs to the space group of $P3m$ (164), with Pearson symbol hP5. Our calculations reveal that Ca$_3$Bi$_2$ undergoes a series phase transitions, i.e., from hP5 to mC20 (space group $C2/m$, 12) at 4 GPa and mC20 to oP5 (space group $R3m$ 166) at about 59 GPa. The calculated phonon dispersion of hP5-Ca$_3$Bi$_2$ indicates that the phonon mode along the $A$-H direction is imaginary at 0 GPa, and it will be dynamically stable at high pressure, which can be seen in Fig. 3 (further study shows that the imaginary phonon mode along the $A$-H direction will disappear at above 0.5 ~ 0.6 GPa, which can be seen in Figure S1). We also observed a high-pressure phase transition in Ca$_3$Bi$_2$, which is from $t12$ to $o12$ (space group $I4/mmm$, 139) to $o12$ (space group $Cmmm$, 65) at 14 GPa and from $o12$ to $hP6$ (space group $P6_3/mmc$, 194) at 33GPa. For CaBi$_3$, we predict an oS12 structure (space group $Pmcm$, 63) with lattice constants $a = 4.738$ Å, $b = 17.160$ Å, $c = 4.598$ Å at 0 GPa compared with the previously reported $a = 4.701$ Å, $b = 17.053$ Å, $c = 4.613$ Å$^{29}$, which lies on the convex hull at ambient and high pressure, and is both dynamically and thermodynamically stable.

The previously reported Ca-Bi phase diagrams$^{26}$ mentioned two phases, CaBi$_3$ and CaBi, without structural information. This work suggests a cubic $cF4$ structure for CaBi$_3$ (space group $Pm3m$, 221) and a tetragonal $t12$ structure for CaBi (space group $P4/mmm$, 123), which are thermodynamically unstable at ambient pressure and can be stable at high pressure. The $cF4$-CaBi$_3$ is very close to the convex hull curve but lies a little above it. In addition, another tetragonal $t12$ structure of CaBi (space group $I4/macd$, 141) was also predicted, which is proved to be thermodynamically more stable at above 45 GPa. Besides, our research also predicted a new phase of Ca-Bi system, i.e., $cF4$-Ca$_2$Bi, the space group of which is the same with $cF4$-CaBi$_3$ and can be thermodynamically stable at high pressure. In $cF4$-Ca$_2$Bi, the Ca and Bi atoms occupy Wyckoff 3c and 1a positions, respectively. However, the situation of the occupancy is just the opposite in $cF4$-CaBi$_3$, which can be seen in Figs. 2d and 2e. The structural parameters for the predicted structures are listed in Table 1.

**Electronic structures.** We calculated the band structures and density of states of all the predicted structures. All the calcium bismuthides are metallic except for the $hP5$-Ca$_3$Bi$_2$ structure, which is semiconductive at 0 GPa, with a narrow band gap of 0.42 eV and becomes metallic at around 20 GPa. Through the calculations we can conclude that the ratio of Ca and Bi will affect their contributions to the DOS at the Fermi level ($E_F$). For example, if a calcium rich structure of Ca$_3$Bi$_{1.5}$, i.e., $x > 0.5$, the density of states at $E_F$ comes mainly from the calcium atoms, in particular Ca $d$ states and bismuth $p$ orbital contributes most to bismuth states. On the contrary, the density of states at $E_F$ comes mainly from the bismuth atoms in a bismuth rich structure, in particular Bi $p$ states, and calcium $d$ orbital contributes most to calcium states at the Fermi level. Fig. 4 shows the band structures and DOS of the $cF4$-Ca$_3$Bi and $cF4$-CaBi$_3$ structures. The density of states at $E_F$ of these two structures is 0.32 and 0.20 states/eV, respectively. A careful examination of the band structures show multiple steep bands crossing the Fermi level as well as flat bands, which is considered to be a necessary condition for superconductivity to occur$^{34}$. As bismuth based materials may have strong spin-orbital coupling (SOC) effect$^{23}$, the electronic structures of $cF4$-Ca$_3$Bi and $cF4$-CaBi$_3$ have been calculated by including the SOC effect and compared with those without SOC effect, as shown in Figure S2 and S3.

**Superconductivity properties.** The superconductivity of the selected structures can be conveniently studied by EPC calculation. The calculated Eliashberg spectral function and the electron-phonon coupling strength $\lambda$ are shown in Fig. 5 for $cF4$-Ca$_3$Bi and $cF4$-CaBi$_3$ at 60 and 30 GPa, respectively. The superconducting critical temperature can be estimated from the Allen-Dynes modified McMillan equation$^{34}$

$$T_C = \frac{\Theta_D}{1.2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right),$$

(1)

where the electron-phonon coupling constant is calculated as
Figure 2 | Crystal structures for (a): t112-Ca2Bi, (b): hP5-Ca3Bi2, (c): oS12-CaBi2, (d): cF4-Ca3Bi and (e): cF4-CaBi3.

Figure 3 | Phonon dispersion curves for the hP5-Ca3Bi2 at 0 GPa and 5 GPa.
Table 1 | Crystal parameters for the predicted structures

| Compound | Space group | Pearson symbol | Lattice constants (Å) | Atom position (Wyckoff position) |
|----------|-------------|----------------|-----------------------|----------------------------------|
| Ca₂Bi   | Cmcm        | oS             | a = 4.851 Å, b = 5.13 Å, c = 16.496 Å, α = 4.572 Å | Ca (4a) [0.0, 0.5, 0.0], Bi (4c) [0.5, 0.5, 0.0] |
| Ca₂Bi₂  | Cmcm        | oS             | a = 5.3150 Å, b = 4.782 Å, c = 4.598 Å | Ca (4a) [0.0, 0.5, 0.0], Bi (4c) [0.5, 0.5, 0.0] |
| Ca₂Bi₃  | Cmcm        | oS             | a = 3.786 Å, b = 4.355 Å, c = 11.56 Å | Ca (4a) [0.0, 0.5, 0.0], Bi (4c) [0.5, 0.5, 0.0] |
| Ca₃Bi   | Cmcm        | oS             | a = 4.998 Å | Ca (4a) [0.0, 0.5, 0.0], Bi (4c) [0.5, 0.5, 0.0] |

\[ \lambda = 2 \int_0^\infty \frac{x^2 F(\omega)}{\omega} d\omega, \]  
(2)

the logarithmic frequency average is

\[ \omega_{\log} = \exp \left( \frac{2}{\lambda} \int_0^\infty \log \frac{x^2 F(\omega)}{\omega} d\omega \right). \]  
(3)

Our calculations suggest that cF₄-Ca₃Bi shows no superconductivity behavior below 25 GPa. Its superconducting transition temperature rises as the pressure increases. The dynamic instability of cF₄-Ca₃Bi is confirmed as the phonon spectrum displays imaginary frequencies above 60 GPa, at which we predict that cF₄-Ca₃Bi will be a superconductor with a \( T_c \) of 5.25 K, total \( \lambda \) of 0.96 and \( \omega_{\log} \) of 146.1 cm⁻¹. 72% of the total \( \lambda \) results from modes below 140 cm⁻¹, which are mainly displacements of bismuth atoms. The decomposition of the phonon density of states into contributions from the atoms (Fig. 5a) shows that the calcium atoms (below 140 cm⁻¹) has a slight contribution to the electron-phonon coupling in this compound. On the contrary, cF₄-CaBi₃ can be a superconductor at 0 GPa with a \( T_c \) of 5.16 K, total \( \lambda \) of 1.23 and \( \omega_{\log} \) of 56.2 cm⁻¹, which will accordingly turn into 0.61 K, 0.41 and 127.8 cm⁻¹ at 30 GPa. 84% of the total \( \lambda \) results from modes below 125 cm⁻¹, which are mainly displacements of bismuth atoms, the same with cF₄-Ca₃Bi. A further study of the phonon density of states of cF₄-CaBi₃ indicates that the calcium atoms (below 180 cm⁻¹) has a negligible contribution to the electron-phonon coupling in this compound (Fig. 5b). The calculated \( \lambda, \omega_{\log} \) and \( T_c \) at different pressure for cF₄-Ca₃Bi and cF₄-CaBi₃ are listed in Table 2 and Table 3.

Figure 4 | Band structure and partial density of states for cF₄-Ca₃Bi and cF₄-CaBi₃.
respectively. The $tI_2$-CaBi exhibits different superconductivity behavior through a brief study of our calculation as the $T_c$ will reach a maximum value of 2.27 K at around 10 GPa, as is shown in Fig. 6. A further analysis of the result shows that bismuth phonon mode is thought to play a large role in the superconductivity of $cF_4$-Ca$_3$Bi and $cF_4$-CaBi$_3$.

**Discussion**

In summary, by using the variable-composition evolutionary algorithm, we performed a systematic search for all possible compositions in the Ca-Bi system at different pressures. Except the previously reported $oP_{32}$-Ca$_5$Bi$_3$ and $tI_{84}$-Ca$_{11}$Bi$_{10}$, we found 10 novel structures either totally unreported or only mentioned but no detailed information. In addition, we predicted a series of phase transitions in Ca$_2$Bi, Ca$_3$Bi$_2$ and CaBi$_3$ and also one stoichiometry (Ca$_3$Bi$_2$) with a $cF_4$ structure. All the newly predicted structures can be both dynamically and thermodynamically stable as the pressure increases. Based on conventional BCS theory, $cF_4$-CaBi$_3$ is superconductor with a $T_c$ of 5.16 K at 0 GPa and will drop with pressure increases. While $cF_4$-Ca$_3$Bi shows no superconductive behavior below 25 GPa and the $T_c$ value is enhanced with increasing pressure and reaches 5.25 K at 60 GPa. Compared to the above, $tI_2$-CaBi is much different as the $T_c$ will reach a maximum value of 2.27 K at around 10 GPa. The newly predicted structures of calcium bismuthides and superconductivity behavior of $cF_4$-CaBi$_3$, $tI_2$-CaBi and $cF_4$-Ca$_3$Bi would stimulate further experimental and theoretical studies on alkaline earth metal bismuthides and pnictide.

**Methods**

We used the evolutionary algorithm USPEX to search for low-enthalpy stable structures as implemented in the USPEX code $^{35,36}$, which has been widely used to predict stable high-pressure crystal structures without requiring any experimental information. The underlying structural relaxations and electronic structure calculations of Ca-Bi over a wide range of the pressure presented here were performed within the density functional theory (DFT), using the all electron projector augmented wave (PAW) method$^{15}$ as implemented in the Vienna $ab$ initio simulation package (VASP)$^{16}$. The 3s$^2$3p$^4$4s$^2$ and 5d$^10$6s$^2$6p$^3$ electrons are treated as valence electrons for Ca and Bi atoms,

![Table 2](image1.png)

| Pressure(GPa) | $\lambda$ | $\omega_{\text{log}}$(cm$^{-1}$) | $T_c$(K) |
|--------------|-----------|-------------------------------|----------|
| 30           | 0.24      | 236.4                         | 0.01     |
| 40           | 0.33      | 228.3                         | 0.24     |
| 50           | 0.47      | 197.9                         | 1.08     |
| 60           | 0.96      | 146.1                         | 5.25     |

![Table 3](image2.png)

| Pressure(GPa) | $\lambda$ | $\omega_{\text{log}}$(cm$^{-1}$) | $T_c$(K) |
|--------------|-----------|-------------------------------|----------|
| 0            | 1.23      | 56.2                          | 5.16     |
| 10           | 0.65      | 88.0                          | 2.55     |
| 20           | 0.49      | 110.9                         | 1.24     |
| 30           | 0.41      | 127.8                         | 0.61     |
respectively. The exchange-correlation energy was treated within the generalized gradient approximation (GGA), using the functional of Perdew-Burke-Ernzerhof \(^39\) for both Ca and Bi. A plane-wave cutoff energy of 500 eV and dense Monkhorst-Pack \(^{40}\) k-point meshes \(^{48}\) with the reciprocal space resolution of \(2\pi \times 0.03 \text{ Å}^{-1}\) were used for all structures to ensure that the enthalpy calculations are converged to better than 1 meV/atom.

The calculation of electron-phonon coupling (EPC) parameter \(\lambda\) are performed using the pseudopotential plane-wave method within the density functional perturbation theory (DFPT) as implemented in the Quantum ESPRESSO package \(^{41}\) using Martins Troullier-type norm-conserving pseudopotential with cutoff energies of 80 and 360 Ry for the wave functions and the charge density, respectively. In order to interpolate the interatomic force constant matrix for the phonon dispersions, \(4 \times 4 \times 4 \times 4 \times 4 \times 4\) and \(4 \times 4 \times 4\) \(\times 3\)-meshes in the first Brillouin zone (BZ) were used for interpolation for \(\text{F}_4\text{CaBi}, \text{F}_4\text{Ca-Bi}\) and \(\text{I}_2\text{CaBi}\), respectively. The denser \(24 \times 24 \times 24 \times 24 \times 24 \times 24\) grids were sufficient to ensure the convergence needed for the EPC calculations for the three calcium bismuthides, respectively.

To ensure the dynamical stability of the newly predicted structures, the phonon dispersion curves were calculated throughout the Brillouin zone using the finite-displacement approach as implemented in the PHONOPY code \(^{29}\).

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**Figure 6** The calculated logarithmic average phonon frequency (\(\omega_{\text{avg}}\)) EPC (\(\lambda\)) and critical temperature \(T_c\) for \(\text{tI}_2\text{-CaBi}\) as a function of pressure. (1994)

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**Acknowledgments**

This work was supported by the Research Foundation of Education Bureau of Hebei Province (2012013039), the Natural Science Foundation of Hebei Province (E2014203243) and the NSFC (Grant No. 51121061), which is gratefully acknowledged.

**Author contributions**

C.Z.F. conceived the idea. X.D. performed the ab initio evolutionary simulations and the superconductivity properties calculations. C.Z.F. and X.D. wrote the manuscript.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Dong, X. & Fan, C. Rich stoichiometries of stable Ca-Bi system: Structure prediction and superconductivity. *Sci. Rep.* **5**, 9326; DOI:10.1038/srep09326 (2015).
