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Tetragonal Allotrope of Group 14 Elements

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Supporting Information

ABSTRACT: Group 14 elements (C, Si, and Ge) exist as various stable and metastable allotropes, some of which have been widely applied in industry. The discovery of new allotropes of these elements has long attracted considerable attention; however, the search is far from complete. Here we computationally discovered a tetragonal allotrope (12 atoms/cell, named T12) commonly found in C, Si, and Ge through a particle swarm structural search. The T12 structure employs sp^3 bonding and contains extended helical six-membered rings interconnected by pairs of five- and seven-membered rings. This arrangement results in favorable thermodynamic conditions compared with most other experimentally or theoretically known sp^3 species of group 14 elements. The T12 polymorph naturally accounts for the experimental *d* spacings and Raman spectra of synthesized metastable Ge and Si-XIII phases with long-puzzling unknown structures, respectively. We rationalized an alternative experimental route for the synthesis of the T12 phase via decompression from the high-pressure Si- or Ge-II phase.

Group 14 elements (C, Si, and Ge) have been the subject of extensive theoretical and experimental studies because of their scientific and technological importance.[1] Carbon exists in two natural allotropes, graphite and diamond, which exhibit dramatically different physical properties (e.g., ultrasoft graphite vs the hardest known diamond) because of their different bonding patterns. Both Si and Ge crystallize in a diamond structure under ambient conditions and are among the most important materials widely applied in the semiconductor industry in electronic and photovoltaic devices.

The physical and chemical properties of materials are intimately related to their structures. Scientists have been searching for new allotropes of group 14 elements that may have other important applications. The ability of C, Si, and Ge to form sp-, sp^2-, and sp^3-hybridized chemical bonds has led to the discovery of their various technologically important allotropes under ambient conditions. In particular, carbon fullerenes, nanotubes, graphene, graphyne, and graphdiyne have been successfully synthesized.[2] Various forms of Si and Ge nanotubes, allo phases, clathrates, and silicene have also been fabricated.[3]

Pressure causes profound changes in the chemical bonds of compounds and thus has become an important tool in the search for new materials. Under high pressure, a variety of C allotropes, including one-, two-, and three-dimensional fullerene or nanotube polymers, superhard post-graphite phase, and diamond-like amorphous carbon, have been synthesized experimentally, with some of them quenchable under ambient pressure.[4] High-pressure polymorphs of β-Sn (*Imma*, *sh*, *Cmca*, and *hcp*) have been observed for Si and Ge at elevated pressures.[5] However, these high-pressure phases are not recoverable upon the release of pressure to ambient conditions; instead, other tetrahedrally bonded metastable phases are stabilized. The formation of the metastable phases depends on the decompression rate. Metastable Si-XII (R8), Si-III (BC8), and Ge-III (ST12) phases can be achieved by slowly releasing the pressure from the high-pressure β-Sn phases of Si and Ge (Si-II or Ge-II).[6] However, rapid depressurization results in the formation of the Ge-IV (BC8) phase as well as the structurally unknown tetragonal Si-VIII/IX phases.[7] When metastable Si-III/XII is heated at ambient pressure, the intermediate Si-XIII is formed, but its structure remains unknown.[8]

Extensive theoretical structure predictions have been performed to search for new polymorphs or to understand structurally unknown phases of C under high pressure. Two C models, Cco-C_8 and *P*-carbon, have been proposed to account for a quenched product recovered from cold-compressed nanotube bundles.[9] Other C models such as *M*-carbon, Bct-C_4, *W*-carbon, *Z*-carbon (or so-called *o*C16-II, *Z*-carbon-8, and Cco-C_8), *F*-carbon (or so-called *S*-carbon, *Z*-carbon-1, and *M*10-carbon), *O*-carbon (or so-called *R*-carbon and *H*-carbon), Z4-A3B1 (or so-called *P*-carbon), *C*-carbon, *X*-carbon, and *Y*-carbon have been proposed to account for the experimentally observed post-graphite superhard phase.[9,10] In addition, other theoretical carbon structures, including chiral C_6 and the three superdense carbons *h*P3, *t*I12, and *t*P12, were also proposed.[11]

To date, theoretical structural investigations on unknown Si and Ge metastable phases[7,8,12] remain scarce. The recent structure model on the interpretation of the structurally unknown tetragonal Si-IX phase is encouraging,[13] but structural studies on other allotropes have yielded no significant results. In this study, we employed our crystal structure analysis by particle swarm optimization (CALYPSO) code[14] to search low-energy structures for C, Si, and Ge. This method is specially designed to predict the stable structures of given compounds with known chemical compositions and has generated several

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successful applications.[15] Though metastable structures can also be explored by our method, mathematically there is no guarantee on the success rate. We here report the theoretical discovery of a tetragonal sp^3 allotrope (12 atoms/cell, named T12) with extended helical six-membered rings interconnected by pairs of five- and seven-membered rings that commonly exists in C, Si, and Ge and has favorable thermodynamic conditions relative to most experimentally or theoretically known sp^3 structures of group 14 elements. The T12 polymorph can naturally account for the experimental d spacings and Raman data for the structurally unknown metastable Ge[12] and Si-XIII phases,[8] respectively.

Our crystal structure predictions for C, Si, and Ge using CALYPSO[14] were performed with simulation cell sizes of up to 30 atoms at pressures of 0–20 GPa. Underlying structural relaxations were performed using density functional theory (DFT) within the local density approximation (LDA), as implemented in the Vienna Ab Initio Simulation Package (VASP).[16] The subsequent structural optimizations and property predictions were performed using ultrasoft pseudopotentials in the Cambridge Serial Total Energy Package (CASTEP).[17] Plane-wave cutoff energies of 310, 180, and 200 eV were used for C, Si, and Ge, respectively. The electron–electron exchange interaction was described using the exchange–correlation functional of Ceperley and Alder, as parametrized by Perdew and Zunger (CA-PZ), in the LDA.[18] A k-point spacing of $2\pi \times 0.04$ Å^{-1} was used to generate the k-point grid within the Monkhorst–Pack scheme.[19] The phonon frequencies were calculated using linear response theory.[20] The phase transition paths were simulated using the variable-cell nudged elastic band (VC-NEB) method.[10c]

Our structure prediction reproduced a number of previously known experimental and theoretical structures, thereby validating our structural search methodology. In particular, we correctly predicted the structures of graphite, diamond, lonsdaleite, nanotubes, 3D nanotube polymers, M-carbon, W-carbon, F-carbon, Bct-C_4, and Cco-C_8 allotropes of C[9,10] as well as the diamond, lonsdaleite, BC8, and ST12 structures of Si and Ge.[6,7,21] In addition, we uncovered an exotic tetragonal structure, T12 (Figure 1), that is commonly exhibited by C, Si, and Ge. This structure (Figure 1b) adopts fully sp^3-hybridized bonding patterns and can be seen as extended helical six-membered rings interconnected through buckled five- and seven-membered rings with five distorted bond angles (102.7°, 105.5°, 108.6°, 109.4°, and 111.3°) that slightly deviate from the angle of 109.5° in the diamond structure. The helical six-membered rings are very unique, dramatically distinct from those of the recently proposed structural models for the understanding of cold-compressed superhard graphite.[9,10] There, though six-membered rings also exist, they extend along the wrinkled graphene layers.[9,10] The dynamical stabilities of the T12 structures of C, Si, and Ge at ambient pressure were examined by explicitly calculating their phonon dispersion spectra (Figure S1 in the Supporting Information). No imaginary frequencies in the Brillouin zone were found for any of these phases.

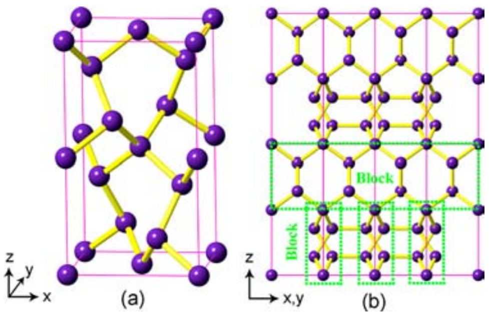

Figure 1. Crystal structure of the T12 phase: (a) 3D view; (b) view along the (110) crystal plane. The T12 structure adopts a $P42/ncm$ space group (No. 138) and contains 12 atoms/cell, wherein atoms occupy the 4b (0, 1, 0.5) and 8i (−0.164, 0.336, 0.357) positions. At ambient pressure, the optimized structural parameters are a = 3.388 Å and c = 6.011 Å for C, a = 5.135 Å and c = 9.167 Å for Si, and a = 5.292 Å and c = 9.346 Å for Ge. The green blocks indicate the wrinkled six-membered rings.

The T12 structure is energetically favorable compared with most known experimental and theoretical structures of C, Si, and Ge under ambient conditions. Figure 2 shows plots of the calculated enthalpies for the different structures against pressure. The T12 structure of C becomes preferable to graphite above 8.5 GPa and is more stable than most earlier theoretical structures (Figure 2a).[9,10] For Si (Figure 2b) and Ge (Figure 2c), the T12 phase is less stable than the diamond and lonsdaleite structures but more favorable than other experimentally synthesized allotropes below 3.7 GPa for Si and 4.5 GPa for Ge.[3,6,7,22] The structural data for various metastable C, Si, and Ge phases at ambient pressure are listed in Tables S1 and S2. The calculated band gap results indicate that T12-structured C, Si, and Ge are semiconductors with indirect band gaps ranging from 3.59 to 0.41 eV (Figure S2 and Table S3). Because DFT systematically underestimates the band gap by 30–40%, the actual band gaps are expected to be larger. Originating from the full sp^3 bonding nature in the T12 structure, the Vickers hardness of the T12-structured C was estimated by our hardness model[23] to have the high value of 94.0 GPa (Table S3), thereby illustrating the superhard nature of the T12 structure.

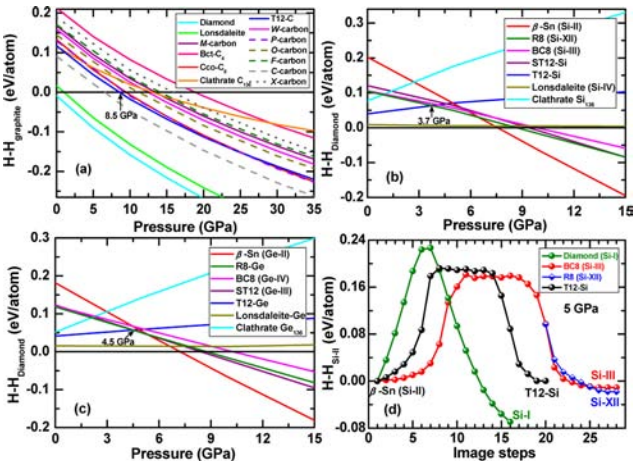

Figure 2. (a–c) Enthalpy vs pressure curves for various (a) C, (b) Si, and (c) Ge allotropes relative to the (a) graphite and (b, c) diamond structures. (d) Transition energy barriers from Si-II to the Si-I, Si-III, Si-XII, and T12 structures at 5 GPa.

With the T12 structure in hand, we explored whether or not this allotrope has already been experimentally synthesized in Si and Ge. By accident, we found that the T12 structure could actually be the structure of an experimentally synthesized metastable Ge phase, the structure of which has remained unsolved for several decades.[12] Two sets of findings support our arguments. First, the calculated lattice parameters of the T12 structure agree well with the a = 5.37 Å and c = 9.04 Å experimental values for the metastable Ge phase. Second, a careful comparison of the calculated T12 d spacings and the observed data for the metastable Ge phase at ambient pressure (Table S4) showed excellent agreement. These findings allow an unambiguous determination of the T12 structure for the unknown Ge metastable phase. It should be noted that this Ge phase was found to show peculiar strong visible photoluminescence at room temperature,[12c] making its optoelectronic applications possible.

Through a long survey of various synthesized Si products with still unknown structures, we established that the T12 structure is a good candidate for the Si-XIII phase.[8] We simulated the Raman spectra of T12-structured Si and compared the results with the experimental data (Figure 3).

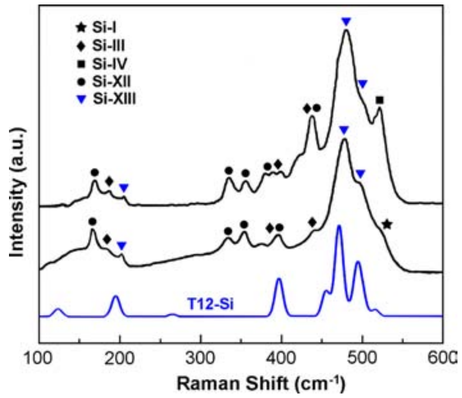

Figure 3. Simulated Raman spectrum of T12-structured Si at ambient pressure (blue) compared with experimental data (black).[8] The peaks associated with Si-I, Si-III, Si-IV, Si-XII, and Si-XIII are labeled.[8,24]

The Si-XIII phase experimentally coexists with several other Si polytypes, such as Si-I (diamond), Si-III, Si-IV (lonsdaleite), and Si-XII. In particular, the Raman peaks at 520 cm^{-1} (★) and 510 cm^{-1} (■) were assigned to Si-I and Si-IV, respectively, and peaks labeled with ◆ and ● were ascribed to Si-III and Si-XII. The latter two phases have similar structures, thereby resulting in very similar vibrational frequencies. In addition to these identified peaks, three new Raman peaks at 200, 475, and 497 cm^{-1} (blue ▼) are the characteristic modes of Si-XIII.[8] The simulated Raman peaks of the T12 phase at 192, 471, and 494 cm^{-1} are in excellent agreement with the experimental data in terms of the positions and intensities. Furthermore, the calculated d spacing of the T12 structure (3.06 Å) is in excellent agreement with the observed d spacing of Si-XIII (3.1 Å),[8] lending additional support to the validity of the T12 structural model. Therefore, it is not unreasonable to consider that Si-XIII adopts the T12 structure.

The Si-III/VIII/IX/XII, Ge-III/IV, and Ge R8 phases were experimentally synthesized by releasing the pressure on the high-pressure Si- and Ge-II phases at different rates.[6,7,22] These remarkable experimental observations motivated us to determine whether the T12 structure could be synthesized through a similar decompression approach. We then calculated the kinetic transition barriers from Si-II to the different Si structures (Figure 2d); the proposed transition paths are shown in Figures S3−S5. Si-III and Si-XII have similar structures and therefore appear energetically competitive in the transition path, in good accordance with experimental observations.[6] The calculated kinetic barriers from Si-II to Si-I, Si-III/Si-XII, and the T12 structure at 5 GPa are 0.227, 0.181, and 0.192 eV/atom, respectively. Our simulations illustrate the actual low-temperature experimental syntheses of the metastable Si-III and Si-XII phases rather than the thermodynamically more favorable Si-I phase.[6] In addition, our calculations indicate the possibility of recovery of the T12 phase from the Si-II phase. Although the barrier for the Si-II → T12 transition is slightly higher than that for Si-II → Si-III/Si-XII, the appropriate heating procedure may readily promote the transformation to the T12 structure. Notably, the Si-II → Si-I and Ge-II → Ge-I transformations were experimentally observed upon decompression at high temperature (above 400 K).[25]

The group 14 elements C, Si, and Ge are fascinating simply because of their ability to adopt a variety of allotropes, most of which are beyond our imagination. The recent success in the syntheses of two-dimensional graphene, graphyne, graphdiyne, and silicene is remarkable,[2,3] but this points out a matter of fact: it is unpredictable what will be the next star material from group 14 elements. Our current findings provide a hint to future experimental explorations. Moreover, the established zero-temperature phase diagrams in Figure 2 reveal that large energy differences (e.g., ~0.1 eV/atom between the T12 and diamond structures for C and ~0.2 eV/atom between the β-Sn and diamond structures for Si and Ge at ambient pressure) remain open. Other low-energy structures can emerge and fill up these gaps. The experimental syntheses of these low-energy phases are thermodynamically possible, especially if heating is considered.

In summary, the T12 structure, a tetragonal sp^3-bonded structure for the group 14 elements C, Si, and Ge, was discovered theoretically using first-principles structural searches. The T12 structure is energetically more stable than most known experimental or theoretical sp^3 species of group 14 elements and was found to be the long-puzzling structure of the experimentally synthesized metastable Ge and Si-XIII phases. The T12 phase of C has physical properties resembling those of diamond phases (e.g., energy gap, bulk modulus, shear modulus, and Vickers hardness). Our simulations of kinetic transition barriers have allowed the rationalization of an alternative experimental route for the synthesis of the Si and Ge T12 phases via decompression from the high-pressure Si-II and Ge-II phases.

■ ASSOCIATED CONTENT

S Supporting Information

Detailed calculation method; crystal structure information, electronic properties, and mechanical properties for various C, Si, and Ge allotropes; comparison of the observed d spacings of experimental metastable Ge and the calculated d spacings of the predicted T12 structure; phonon dispersion curves and band structures of T12-structured C, Si, and Ge; and the proposed transition paths. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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