New tetrahedral polymorphs of the group-14 elements

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Abstract. In this short communication we present the main results of an ab initio structural search for new polymorphs of the group-14 elements C, Si, and Ge, with a focus on low-density and energetically favorable $sp^3$-bonded tetrahedral polymorphs which could constitute candidate phases to be synthesized in the laboratory. We propose new orthorhombic and tetragonal polymorphs with enthalpies that are lower or comparable to those of other polymorphs of the group-14 elements that have either been experimentally synthesized or recently proposed as the structure of unknown phases obtained in experiments. The new phases have interesting structural and electronics properties. These include an orthorhombic phase that in Si is found to have a quasi-direct band gap at the zone center of about the right size for optimal photovoltaic applications, and a tetragonal phase with a chiral topology that displays an exotic pentagonal pattern and whose vibrational properties match those of an unknown phase of Si.

1. Introduction

The polymorphism of the technologically relevant group-14 elements carbon, silicon, and germanium has been intensively studied over the years and is still attracting much interest. A number of high pressure phases have been obtained by applying pressure to the cubic diamond ambient forms of silicon and germanium [1] whereas the versatility that stems from the ability of carbon to form $sp$, $sp^2$, and $sp^3$ hybrid bonds has resulted in a variety of synthetic carbon allotropes with a wide range of different structures and properties [2-6]. A number of zero-pressure metastable tetrahedral polymorphs of these materials, with both higher and lower densities than the corresponding diamond phases, have been experimentally observed after release of pressure from the stable high-pressure phases, in nanoindentation experiments or by other synthesis methods which involve the use of high pressure [1,6-8].

In this short conference communication (a fuller account of this study can be found in [9]) we present several energetically favorable and dynamically stable tetrahedral polymorphs of the group-14 elements that have been theoretically obtained by an ab initio random structure search performed within the framework of the density functional theory. These hypothetical structural forms make promising candidate metastable phases with the potential to be synthesized experimentally and have interesting crystallographic and electronics properties, including an
orthorhombic phase with 24 atoms per unit cell that in Si is found to have a quasi-direct band gap at the zone center of about the right size for optimal photovoltaic applications, and a tetragonal phase with 20 atoms per unit cell with a chiral topology that displays an exotic pentagonal pattern.

2. Details of the calculations
All total-energy calculations were performed within the framework of the density functional theory (DFT) whereas the computational searches for low-energy structures were performed using the \textit{ab initio} random structure searching (AIRSS) approach developed by Pickard and Needs [10]. In AIRSS, ensembles of randomly chosen initial structures are relaxed to minima of the energy. This scheme has been successfully used in finding low-energy structures in many systems and the details of the present searches are similar to those reported in previous AIRSS studies [10]. We performed searches for structures with up to 24 atoms per unit cell, using the \textsc{castep} [11] DFT code and the Perdew-Burke-Ernzerhof (PBE) [12] generalized gradient approximation (GGA) to the exchange-correlation (XC) functional in a plane-waves scheme that used ultrasoft pseudopotentials [13] with the outermost four valence electrons of each group-14 atom being treated explicitly and the innermost core electrons considered frozen. Default basis-set kinetic-energy cutoffs (as implemented in the \textsc{castep} package) and convergence parameters were used for a first screening of candidate structures, further relaxing the configurations of interest to a higher level of accuracy, using a $k$-point grid of spacing $2\pi \times 0.03$ Å$^{-1}$ for the Brillouin zone integrations [14].

These structures were then further relaxed to a very high accuracy and exhaustively studied (energetics, vibrational and electronic properties, pressure evolution, as well as the effect of different XC functionals, namely the LSDA and PBEsol [15]) using the Vienna \textit{ab initio} simulation package (\textsc{vasp}) [16], which implements DFT within a projector augmented-wave (PAW) scheme [17], obtaining results in very good agreement with those obtained with \textsc{castep}, which is a useful crosscheck. At this point we also studied the effect of the semicore 3$d$ electrons of Ge on the energetics of the tetrahedral phases that resulted from our study, which was found to be very small. The cutoff in the kinetic energies of the plane wave basis set used in the \textsc{vasp}
calculations with the PBE were 520 eV (C), 320 eV (Si), and 230 eV (Ge, or 375 eV when the 3d electrons were explicitly included), with dense k-point meshes for the integrations within the Brillouin zones of each of the phases (e.g. $8 \times 8 \times 8$ for the Pbam and P4$_12$12 phases, with 24 and 20 atoms per cell, respectively, see below).

All calculations shown here are for hydrostatic conditions and zero temperature, and the small zero-point energy was neglected. Under hydrostatic conditions, the structural optimization was conducted using the calculated forces on the atoms and the stress tensor, and full convergence was considered to have been achieved when the forces were less than 5 meV Å$^{-1}$ and the anisotropy in the diagonal components of the stress tensor was less than 0.1 GPa. For each phase, the calculated total energy, $E$, as a function of volume, $V$, was fitted using a fourth-order Birch-Murnaghan equation of state (EoS) [18] from which the pressure, $p$, and the enthalpy, $H = E + pV$, were obtained, as well as volumes and bulk moduli at equilibrium. Phonon frequencies were calculated within the finite displacement supercell method using the PHON code [19]. The phonon band structures were used to investigate the dynamical stability of the new phases.

![Figure 2](image1.png) **Figure 2.** Energy-volume curves for several selected phases of Si, with the different symbols corresponding to our calculated $E$-$V$ values using VASP and the PBE. The novel phases discussed in the main text are shown in thicker line and solid symbols. The meaning of each curve’s label is given in the main text.

![Figure 3](image2.png) **Figure 3.** Energy-volume curves for several selected phases of Ge, with the different symbols corresponding to our calculated $E$-$V$ values using VASP and the PBE. The novel phases discussed in the main text are shown in thicker line and solid symbols. The meaning of each curve’s label is given in the main text.

### 3. Results and discussion

Figures 1-3 show the calculated energy-volume ($E$-$V$) curves for a selection of structural phases of C, Si, and Ge, respectively. In these figures we have used standard abbreviations for well known phases (see for example Ref. [1]) whereas we have followed the standard practice of using the space group symbol for denoting the novel tetrahedral phases. In this brief account we will summarily comment on several of these novel phases and direct the reader to Ref. [9] for a fuller report of our study. Among the well known phases included in Figures 1-3 we notice the cubic
and hexagonal diamond phases (cd and hd, respectively), the metallic high-pressure β-Sn and simple hexagonal (sh) phases, and the high-density tetrahedral polymorphs known as bc8, r8, and st12 [1]. Ia3d is the same structure reported for C in [20]. The structure labelled cintet in Figures 2 and 3 is the elemental analog of the tetrahedral variant of the cinnabar structure observed at high pressures in ZnTe and GaAs [1], whereas the high-density polymorph I41/a was found to play an important role in the decompression kinetics from the high-pressure phases of Si and Ge [21]. All these structures came out during the search process.

Figures 4 and 5 show the structures of the low-density orthorhombic Pbam and tetragonal P41212 phases, found with AIRSS, and which according to our calculations are dynamically stable and quite low in energy for each of the group-14 elements studied (see Fig. 1-3), and should thus be considered energetically competitive polymorphs for these materials at zero or low pressure. Both Pbam and P41212 are slightly expanded with respect to the corresponding diamond phases, with equilibrium volumes larger than diamond by 2%-3%, and bulk moduli slightly below those of the diamond forms [9]. For comparison, the low-density clathrates of types I and II (referred to as clat46 and clat34, respectively) are also shown in Figures 1-3, as well as the P6522 chiral framework structure previously obtained by Pickard and Needs [22], whose density is intermediate between that of the clathrates and that of Pbam and P41212.

**Figure 4.** A plot of the Pbam structure viewed along the z axis, with its six different Wyckoff sites represented by different colors. Fivefold and sevenfold rings are clearly visible.

**Figure 5.** A plot of the P41212 structure viewed along its fourfold axis, with the three different Wyckoff sites represented by different colors. The characteristic Cairo-type pattern is apparent in this plot.

The P41212 form (20 atoms per unit cell at 2×8b and 4a Wyckoff sites, see [9]) is also a chiral framework structure, based on interconnected fivefold spirals chains. The presence of fivefold spirals is a rather unusual feature of this structure, as well as the large proportion of fivefold rings. Another exotic feature is that the two dimensional pattern of P41212, when viewed along its fourfold main axis, corresponds to the so-called Cairo pentagonal tiling, reported in Islamic decoration and apparent in Figure 5. In C, P41212 is close in energy to the Cmmm and Cmca phases (which are essentially mutually degenerate in energy for each of the three materials and indistinguishable in practice in Figures 1-3). Cmmm has been previously proposed for the structure of cold-compressed carbon nanotubes [6,23], and Cmca can be considered as a variant.
of this structure which shares the same structural motifs of fourfold, sixfold, and eightfold ring patterns as Cmmm, in a mutated arrangement. The tetragonal \( P_4_{2}/ncm \) structure reported by Zhao et al. [24] also appeared in our search. \( P_4_{2}/ncm \) (12 atoms per cell, at 4b and 8i sites) is made of slabs of corner-sharing diamondlike tetrahedra. Adjacent tetrahedra appear tilted through the direction of the fourfold axis in \( P_4_{2}/ncm \) with respect to the arrangement found in the diamond structure, but are otherwise remarkably close to being ideal (see Fig. 5 in Ref. [9]). The nearest-neighbor environment of each site in Pbam (24 atoms per cell at \( 3 \times 4h \) and \( 3 \times 4g \) sites [9]) is also tetrahedral, but in a sense much more distorted, with fivefold, sixfold, and sevenfold rings of atoms visible in the \( xy \) projection shown in Fig. 4. These can be interpreted as the result of strong rebonding in a diamond network, which however preserves a large number of sixfold chairlike diamond-type rings perpendicular to the \( xy \) plane. Angular distortion is consequently large. In both Pbam and \( P_4_{1}2_{1}2 \), nearest-neighbor distances spread around the value for the perfectly tetrahedral network, viz. cd (diamond), with a similar response to compression and a large deviation in the orientation of the bonds.

The calculated electronic band structures of C-Pbam and C-\( P_4_{1}2_{1}2 \) (at the DFT-PBE level) show them to be insulating with band gaps of 4.57 and 4.70 eV, respectively, whereas for C-cd our calculations yield 4.13 eV [9]. Band gaps are expected to be underestimated in DFT when calculated using a semilocal form for the XC density functional, as in the PBE approximation. Improving over the PBE values using a first-principles self-energy approach is very costly, but a measure of correction can nonetheless be attempted in order to discern an approximate trend for the true gaps. For example, our calculated PBE band gaps are 0.86 eV for Si-Pbam and 1.23 eV for Si-\( P_4_{1}2_{1}2 \), which are larger than the calculated band gap for Si-cd of 0.63 eV. This value for Si-cd is in turn approximately half the experimental value of 1.17 eV. Roughly correcting the calculated band gaps of Si-Pbam and Si-\( P_4_{1}2_{1}2 \) by adding the difference between the known experimental and theoretical values of the diamond phase (0.54 eV) results in an estimate of 1.4 eV for Si-Pbam and 1.77 eV for Si-\( P_4_{1}2_{1}2 \). These values are close to the value considered optimal for photovoltaic conversion, \(~1.5\) eV. In particular, the estimated quasi-direct band gap of \(~1.4\) eV for Si-Pbam at the zone center makes it a very interesting phase in that respect. For Ge, the calculated band gap of the Pbam phase is close to zero (direct at the zone center) whereas for the \( P_4_{1}2_{1}2 \) phase is indirect (1.00 eV).

Finally, in respect to vibrational properties, our simulation of the Raman spectrum of Si-\( P_4_{1}2_{1}2 \) at equilibrium shows a strong Raman peak at a frequency around 480 cm\(^{-1}\), significant Raman activity just below 200 cm\(^{-1}\) and weak Raman activity around 330 cm\(^{-1}\), see Fig. 10 in Ref. [9]. Simulated Raman spectra can be a great advantage in the identification of phases obtained in the laboratory, and this can be the case with the hypothetical Si-\( P_4_{1}2_{1}2 \) phase. In particular, the unknown structure of Si-XIII, which is formed in the laboratory under nanoindentation, has been examined in detail by Ruffell et al. [7] who concluded the existence of three signature peaks which are characteristic of the Raman spectrum of Si-XIII, at frequencies of 202, 333, and 478 cm\(^{-1}\). These values agree quite well with the values calculated by us for the Raman peaks of the Pbam phase is close to zero (direct at the zone center) whereas for the \( P_4_{1}2_{1}2 \) phase is indirect (1.00 eV).

4. Summary
In summary, we have outlined the results of our structural search for new polymorphs of the group-14 elements C, Si, and Ge, focusing mainly on low-density, energetically favorable polymorphs with tetrahedral coordination and \( sp^3 \) bonding. We have discussed the energetics, structure, and electronic and vibrational properties of several novel phases which can be compared with those of other observed and hypothetical phases of these materials. We have found a chiral structure with \( P_4_{1}2_{1}2 \) symmetry and 20 atoms per cell which is low in energy
and significantly different from any other structure previously proposed for these materials, exhibiting a characteristic Cairo-type two-dimensional pentagonal tiling. The calculated Raman data for the Si-P4\textsubscript{1}2\textsubscript{2}2 phase show good compatibility with those experimentally obtained for the unknown Si-XIII phase [7]. Of interest is also the orthorhombic structure with 24 atoms per cell and Pbam symmetry, which in the case of Si has an estimated quasi-direct band gap at the zone center optimal for photovoltaic applications. Recent experimental studies have demonstrated the possibility of synthesizing structures similar to Si-Pbam in the laboratory [8] and we hope that our results may entice further experimental research within this area, leading to new findings. The interested reader is referred to Ref. [9] and its supplemental material for an extended account of our survey on the polymorphism of the group-14 elements.

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