

Comment on "Towards Direct-Gap Silicon Phases by the Inverse Band Structure Design Approach"

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Comment on “Towards Direct-Gap Silicon Phases by the Inverse Band Structure Design Approach”

In the Letter of Xiang *et al.* [1], a novel, metastable cubic silicon phase $\text{Si}_{20}\text{-T}$ was theoretically predicted by the modified particle swarm optimization method CALYPSO [2]. The optical absorption of this phase was computed and compared to that of diamond silicon. $\text{Si}_{20}\text{-T}$ exhibits a quasidirect gap of 1.55 eV and has a stronger absorption in the visible compared to diamond silicon, which makes it a candidate as a solar energy absorber. However, we have strong reasons to believe that this phase cannot be experimentally synthesized via strong compression or decompression or through molecular encapsulation as proposed by the authors [3].

According to our density functional theory calculations with the Perdew-Burke-Ernzerhof functional, and in agreement with the data reported in Ref. [1], the energy differences at ambient conditions of $\text{Si}_{20}\text{-T}$ with respect to diamond silicon and to the type II silicon clathrate are 286 and 233 meV/Si, respectively. In fact, Botti *et al.* [4] predicted a plethora of energetically much more favorable silicon polymorphs, some of which are equally well suited for photovoltaic applications, by employing the minima hopping method [5,6]. In view of that, even in the unlikely case that $\text{Si}_{20}\text{-T}$ could be synthesized, its stability is highly questionable since it would quickly and highly exothermically decay to some more favorable metastructure, such as those of Ref. [4].

Furthermore, the configurational density of states increases with energy and essentially explodes [7] when amorphous silicon becomes accessible at roughly 290 meV/Si above silicon diamond [8]. A huge number of structures therefore compete thermodynamically with $\text{Si}_{20}\text{-T}$ such that a crystallization in this phase is very unlikely. To address the above issues, Botti *et al.* [4] systematically rejected all phases with higher energies than 150 meV/Si above diamond silicon.

Although compression or expansion of silicon is a valid and promising approach to synthesize novel silicon polymorphs, we are convinced that this approach is not applicable to obtain $\text{Si}_{20}\text{-T}$. Xiang *et al.* [1] conclude that $\text{Si}_{20}\text{-T}$ can be synthesized at cell volumes below $15.6 \text{ \AA}^3/\text{Si}$ or above $37.0 \text{ \AA}^3/\text{Si}$ by boldly comparing its energy/atom curve as a function of volume/atom with respect to diamond silicon alone, ignoring all other lower-energy metastable polymorphs. This complete neglect of the complex phase diagram of silicon, which undergoes several phase transitions as a function of pressure, is the origin of their erroneous conclusions. The energies of the various silicon phases as a function of atomic volume are shown in Fig. 1. With the full phase diagram in mind, we can clearly see that the $\beta\text{-tin}$ phase is by far energetically

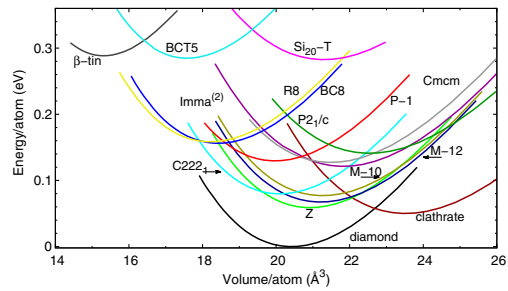


FIG. 1 (color online). Energy/atom as function of volume/atom for the structures in Ref. [4], together with $\text{Si}_{20}\text{-T}$.

favored over $\text{Si}_{20}\text{-T}$ at $16 \text{ \AA}^3/\text{Si}$ (170 meV/Si), while silicon clathrates are favored in the high volume range (156 meV/Si at $37.0 \text{ \AA}^3/\text{Si}$). Note that at this high volume, which corresponds to a negative pressure of -1.8 GPa, our calculations show that $\text{Si}_{20}\text{-T}$ silicon is dynamically unstable, making it therefore irrelevant to propose the synthesis beyond $37.0 \text{ \AA}^3/\text{Si}$.

Xiang *et al.* [1] also proposed molecular encapsulation to synthesize $\text{Si}_{20}\text{-T}$ with intercalated CH_4 . Again, the authors neglected the energetically more favorable silicon clathrates in their comparison. By inserting CH_4 in the clathrate's polyhedra the cell volume expands by merely 1.6%, compared to 8.3% volume expansion in $\text{Si}_{20}\text{-T}$, resulting in a significantly stronger strained structure. Therefore it is not surprising that, according to our calculations, the clathrate with encapsulated CH_4 is favored by 458 meV/Si.

In conclusion, optimizing a single physical property alone when designing novel functional materials is by no means sufficient to predict promising structures, but a rigorous study of the thermodynamic stability is essential when evaluating their synthesizability.

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