

Apparent Scarcity of Low-Density Polymorphs of Inorganic Solids

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For most inorganic solids, very few dense polymorphs and no low-density polymorphs are observed. Taking a wide range of tetrahedrally-coordinated binary solids (e.g., ZnO, GaN) as a prototypical system, we show that the apparent scarcity of low-density polymorphs is not due to significant structural or energetic limitations. Using databases of periodic networks as sources of novel crystal structures, followed by *ab initio* energy minimization, we predict a dense spectrum of low-density low-energy polymorphs. The diverse range of materials considered indicates that this is likely to be a general phenomenon.

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The structure and properties of inorganic solids are intimately linked to such an extent that even different structures of the same composition (so-called polymorphs) often have widely differing properties and applications. For boron nitride (BN), for example, the soft hexagonal layered polymorph (*h*-BN) is used as a lubricant, while the cubic polymorph (wurtzite structure) is extremely hard and is employed as an industrial abrasive. Germanium also exhibits more than one polymorph (or more strictly “allotrope” for elemental systems) having very different optical properties; with the diamond structured α -germanium having an indirect band gap, and the recently synthesized low-density clathrate-II structure [1] a direct gap. Evidently, having access to more than one polymorph can significantly extend the range of properties and applications of a particular compound. For the vast majority of inorganic solids, however, typically only three or fewer distinct polymorphs have been prepared experimentally and a similarly small number of hypothetical polymorphs have been proposed. Moreover, where more than one polymorph is known, these extra phases very rarely have a significantly lower density than the most stable polymorph.

In stark contrast to this situation, silica (SiO₂) has been prepared as more than 40 polymorphs [2], the majority of which are considerably less dense than α -quartz; the most stable polymorph under ambient conditions. The rich polymorphism of silica, especially in its low-density forms, allows for fine-tuning of applications (e.g., gas separation membranes) by choosing the best suited polymorph. In addition, 100 000+ hypothetical silica polymorphs have been predicted theoretically as fourfold-connected networks (4CNs) [3–7], a large fraction of which, after accurate theoretical evaluation as silica materials, were found to have comparable energetics to experimentally prepared polymorphs [8,9]. Similarly rich polymorphism has only been further observed for a select group of other inorganic solids, for example, aluminophosphates (AlPO₄). A tantalizing hint that there may as yet exist a greater pool of

experimentally accessible polymorphs for many other inorganic solids is given by the recent low temperature deposition synthesis of the tetrahedral wurtzite polymorph of LiBr [10] (after previous theoretical prediction [11]). While the wurtzite structure is still generally considered as dense, it is significantly less dense than the closed-packed rocksalt structure normally observed for LiBr. Largely inspired by these studies we have used accurate density functional (DF) calculations to explore the energy landscape of a range of other binary solids (i.e., with atomic composition *AB*) with a view to establishing the prevalence of feasible low-density polymorphs. For all systems we predict a multitude of structures, many having remarkably open frameworks, lying surprisingly low in energy, thereby demonstrating that the apparent scarcity of low-density polymorphs is not due to significant structural and/or energetic limitations.

In our investigation we concentrate on a wide selection of the extensive class of 1:1 binary solids that crystallize experimentally at ambient conditions as tetrahedral polymorphs, reminiscent of those of silica. Just as for the silicon atoms in silica polymorphs, the atoms of these tetrahedrally-coordinated binary solids (hereafter referred to as TBSs) can be abstractly regarded as vertices of 4CNs. TBSs have been generally prepared in only two tetrahedral polymorphs (wurtzite and zincblende), a number of intergrowths in between these two (so-called polytypes [12]) and at high pressure as the octahedral rocksalt polymorph [13,14]. Only one further polymorph is observed for TBSs experimentally: the β -BeO or BCT structure (where the three letter code, here and throughout, refers to an International Zeolite Association framework type [15]), as displayed by BeO (i.e., BCT-BeO) at high temperatures [16], sharing the same 4CN as the silicate Mg-BCTT.

Previous theoretical work addressing the energy landscape of TBSs has identified a number of hypothetical polymorphs, many of which lie much higher in energy than wurtzite and zincblende. The two lowest energy

hypothetical TBS polymorphs predicted to date are (i) BCT, although known experimentally for BeO, has also been proposed as a possible extended phase in ZnO and ZnS nanostructures (BCT-ZnO [17,18], BCT-ZnS [19]) and, (ii) the SOD polymorph (sharing the same underlying 4CN as the low-density silicate sodalite [15]) recently proposed for ZnO (SOD-ZnO [20]) and SiC (SOD-SiC [21]). Furthermore, for BN, which is not strictly a TBS as it crystallizes under ambient conditions as the three-connected *h*-BN polymorph, ABW-BN (again with a 4CN originally found as a silicate) and BCT-BN have been predicted [22]. Such studies have not exploited the huge resource of enumerated 4CNs, but have instead derived TBS polymorphs based on methods inspired by physical processes (e.g., simulated thermal [22] and mechanical annealing [17], cluster assembly [20,21]). Arguably, the most thorough study of the energy landscape of any TBS-like system to date was that recently applied to BN [22] which sampled systems with up to only eight atoms per unit cell finding only two hypothetical TBS polymorphs (see above). Evidently, to date, such studies have yielded only a very small number of hypothetical TBS polymorphs with respect to those derived for silica from the enumeration of 4CNs [3–7]. Following this latter topological approach we here sample directly the large and diverse set of 4CNs (with up to 48 atoms per unit cell when realized as a TBS) from a variety of sources.

We initially started our exploration with 4CNs realized as ZnO materials. Taking a representative sample of 55 4CNs, all of which only contained even rings (the atomic ordering of TBSs does not allow for 4CNs with odd rings), we then constructed them as appropriately scaled ZnO structures. In a screening step, we next energy minimized the structures of all resulting ZnO materials using the GULP [23] code and the empirical potential of Whitmore *et al.* [24], which were then checked to be true energy minima by phonon calculations. Subsequently, we selected the 26 structures with the lowest energy, some of which are shown in Fig. 1. This selection was then reoptimized using periodic DF calculations for ZnO and a range of other TBSs: those from groups I–VII (AgI), II–VI (ZnS, CdS), III–V (GaP, GaN) and IV (SiC). The initial structures for the rest of the materials considered were obtained by rescaling the optimized ZnO structures to obtain suitable bond lengths. In all DF calculations a combination of the gradient corrected PW91 [25] functional and projector augmented waves [26], as implemented in the VASP [27] code, were employed. To minimize spurious dependency of basis-set quality on unit-cell size, all reported energies and structures are after two sequential optimizations of both atomic positions and cell parameters and a final single point calculation. Calculations employed a 550 eV plane-wave cutoff, with *k*-point grids chosen such that the energy differences between different polymorphs were converged to within 1 kJ/mol.

Figure 2 shows the resulting relative energies of the different polymorphs for the different TBSs plotted against

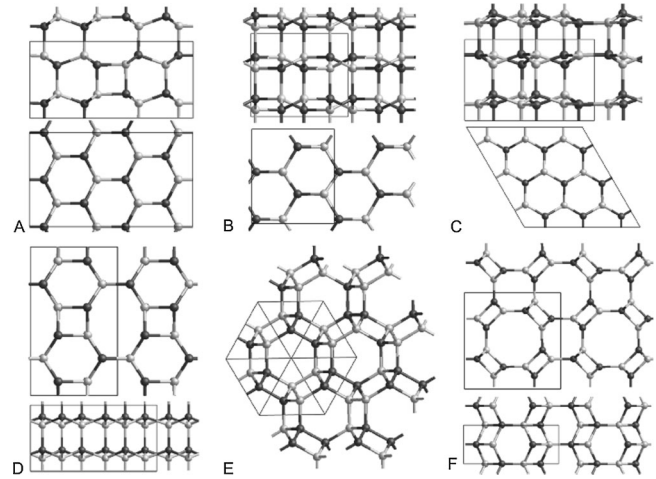


FIG. 1. Structures of selected low-energy hypothetical TBSs: (a) 59_4_280312 (3 kJ/mol), (b) 64_1_1 (5 kJ/mol), (c) 189_3_1615 (8 kJ/mol), (d) ATV (13 kJ/mol), (e) SOD (13 kJ/mol), (f) ATN (17 kJ/mol). (a), (b), and (c) are based upon 4CNs from the database of Treacy *et al.* [1,4,38] and (d), (e), and (f) are derived from 4CNs known for porous crystalline silicates (i.e., zeolites) [15]. Energies in parentheses correspond to the energy difference of the ZnO form of the polymorph with respect to wurtzite-ZnO. The unit cell is boxed in each case.

their relative molecular volume ($V_m/V_{m \text{ wurtzite}}$) and allows for three clear observations. First on a methodological note, in all cases the wurtzite and zincblende polymorphs and the $4H$ and $6H$ polytypes lie lowest in energy and their order of stability follows that found by calorimetry [28,29] and, where experimental data is currently unavailable, by previous theoretical work [30–32]. Second, for all TBSs studied we find a dense spectrum of polymorphs that are approximately evenly spaced over a wide range of relative molecular volumes, reaching up to relative molecular volumes at least 20% larger than that of wurtzite. When ordered with respect to energy, the average energy gap between each subsequent pair of polymorphs ranges from 0.4 kJ/mol *AB* for AgI to 2 kJ/mol *AB* for SiC. As this measure is likely to decrease even further when considering more than 26 polymorphs, it provides an effective upper boundary to the coarseness of the polymorph spectrum. This suggests that the dense spectrum of low-density polymorphs observed for silica is not an exceptional property but general to all tetrahedrally-coordinated solids, and perhaps, more speculatively, all simple solids. Third, both the overall energetic ordering of polymorphs and the shapes of the curves for the different TBSs in Fig. 2 are very similar. This suggests that, even though the various TBSs considered contain different combinations of elements, the underlying physical relationship between topology and energy is strikingly similar.

The energy range spanned by the 26 polymorphs differs strongly between the different TBSs, from 0–9 kJ/mol *AB* for AgI to 0–45 kJ/mol *AB* for SiC and as shown in Fig. 3 appears to increase with the formal charges of the constituent ions. A significant component of the energy of TBS

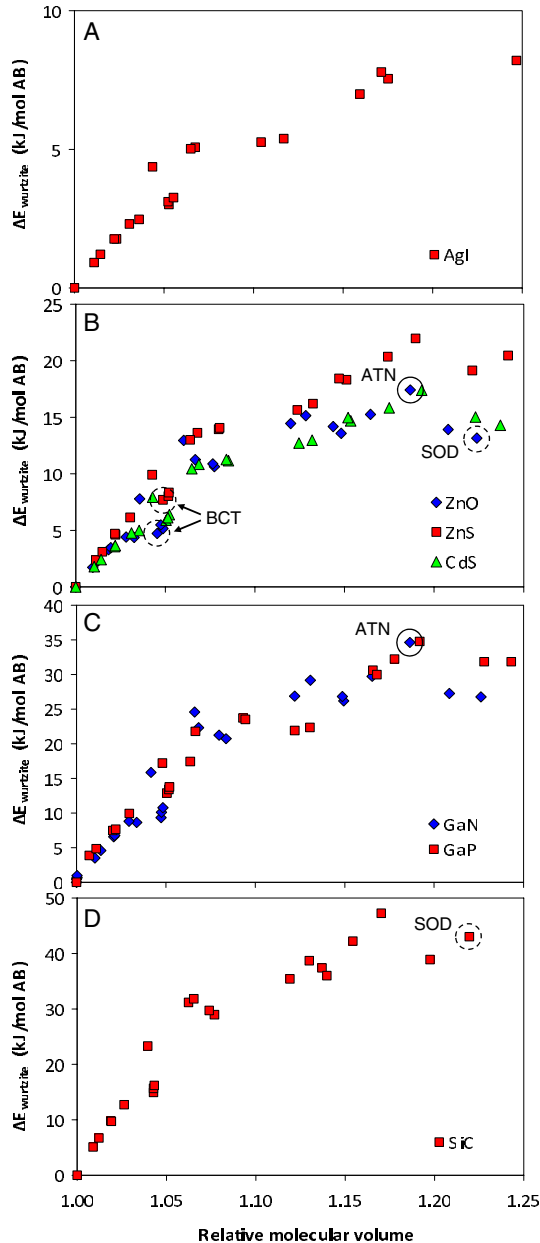


FIG. 2 (color online). Energies with respect to the wurtzite structure ($\Delta E_{\text{wurtzite}}$) of a range of TBSs based on monovalent ions (a), divalent ions (b), trivalent ions (c), and tetravalent ions (d), plotted against their relative molecular volume ($V_m/V_{m,\text{wurtzite}}$). Points corresponding to previously predicted TBSs (Refs. [17–21]) are circled by dashed lines, while doped experimental TBSs are circled in black (Refs. [36,37]).

polymorphs and its link with topology is thus most likely electrostatic in nature. To put the above energy ranges in perspective, the rocksalt polymorph, that has been experimentally prepared and found to be metastable at atmospheric pressure for three TBSs (ZnO [33], CdS [34] and GaN [35]), is calculated for all TBSs to lie significantly higher in energy than all 26 polymorphs considered (e.g., +29 kJ/mol AB for ZnO, +25 kJ/mol AB for CdS, and +94 kJ/mol AB for GaN).

The advantage of exploring the energy landscape of well-defined crystalline solids by first identifying likely minima via a topological approach can be seen by considering the number of new hypothetical low-energy, low-density TBS polymorphs found herein with respect to those previously predicted (i.e., ABW, BCT and SOD, see above). For all compositions studied over 90% of our 19 newly proposed hypothetical TBS polymorphs are found to lie lower in energy than SOD and ABW, while 20%–25% lie energetically below BCT. Other methods of searching for new TBS polymorphs which physically sample the energy landscape more directly may struggle to find these new polymorphs due to the combination of high structural diversity and the wide range of atoms per unit cell (4–48) and unit-cell volumes (e.g., $\sim 40\text{--}80 \text{ \AA}^3$ for ZnO) covered.

As a further note, it is tantalizing to observe that one low-density polymorph in our set of hypothetical polymorphs [ATN, see Fig. 1(f)] has been synthesized twice as a doped TBS: for ZnO as $[\text{K}, \text{Rb}][\text{Zn}_3\text{LiO}_4]$ [36] and for GaN as $[\text{Sr}][\text{Ga}_2\text{Mg}_2\text{N}_4]$ [37] (see highlighted points in Fig. 2 for undoped ATN-ZnO and ATN-GaN). To investigate the stabilizing influence of doping we used DF calculations to probe the thermodynamic favorability of introducing dopants into TBSs and to assess the relative energies of different K-Li-doped ZnO polymorphs (wurtzite, ATN and SOD). In all cases care was taken to find the lowest energy dopant positions. These calculations demonstrate that synthesis of ATN- $[\text{K}][\text{Zn}_3\text{LiO}_4]$ from the corresponding binary oxides (i.e., $\text{ZnO}_{\text{wurtzite}}$, K_2O , Li_2O) is thermodynamically favored ($-15 \text{ kJ/mol } [\text{K}]_{1/4}[\text{Zn}_{3/4}\text{Li}_{1/4}\text{O}]$) helping to rationalize the corresponding experimental synthesis. We also find that the hypothetical SOD- $[\text{K}][\text{Zn}_2\text{LiO}_3]$ structure is also similarly energetically favored ($-14 \text{ kJ/mol } [\text{K}]_{1/3}[\text{Zn}_{2/3}\text{Li}_{1/3}\text{O}]$). Further, in both cases these polymorphs become (upon doping) more stable than the correspondingly doped wurtzite-ZnO structure (by $9 \text{ kJ/mol } [\text{K}]_{1/4}[\text{Zn}_{3/4}\text{Li}_{1/4}\text{O}]$ for doped ATN and by $5 \text{ kJ/mol } [\text{K}]_{1/3}[\text{Zn}_{2/3}\text{Li}_{1/3}\text{O}]$ for doped SOD). We note that with increasing doping, wurtzite-ZnO develops internal voids and/or layers indicative of the instability of doping this relatively dense structure. These calculations suggest that doping with pairs of charge-compensating cations, analogous to methods routinely used to prepare low-density silicate zeolites [15], may be a promising alternative to the synthesis of undoped phases using the low temperature deposition route as employed by Jansen *et al.* [10]. Nevertheless, based on their calculated low energy and structural stability, we reiterate that there is no compelling reason to suppose that many of our predicted undoped polymorphs cannot be synthesized directly.

In summary our detailed theoretical investigation shows that the paucity of low-density polymorphs observed for the majority of inorganic solids is very likely not due to significant energetic or structural constraints. Rather to the contrary, our wide ranging study suggests that the dense

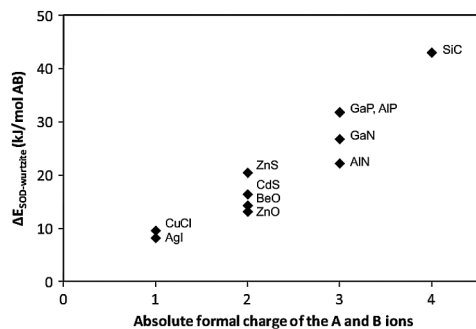


FIG. 3. Energy differences between the SOD and wurtzite polymorphs ($\Delta E_{\text{SOD-wurtzite}}$) for a range of TBSs plotted against the absolute formal charges of the constituent ions. To highlight the generality of the observed correlation, points for other TBSs are also included (CuCl, BeO, AlN, AlP).

spectrum of low-density polymorphs (experimentally observed for silica) is a general property of tetrahedrally-coordinated solids and perhaps all simple solids. We hope that our predictive study will inspire more experimental efforts into investigating low-density polymorphism in inorganic systems.

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