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Metastable Phases

Synthesis and Identification of Metastable Compounds: Black Arsenic—Science or Fiction?**

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Dedicated to Professor Rudolf Hoppe on the occasion of his 90th birthday

The prediction and identification of stable and particularly of metastable compounds is important in achieving innovative materials.[1] With this objective in mind, approaches containing both theoretical examinations of phase stabilities and concepts of a rational synthesis[2] are gaining increasing importance. Thus, an investigation of energy landscapes[3] provides important information about local and global minima to predict the existence of new compounds and structures.

Herein, we introduce a combination of quantum-chemical calculations and thermodynamic considerations to realize target-oriented planning and optimization of chemical synthesis. The analysis of phase formation is acquired with an in situ method for monitoring gas-phase reactions. Using the system P-As, we investigated a textbook example of monotropic phase transitions, which features a variety of known and postulated allotropes.[4]

To estimate the relative stabilities of the compounds under discussion, structure allotropes of N, P, and As were modeled by means of DFT calculations. The calculated electronic energies (normalized to one atom *Pn*) for molecular Pn_2 and Pn_4, the black/orthorhombic (*o-Pn*), gray/trigonal (*t-Pn*), and the simple-cubic (*c-Pn*) allotrope as well as the tubular polymeric forms of Hittorf (*H-Pn*),[5] Ruck (*R-Pn*),[6] and Pfitzner (*P-Pn*),[7] which are known for phosphorus, are shown in Figure 1. The high stability of N_2 can be observed as well as the preference for solid-state structures for P and As. Figure 1b emphasizes the results for the *t* and *o* forms of P and As. The known stability of *o*-P compared to the high-pressure modifications *t*-P and *c*-P is correctly predicted as well as the stability of gray *t*-As compared to the known high-pressure modification *c*-As, hypothetical tubular As allotropes, and predicted *o*-As. Does this mean that *o*-As can be synthesized as a metastable compound?[8a]

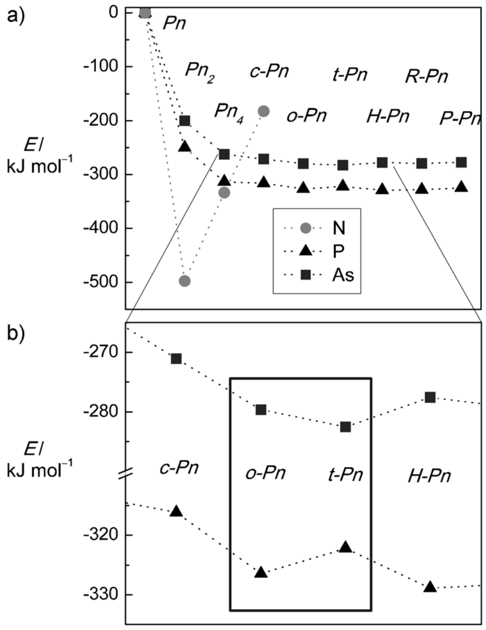

Figure 1. a) Calculated total energies (0 K) of the allotropes, normalized to one atom *Pn* (*Pn* = N, P, and As). b) Enlarged section of selected allotropes. Pn_4 = molecular Pn_4, *c* = simple-cubic, *o* = orthorhombic, *t* = trigonal, *H* = Hittorf, *R* = Ruck, *P* = Pfitzner.

The calculated values of the total electronic energies correctly express the higher stability of *o*-P compared with the high-pressure phase *t*-P and also *t*-As compared to *o*-As. From the computed values $\Delta E_{el} = E_{el}(o) - E_{el}(t)$ of $-4\,\text{kJ}\,\text{mol}^{-1}$ for P and $+2.5\,\text{kJ}\,\text{mol}^{-1}$ for As, a transition from the *o*- to the *t*-structure in the ideal solution As_xP_{1-x} can be estimated to be about $x = 0.6$ (Figure 2). Taking thermodynamic energy terms into consideration (for details, see the Supporting Information), a distinctive stabilization of the *o* phase is calculated and the *o–t* transition shifts to a higher As content ($x = 0.9$). According to the calculated values, very low energy differences decide whether or not *o*-As can actually be synthesized.[8b]

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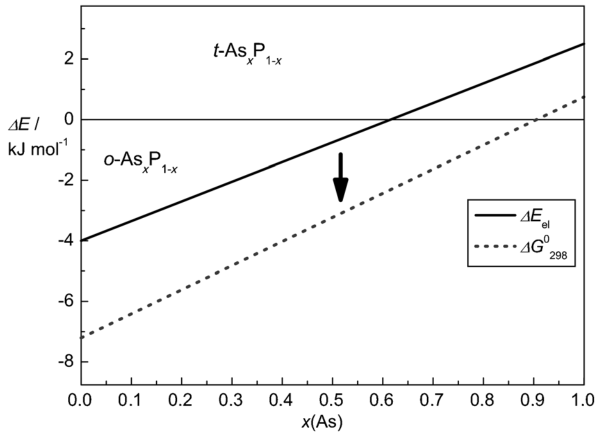

Figure 2. ΔE_{el} and ΔG_{298} values [kJ mol^{-1}] derived from DFT calculations to evaluate the stability of o-As$_x$P$_{1-x}$. $\Delta G_{298} < 0$: stable; $\Delta G_{298} > 0$: metastable.

The synthesis of representatives of the solid solution As$_x$P$_{1-x}$ is not only determined by thermodynamic aspects; the kinetic behavior of the reactions also plays an important role.

A reasonable approach to combine thermodynamics and kinetics is given by the in situ method of gas-phase reaction monitoring.[9] The equilibrium between the solid state and a corresponding gas phase can be analyzed by pressure measurements, even though a metastable solid is concerned. The attainment of the solid–solid equilibrium with the formation of the thermodynamically stable phase is significantly slower. To identify the different allotropes, the individual K_p functions are required. Their determination is based on known G functions[10] and DFT-calculated ΔG values of the metastable phases. An energy difference $\Delta G \leq 4\,\text{kJ mol}^{-1}$ between the allotropes results in a deviation in vapor pressure of $\Delta(\lg p/\text{bar}) = \Delta G/(2.3\,R\,T) \leq 209\,T^{-1}/\text{K}^{-1}$. This implies pressure differences of $\geq 10^{-1}$ bar for temperatures above 400 °C. Consequently, a metastable phase is clearly distinguishable from stable allotropes until a thermodynamic equilibrium of the solid phase is obtained. In this way, the kinetics of phase formation can be traced through various intermediates.

The theoretical pressure curves of P$_{red}$, o-P, H-P, and t-As are shown as dashed lines in Figure 3. Measurements of the pure phases are in perfect agreement with these curves (see Figure S7 in the Supporting Information). In the course of phase formations or phase transitions, characteristic effects can be observed:

I. The pressure of a metastable phase is higher than the pressure of a stable phase.
II. The establishment of equilibrium from a metastable to a stable solid phase is indicated by a decrease of pressure.
III. The establishment of equilibrium can be obtained via several metastable states.
IV. The transition from a low temperature to a high temperature modification involves a kink in the curve.

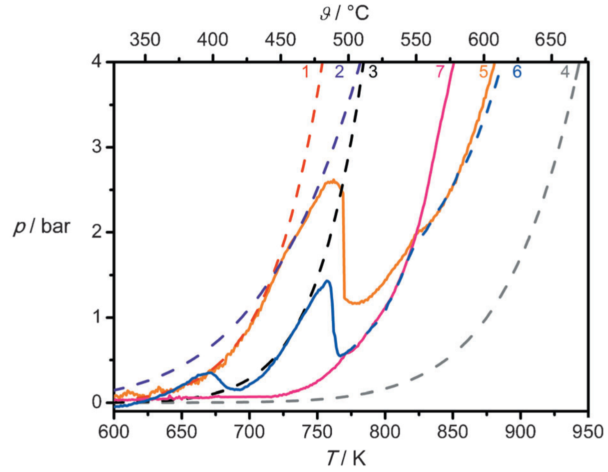

Figure 3. Comparison of the theoretical pressure curves of the allotropes of phosphorus and t-As (dashed curves) with the measured pressures (solid lines) of a mixture As/P = 7:3: 1) -----P$_{red}$; 2) -----H-P; 3) -----o-P; 4) -----t-As; 5) ——7 As + 3 P$_{red}$; 6) ——7 As + 3 P$_{red}$ + mineralizator (PbI$_2$); 7) ——7 As + 3 P$_{red}$ + 2 Au + 3 Pb + mineralizator (PbI$_2$)

Figure 3 exhibits the total pressures of the allotropes of P (curves 1, 2, 3) and t-As (4) as well as the representative pressure curves in the formation of As$_{0.7}$P$_{0.3}$.

Using P$_{red}$ and t-As (curve 5) as starting materials, the pressure follows the curve of P$_{red}$ until the formation of H-P (effect IV). Both phases are metastable in the overall system, as their pressures are above the curves of o-P (3) and o-As$_{0.7}$P$_{0.3}$ (4; effect I). At 500 °C, a drop in pressure occurs owing to the formation of o-As$_{0.7}$P$_{0.3}$ as thermodynamically stable phase of the overall system (II). At 550 °C, the high-temperature phase t-As$_{0.7}$P$_{0.3}$ is formed (IV).

The phase formation develops in a different way (curve 6) if PbI$_2$ is added to the same initial compounds. In this case, the mineralizator principle[11] for the kinetically controlled synthesis of o-P is applied to the formation of o-As$_x$P$_{1-x}$. Initially, the pressure rises along P$_{red}$ but shows a decrease down to curve 3 at 400 °C according to the formation of o-P (effect II). Up to about 490 °C, the pressure follows curve 3 until o-As$_{0.7}$P$_{0.3}$ is formed. Both P$_{red}$ and o-P are metastable with respect to the overall system, so several steps led to the formation of the stable phase o-As$_{0.7}$P$_{0.3}$ (III). In mass spectrometry investigations, only the molecular species As$_4$(g), As$_3$P(g), As$_2$P$_2$(g), AsP$_3$(g), and P$_4$(g) could be detected (see the Supporting Information). The mineralizator is instrumental in the heterogeneous equilibrium during the condensation of a solid. With the addition of Au, Pb, and PbI$_2$ (curve 7), o-As$_{0.7}$P$_{0.3}$ is synthesized without the formation of intermediate element allotropes. Initially, phosphorus is condensed into Au$_2$P$_3$, which then decomposes directly to o-As$_{0.7}$P$_{0.3}$. It is quite remarkable that o-As$_{0.7}$P$_{0.3}$ remains metastable above 550 °C (I) when the pressure curve is located above that of t-As$_{0.7}$P$_{0.3}$ (curve 6). For both the direct formation of o-As$_{0.7}$P$_{0.3}$ and its conservation at high temperatures, surface effects of an additional Au$_2$PbP$_2$[12] phase could be a plausible explanation.[11]

The presented method, which was successfully applied to the system As/P, is generally applicable to all reaction types that are dominated by gas-phase chemistry. By combining quantum-chemical and CalPhaD calculations with in situ investigations of phase formations, appropriate reaction parameters for the synthesis of metastable and stable phases can be derived; this drastically reduces the number of attempts at synthesis. It is therefore another important step towards a rational and efficient synthesis planning. The importance of such a method for the examination of kinetically dominated reactions will be illustrated below.

Applying the synthesis pathways and parameters evaluated for $As_{0.7}P_{0.3}$, the formation of a complete series of *o*-As_xP_{1-x} was aspired. In the literature, a complete non-ideal solid solution of *o*-As_xP_{1-x} was postulated.[13] For high As contents, however, the structural parameters significantly differ from Vegard behavior[14] (see Figure S1 in the Supporting Information), and some data for pure *o*-As turned out to be inconsistent.

All attempts at synthesis with and without addition of a mineralizator demonstrate a consistent behavior: The *o-Pn* structure type could be detected up to a composition of $As_{0.83}P_{0.17}$ (Figure 4).[15] Higher As contents resulted in the *t*-As type, which qualitatively confirms the prediction of the quantum-chemical calculations (61 atom% As from 0 K-GGA and 90 atom% from 298 K-GGA).

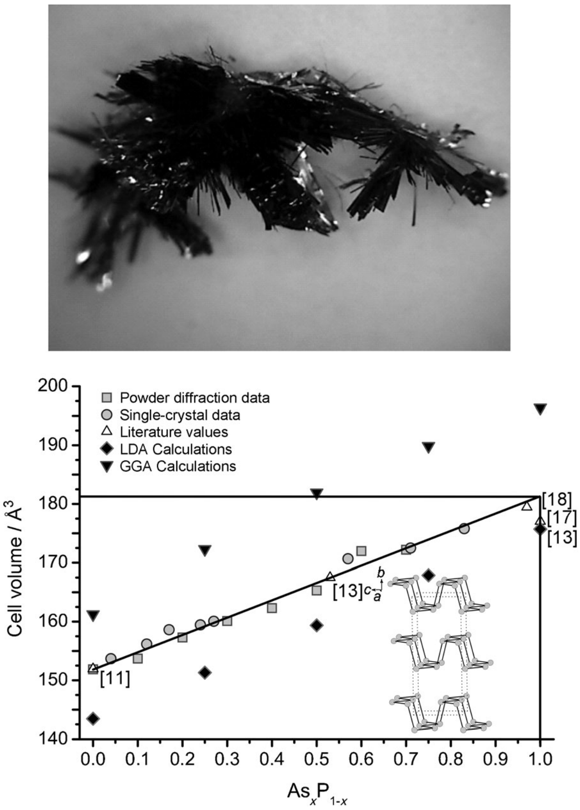

Figure 4. Cell volume derived from powder and single-crystal XRD experiments of the solid solution *o*-As_xP_{1-x} with $x = 0$–0.83, as well as 0 K-LDA and GGA optimizations. A Vegard-like increase of the cell volume is observed up to the maximum As content of 83 atom%.[19] Photo: Crystals of *o*-As_xP_{1-x} with $x = 0.83$ (size up to 0.5 cm).

Up to a content $x = 0.83$, the results from powder refinements as well as single crystal data show a linear increase in volume for *o*-As_xP_{1-x}. An extrapolation of the data to $x = 1$ allows the cell volume of *o*-As to be estimated. This estimation agrees well with the calculated energy values for the geometry optimization of the structure (see the Supporting Information). From the 0 K-GGA (LDA) calculations, bond lengths $d_{As-As} = 2.57$ Å (2.52 Å) and distances between corrugated As layers of 3.29 Å (3.10 Å) could be derived for *o*-As. This reflects the prevalent systematic over- (GGA) or underestimation (LDA) of bond lengths, although Vegard behavior is postulated with both functionals.

The nonlinear behavior reported in the literature indicates a misinterpretation of the phase relations. Whereas the experimental cell volumes up to $x < 0.8$ match those presented herein, all of the literature values for *o*-As are located below the extrapolated straight line. The cell parameters for pure *o*-As,[16] which were postulated in an investigation of the solid solution As_xP_{1-x}, coincide with those found for the limiting composition *o*-$As_{0.83}P_{0.17}$. Elsewhere, it was explicitly referred to contaminations of *o*-As with mercury[17] or oxygen.[18] Summing up all of the the known facts (Figure 4), it is reasonable to conclude that, to date, *o*-As could only be stabilized by impurities. Pure *o*-As is metastable according to our calculations and it is still waiting to be prepared by a kinetically controlled synthesis.

The presented combination of quantum-chemical methods and CalPhaD investigations is universally applicable for all kinds of reactions that are dominated by gas-phase chemistry. By means of straightforward investigations, thermodynamics and kinetics can be considered simultaneously, and reaction pathways can be established directly. By avoiding trial-and-error methods, a set of process parameters can be determined that will allow the directed formation of new phases and the optimization of processes. The huge potential for all areas of chemistry is obvious. We have shown that even for well-known textbook examples, such as *o*-As, significant new insights can be gained.

Experimental Section

As_xP_{1-x} was prepared from a mixture of Au (Chempur, 99.9+%), Pb (AlfaAesar, 99.9985%), P_{red} (Chempur, 99.999+%), and *t*-As (Chempur, 99.9999%) in the ratio 2:3:(10−*y*):*y* with $y = 1$–8 ($\Delta y = 1$) in evacuated silica ampoules ($l = 10$ cm, $\varnothing_{inner} = 0.8$ cm). As was sublimated twice prior to use in synthesis. PbI_2 (10 mg per 500 mg overall weight; AlfaAesar, 98.5%) was added as mineralization agent. The samples were heated up to 550°C within 8 h, held at this temperature for 24 h, and then cooled down to room temperature within 20 h. X-ray powder diffractograms were collected in transmission geometry on a STOE StadiP diffractometer using $Cu_{K\alpha 1}$ radiation at room temperature (α quartz was used as external standard). Indexing and refinement of the lattice parameters were carried out with the program packet win-Xpow.[20]

Single-crystal data were collected on a STOE IPDSII diffractometer at room temperature ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). Numerical absorption corrections were done on the basis of the symmetry equivalent reflections after the optimization of the crystal shape.[21] The structures were solved with Superflip[22a] and refined with Jana2006.[22b]

Semi-quantitative EDX analyses of selected single crystals were carried out on a ZEISS-scanning electron microscope (Type *EVO MA 10*) with an Oxford EDX unit ($U = 20$ kV). GaP (P) and InAs (As) were used as standards.

The DFT structure optimizations using LDA and GGA (PBE) functionals with all-electron basis sets were performed with respect to the total electronic energy (0 K). The accuracy was checked by convergence concerning the k-points (Gilat and Monkhorst grid). Optimizations of all of the cell parameters and atomic sites were done within a tolerance of 10^{-5} kJ in total energy. All of the stated energy values herein were obtained from GGA optimizations. Supercells were used for calculations with phonon dispersion (298 K) and for modeling of solid solutions with ordered structures.

For the investigation of the temperature-dependent pressure behavior during the formation of As_xP_{1-x} ($p = 0.1$ to 15 bar; $\tau \leq 1000\,°C$), an advanced high-temperature gaseous phase balance invented by Hackert and Plies,[24] was used.[9] The measurements were carried out with an overall weight of 500 mg of starting materials in evacuated silica ampoules ($V = 16\ cm^3$) and applying a heating rate of $5\ K\,h^{-1}$.

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