

Lucky Number 13: A 13-Layer Polytype of the Alkyne Hydrogenation Catalyst CaGaGe

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ABSTRACT: Polytypism, the ability of materials to form crystal structures with different stacking sequences, occasionally causes materials with the same stoichiometry and similar local structures to have profoundly different properties. Herein, we discover a metastable 13-layer trigonal (13T) polytype of CaGaGe, a layered intermetallic phase comprised of $[\text{GaGe}]^{2-}$ honeycombs separated by Ca^{2+} . 13T-CaGaGe is synthesized from arc-melting the elements, and its structure is elucidated via neutron powder diffraction. Air-stable 13T-CaGaGe has one misaligned $[\text{GaGe}]^{2-}$ layer for every 13 and transforms into the more stable 4-layer hexagonal (4H) CaGaGe polytype after annealing at 500 °C. Transition-metal-free 13T-CaGaGe shows remarkable activity in the catalytic hydrogenation of phenylacetylene to styrene and ethylbenzene, much higher than the 4H polytype. This work identifies the first 13-layer polytype for any crystal structure and further establishes the influence of polytypism on catalysis.

Polymorphs, compounds with the same stoichiometry and different crystal structures, are prevalent in materials chemistry. Polytypism is a subset of polymorphism commonly occurring in layered compounds describing materials having nearly identical structures and compositions along two dimensions but stacked into unit cells with different repeating sequences. While most polytypes lead to subtle differences in structure and properties, sometimes dramatic changes are observed. Namely, $\text{TaSe}_{2-x}\text{Te}_x$ exhibits an order of magnitude higher superconducting transition temperature in the 3-layer rhombohedral polytype compared to the 2-layer hexagonal polytype, despite minimal differences in their local coordination.¹ SiC forms many different polytypes of close-packed corner-sharing tetrahedra, and its band gap changes from 2.39 eV (zinc blende) to 3.33 eV (wurtzite).² Finally, there have been significant differences in the catalytic and electrocatalytic behavior between the face-centered-cubic and the 4-layer hexagonal (4H) polytypes of Au and Cu, which have different arrangements of close-packed layers.^{3–6} 4H-Cu has been recently found to exhibit higher electrocatalytic activities and ethylene selectivity in the CO_2 reduction reaction.⁴ Thus, polytypism can significantly influence the catalytic behavior.

An exciting family of materials that feature polytypism are Zintl–Klemm compounds, having structures comprised of layers of main-group elements separated by large electropositive cations.^{7–14} These materials exhibit many exotic physical properties including axis-dependent conduction polarity in NaSn_2As_2 ,¹⁵ hydrogen absorption in SrGa_2 ,¹⁶ and topological insulating properties of BaSn_2 .^{11,17} Examples of polytypism in these phases include CaGe_2 , forming 2- and 6-layer polytypes, and CaAlSi , forming 1-, 5-, and 6-layer polytypes.^{10,18,19}

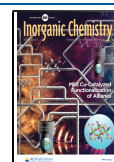
Recently, we discovered that the transition-metal-free layered Zintl–Klemm compound BaGa_2 shows catalytic activities for the hydrogenation of phenylacetylene into styrene and ethylbenzene within an order of magnitude of Pd-based

compounds.²⁰ BaGa_2 consists of planar layers of covalently bonded Ga^- honeycombs, where every Ga formally has 7 valence electrons, ignoring weak intralayer Ga–Ga π bonding. We hypothesized that the valence electron count of 7 makes these phases acidic, promoting adsorption of both H_2 and alkynes. We found other structurally and electronically similar Zintl phases to have appreciable catalytic activity for alkyne hydrogenation.²¹ One such material is CaGaGe, which is comprised of puckered honeycomb $[\text{GaGe}]^{2-}$ layers having an alternating BN-like arrangement, with each layer separated by Ca^{2+} .²² According to the Zintl–Klemm electron-counting rules, each Ga^- and Ge^- formally has 7 and 8 valence electrons, respectively. CaGaGe adopts a 4H-YPTAs structure type, in which the Ga atoms in neighboring layers tilt toward each other, partially stabilizing the lack of an octet. The interlayer Ga–Ga distance is too large (3.57 Å) to form a covalent bond (Figure 1a).²² Because each Ge formally has an octet, the layers tilt to minimize the electrostatic repulsion between the Ge atoms and the nearest Ge or Ga atoms in neighboring layers. Transmission electron microscopy studies suggested that CaGaGe could form a more complex stacking sequence, although the structure was never determined.¹⁰ Herein, we have elucidated a new 13-layer trigonal (13T) polytype of CaGaGe, an air-stable, highly active heterogeneous catalyst for the hydrogenation of alkynes with consistently greater activities than those of the 4H polytype.

CaGaGe was synthesized by arc-melting stoichiometric amounts of the elements. The initial Rietveld refinements

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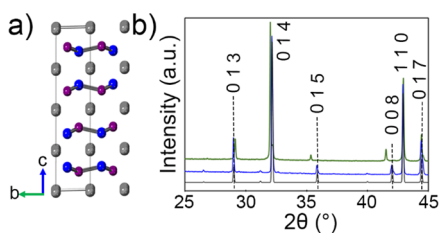


Figure 1. (a) 4H polytype of CaGaGe. (b) XRD patterns of synthesized 13T (green), synthesized 4H (blue), and calculated 4H-CaGaGe (black), with Miller indices labeling the 4H polytype.

were performed using X-ray diffraction (XRD). All attempts to fit the pattern to the 4H $P6_3/mmc$ crystal structure were unsuccessful (Figures 1a,b and S1–S3). When assuming a 4H polytype, all $0kl$ reflections, where l is odd are shifted to either higher or lower 2θ , and additional unindexed weak reflections are present (Figure S2). However, the observed intensity of every reflection is close to that predicted for the 4H polytype, indicating that the majority phase has a similar structure but a different stacking sequence. Indeed, the d spacings of the $0kl$ reflections and the new minor reflections precisely match a 13-layer unit cell (Figure 2a and S3). The 4H-CaGaGe phase is

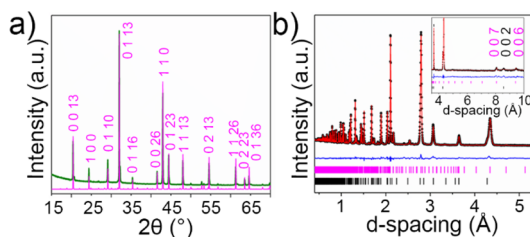


Figure 2. (a) Observed (green) and superimposed calculated (magenta) XRD patterns of P3 CaGaGe. (b) Rietveld refinement of the NPD. The observed data, calculated pattern, and difference curve are represented by black dots, red lines, and blue lines, respectively. The hkl marks for the 13T and 4H phases are magenta and black, respectively. The inset shows another frame highlighting the 006 and 007 reflections of 13T-CaGaGe and the 002 reflection of 4H-CaGaGe.

present as a minor phase (~ 15 wt %), appearing as shoulders on the most intense 13-layer reflections, at slightly larger 2θ . The 13-layer phase transforms into the 4H polytype upon annealing at 500 °C for 18 h (Figure 1b). No well-defined transition is observed with differential scanning calorimetry, suggesting that the polytypes have similar energies (Figure S4).

Time-of-flight neutron powder diffraction (NPD) was performed to elucidate the structure of this 13-layer phase because the neutron scattering factors of Ga and Ge are considerably different ($Ga = 6.83$; $Ge = 8.6$).²³ Rietveld refinement convincingly established a 13-layer unit cell as the majority phase (Figure 2b). The most visually straightforward evidence of the 13-layer structure is the presence of the 006 and 007 reflections at large d spacings (Figure 2b, inset). Between those reflections, the 002 reflection of the minority 4H phase is apparent.

A combination of Rietveld refinements and density functional theory (DFT) calculations indicated that this new polytype crystallizes into a $P3$ space group, as described in Figures S5–S11 and Tables S1 and S2. The refined 13T-CaGaGe $P3$ crystal structure (Figure 3) is nearly identical with the crystal structure of 4H-CaGaGe, except for “layer 8”.

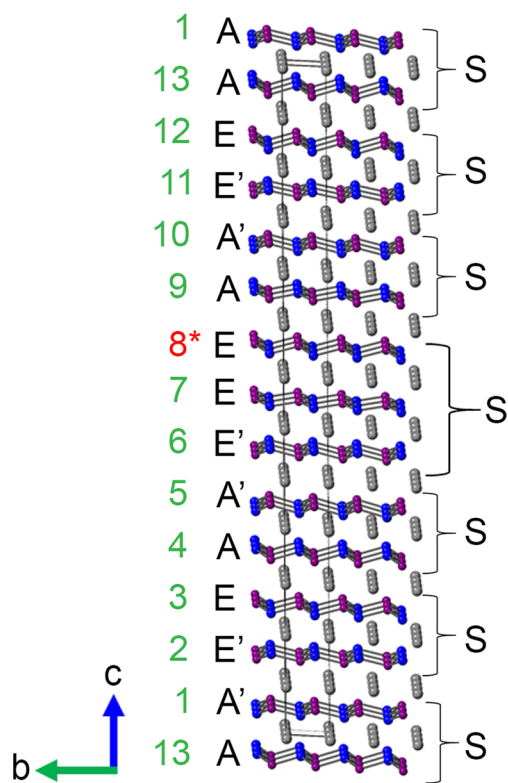


Figure 3. Refined $P3$ crystal structure of CaGaGe. Ca, Ga, and Ge are represented with gray, blue, and purple spheres, respectively. The green text refers to the GaGe layer number. The unique 8th layer is highlighted in red. “A” and “E” in the left column indicate whether “Ga” or “Ge”, respectively, occupy the left ($1/3, 2/3, z$) positions. An apostrophe next to A or E denotes that the right ($2/3, 1/3, z$) atom is above the left ($1/3, 2/3, z$) atom. The “S” label groups layers having the same atoms stacked on top of each other.

Except for this layer, the positions of the Ga and Ge atoms alternate every two layers. The Ga atoms pucker toward each other to partially stabilize the lack of an octet, but the average Ga–Ga interlayer distance [$3.45(14)$ Å] is too large for full covalent bonding. Layer 8 deviates from the 4H-stacking sequence and lacks interlayer Ga–Ga stabilization. In summary, 13T-CaGaGe has an overall repeat unit of $3 \times$ 4H-CaGaGe capped by one deviating CaGaGe layer.

Considering the similarity of the 13T and 4H phases, one could envision other polytypes. DFT calculations of the formation energies of the 4H, $4n + 1$, and $4n - 1$ polytypes ($n = 1-4$) confirmed that the 4H polytype was the most stable structure (Table S3). The energetic penalty of adding or subtracting an additional layer was calculated as a stacking fault energy relative to the 4H polytype and normalized per formula unit of CaGaGe. The stacking fault energies in the 5, 9, 13, and 17 ($4n + 1$) polytypes (67–73 meV) were much smaller than those in the 3, 7, 11, and 15 ($4n - 1$) polytypes (129–139 meV). The extra energetic penalty in the $4n - 1$ polytypes results from the destabilizing influence of having Ge and Ga atoms in the neighboring layers tilted toward each other (Figure S12). This destabilizing interlayer Ge/Ga interaction is absent in the $4n + 1$ polytypes. Although the other $4n + 1$ polytypes are all close in formation energy, no evidence for these structures was observed in the XRD or NPD patterns. Nevertheless, this 13T phase is metastable and can only be accessed from the fast cooling achieved via arc-melting. To the

best of our knowledge, this is the first example of a crystal structure with a 13-layer polytype in any crystalline material, including materials known to have many polytypes (zeolites, SiC, etc.). The only previous claim of a 13-layer polytype was $\text{Ba}_{18}\text{Ti}_{54}\text{Nb}_2\text{O}_{132}$, although its atomic structure remains undetermined.²⁴

The catalytic activities of the 13T and 4H phases in the hydrogenation of phenylacetylene to styrene and ethylbenzene were evaluated in dimethylformamide (DMF) and *n*-butanol (*n*-BuOH) at 51 bar of H_2 (Figure 4a), a common pressure for

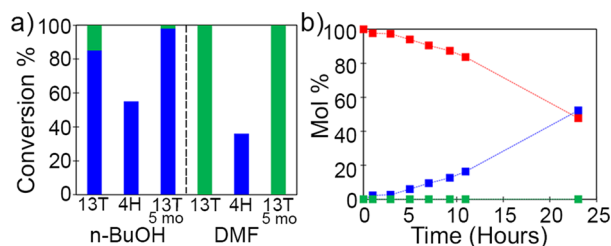


Figure 4. (a) Catalytic hydrogenation of phenylacetylene to styrene (blue) or ethylbenzene (green) using either non-air-exposed 13T- or 4H-CaGaGe and 5 month air-exposed 13T-CaGaGe as catalysts. Reaction conditions are 51 bar of H_2 , 20 h, 2.5 mL of solvent (*n*-BuOH or DMF), 1.82 mmol of phenylacetylene, and 0.12 mmol of CaGaGe (6.2 mol %). (b) Time-dependent conversion of phenylacetylene (red) to styrene (blue) using non-air-exposed 13T-CaGaGe at 1 bar of H_2 , in 2.5 mL of DMF, 0.91 mmol of phenylacetylene, and 0.081 mmol of CaGaGe (8.2 mol %). Ethylbenzene (green) was not detected.

catalyst screening.^{25–27} After 24 h, 13T-CaGaGe completely hydrogenates phenylacetylene to ethylbenzene in DMF and is more selective for semihydrogenation to styrene in *n*-BuOH. Surprisingly, 13T-CaGaGe shows much greater conversion than the 4H-CaGaGe phase, despite a nearly identical structure and an average particle size. This observation is quite robust, and the enhanced activity in 13T-CaGaGe was maintained across three synthetic batches of both polytypes. Additionally, 13T-CaGaGe has enhanced air stability compared to other Zintl–Klemm catalysts, including BaGa_2 , which loses all activity upon immediate exposure to air.^{20,21} After 5 months in air, 13T-CaGaGe retained complete conversion with similar product mixtures in DMF and *n*-BuOH, using these same reaction conditions. No new phases are observed in the diffraction pattern, further evidencing its air stability (Figure S13). Additionally, cyclability experiments in *n*-BuOH demonstrated a minimal loss in activity after 5 cycles (Figure S14).

13T-CaGaGe even exhibited catalytic activity at 1 bar of H_2 (Figure 4b). The time-dependent conversion in DMF shows >50% conversion after 23 h. The surface specific activity (SSA) was estimated by measuring the surface area per gram of catalyst ($0.406 \text{ m}^2 \text{ g}^{-1}$) with the Kr adsorption isotherm Braunauer–Emmett–Teller (BET) method along with conversion versus time (Figure S15). Using the 23 h conversion, the SSA is estimated to be 315 h^{-1} , similar to those of Lindlar’s catalyst (650 h^{-1}) and other highly active Pd- and Au-containing catalysts (Table S4).^{20,21,28} An induction period is apparent, which complicates further kinetic analysis, and makes the estimate of SSA a lower bound. Inductively coupled plasma optical emission spectrometry analysis of the supernatant indicated that the amounts of soluble Ga and Ge were <1 ppm,

suggesting that catalysis is not due to a soluble Ga- or Ge-based impurity.

The difference in activity between these polytypes is unexpected. Because the 4H-CaGaGe phase is prepared by annealing the 13T phase at 500 °C in fused silica, we explored whether the reduced activity in 4H-CaGaGe was caused by greater degrees of surface oxidation upon annealing. However, the X-ray photoelectron spectroscopy (XPS) spectra of the 13T and 4H powders show no differences in the degree of oxidation between the polytypes (Figure S16). Both phases show major Ga $2p_{3/2}$ and $2p_{1/2}$ peaks at 1117.90 and 1144.5 eV, indicative of an oxidized Ga^{3+} , along with shoulders at 1115.7 and 1142.7 eV, which are at lower energies than Ga^0 and thus indicative of an anionic Ga surface species.²⁹ The presence of this anionic Ga surface species was shown to correlate with the catalytic activity in BaGa_2 .²⁰ The relative areas of the anionic Ga shoulders are nearly identical in both 4H-CaGaGe and 13T-CaGaGe, indicating that the degree of surface oxidation is very similar. The Ge 2p and O 1s regions in the XPS spectra of the two polytypes are also similar (Figure S17). Thus, the difference in activity between the polytypes does not result from varying degrees of surface oxidation. The higher activity in the 13T phase could originate from a much more active misfit layer. Another possibility is that the subtle differences in the Ga–Ge bond length lead to enhanced activity. The 13T polytype has, on average, a slightly smaller Ga–Ge bond distance of 2.507(23) Å, ranging from 2.458 to 2.541 Å compared to 4H-CaGaGe [2.530(3) Å]. In other heterogeneous catalysts, similar metal–metal bond length deviations significantly influence the catalytic activity.³⁰ One final possibility is that the surface structure of the arc-melted 13T phase exists in a nonequilibrium state, with a higher concentration of catalytically active defects and amorphous regions. The concentration of these regions is decreased upon annealing to form the 4H phase. Further investigations are needed to conclusively pinpoint the exact nature of the active sites and origin of increased activity in the 13T polytype.

This exotic, metastable 13T-CaGaGe is the first 13-layer polytype and provides an additional example of the unique role of polytypism on the catalytic performance, beyond Cu and Au. Its formation is highly reproducible, and it is the dominant phase that forms through >50 syntheses. This highly active transition-metal-free, air-stable catalyst paves the way for exploration of the reactivity, substrate selectivity and functional group tolerance, robustness, and mechanistic understanding of catalysis with these Zintl–Klemm polytypes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02051>.

Experimental methods, general procedure for refinements, tables of refinement results, XPS, BET, recycling experiments, and air-stability studies (PDF)

Accession Codes

CCDC 2096945 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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