Understanding the Amorphous Lithiation Pathway of the Type I Ba$_8$Ge$_{43}$ Clathrate with Synchrotron X-ray Characterization

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ABSTRACT: Tetrel (Tt = Si, Ge, and Sn) clathrates have highly tunable host–guest structures and have been investigated as novel electrode materials for Li-ion batteries. However, there is little understanding of how the clathrate structure affects the lithiation processes and phase evolution. Herein, the electrochemical lithiation pathway of type I clathrate Ba$_8$Ge$_{43}$ is investigated with synchrotron X-ray diffraction (XRD) and pair distribution function (PDF) analyses and compared to the lithiation of germanium with a diamond cubic structure ($\alpha$-Ge). The results confirm previous laboratory XRD studies showing that Ba$_8$Ge$_{43}$ goes through a solely amorphous phase transformation, which contrasts with the crystalline phase transformations that take place during lithiation of micrometer-sized $\alpha$-Ge particles. The local structure of framework-substituted clathrate Ba$_8$Al$_{16}$Ge$_{30}$ after lithiation is found to proceed through an amorphous phase transformation similar to that in Ba$_8$Ge$_{43}$. In situ PDF and XRD during heating show that the amorphous phases derived from lithiation of Ba$_8$Ge$_{43}$ are structurally related to various Li–Ge phases and crystallize at low temperatures (350–420 K). We conclude that the Ba atoms inside the clathrate structure act to break up the long-range ordering of Li–Ge clusters and kinetically prevent the nucleation and growth of bulk crystalline phases. The amorphous phase evolution of the clathrate structure during lithiation results in electrochemical properties distinct from those in $\alpha$-Ge, such as a single-phase reaction mechanism and lower voltage, suggesting possible advantages of clathrates over elemental phases for use as anodes in Li-ion batteries.

1. INTRODUCTION

Tetrel elements (Tt = Si, Ge, and Sn) are potential candidates for next-generation Li-ion battery anodes due to their intrinsically high capacities originating from a series of complex phase transformations. While the room-temperature lithiation of diamond-structured Si ($\alpha$-Si) proceeds through the formation of amorphous phases until crystallization of Li$_{13}$Si$_4$ at high degrees of lithiation,1,2 Ge and Sn readily crystallize at intermediate Li compositions to form various Li–Tt binary compounds.3–5 The phases that form have direct consequences on the electrochemical properties such as the voltage, rate capability, and stress evolution. Understanding how these properties are affected by the initial host structure and its subsequent lithiated intermediates is important for optimizing the performance of alloying anodes. Much work has been conducted on the role of nanostructuring on the alloying reactions of the elemental tetrels,6–11 but other than comparisons between amorphous and diamond-structured Si (or Ge) electrodes,1,2,6,12–14 less focus has been given to understanding the effect of the initial crystal structure on the subsequent lithiation pathways.

To further this understanding, our group and others have been investigating tetrel clathrates16–22 and other polymorphs28–30 for their electrochemical properties for Li-ion batteries. Tetrel clathrates are host–guest structures, wherein an open framework of covalently bound Tt atoms (all four-coordinated and thus electroneutral) encapsulate metal guest atoms. For example, the type I clathrate adopts the Pm$\bar{3}$n cubic space group with a general unit cell of M$_8$Tt$_{46}$ where M represents an alkali metal or alkaline earth metal guest atom. Clathrates can adopt several different crystalline structures and form with a variety of atomic substitutions and vacancies on guest or framework sites, resulting in a large design space for tuning the material properties of the clathrate.31 The type I Ba–Ge clathrate, Ba$_8$Ge$_{43}$, deviates from the M$_8$Tt$_{46}$ stoichiometry due to the presence of vacancies on Ge sites, which compensate for the excess electrons contributed from the Ba atoms. Substituting group III elements (Al, Ga, and In) for Ge allows for further charge compensation of Ba and results in the ability to tune the material properties of the clathrate. For instance, the electron precise Ba$_8$Al$_{16}$Ge$_{30}$ clathrate is a semiconductor,32 while Ba$_8$Ge$_{43}$ shows metallic-like behavior due to the excess electrons from Ba.33 The structure of Ba$_8$Ge$_{43}$ (Figure 1) is composed of two dodecahedra (Ge$_{20}$) and six tetraakisdecahedra (Ge$_{24}$) per formula unit, where all Ge atoms are in slightly distorted tetrahedral configurations. Much work...
has gone into understanding how the clathrate structure and defects affect the thermoelectric, superconducting, and microstructural properties of these materials; however, their role on the electrochemical and Li-ion alloying properties is less understood. Our goal in this work is to establish structure–property relationships for clathrates within the context of Li-ion battery applications.

Because of the similar covalent bonding within the cage-like framework in tetrel clathrates and their elemental analogues, the clathrates are expected to undergo similar alloying reactions with lithium. However, previous work shows that in some situations, this is not the case. For example, with laboratory X-ray diffraction analysis, we found previously that the type I Ba₈Ge₄₃ (0 < y < 16) clathrates proceed through an amorphous pathway different from the crystalline phase transformations typically seen in lithiation of α-Ge. On the other hand, Si clathrates with a type II structure (Na₆Si₁₁₆, 0 < x < 24) reacted with Li in a similar manner as α-Si, however, if the Na occupancy of the cages was low, the voltage profile looked similar to that seen in the lithiation of amorphous Si. From these studies, it appears that the guest atom type and occupancy in the clathrates are important parameters for determining their electrochemical properties. However, the formation of amorphous phases in the reaction intermediates precludes the use of Bragg diffraction for structural characterization, necessitating local structure characterization methods to understand the nature of the amorphous phases during the lithiation of clathrates.

Atomic X-ray pair distribution function (PDF) analysis has proven to be a vital tool in elucidating the alloying pathways of tetrel elements with alkali metals. The PDF is derived from the total X-ray scattering pattern and provides information about the probability of finding atomic pairs at certain distances. This technique enables the local structure of amorphous and crystalline materials to be investigated, thus, allowing for a better picture of the lithiation intermediates to be attained. From this, differences in electrochemistry between clathrates and the elemental phases can be corroborated by differences in the structures formed during the lithiation reactions. In addition, PDF analysis with in situ heating of electrochemically obtained amorphous phases can illuminate how the amorphous phases that form are related to known crystalline phases. For example, heating experiments on electrochemically synthesized amorphous Li,Si showed that the materials crystallized to Li–Si phases, implying that the local structure in the systems was similar. Obtaining PDFs during this crystallization process could provide insights into how the amorphous structure relates to the crystalline structures.

In this work, the lithiation pathways of the type I clathrate Ba₈Ge₄₃ are investigated in more detail with ex situ synchrotron X-ray PDF analysis and X-ray diffraction and compared to α-Ge at similar states of lithiation. The PDF results confirm that Ba₈Ge₄₃ proceeds through an amorphous pathway during lithiation, with no atomic correlations associated with long-range order observed beyond 10–30 Å. This contrasts with the crystalline phase transformations observed during lithiation of α-Ge micrometer-sized particles, which are characterized by long-range order in both the XRD and PDF results. The local structure of the lithiated Ba₈Al₄₃Ge₃₀ clathrate, where Al is substituted on the Ge site, is found to be very similar to that seen in Ba₈Ge₄₃ after electrochemical reaction with lithium. In situ heating during XRD and PDF measurements was conducted to evaluate the thermal stability of the amorphous phases and identify crystallization events and the phases that formed. Heating of the lithiated clathrate materials caused the amorphous Li–Ba–Ge phases to crystallize to Li–Ge binary compounds at low temperatures (350–420 K), suggesting structural relationships between the amorphous and crystalline phases. Our results show that analysis of the lithiation pathway of type I Ba₈Ge₄₃ clathrate and comparison to the elemental analogue can provide an understanding of the effects of guest atoms and framework atoms on the lithiation pathways and their implications for Li-ion battery anodes.

2. EXPERIMENTAL METHODS

The Ba₈Ge₄₃ and Ba₈Al₄₃Ge₃₀ clathrates were synthesized and prepared into electrodes in a similar manner as described in our previous work. Electrodes were lithiated galvanostatically in half-cells with lithium metal as counter electrode and then extracted for ex situ measurements. Synchrotron X-ray pair distribution (PDF) measurements were conducted at the Diamond Light Source (Didcot, United Kingdom) at the I15-I dedicated PDF beamline with \( λ = 0.161669 \) Å. The atomic PDF, \( G(r) \) as defined by Farrow and Billinge, was generated from the total scattering data using PDFgetX3 within the xPDFsuite software package. Synchrotron X-ray diffraction measurements were performed at the P02.1 powder diffraction beamline at PETRA III at the Deutsches Elektronen-Synchrotron (DESY) with \( λ = 0.20733 \) Å. More detailed descriptions of the synthesis, electrochemical and synchrotron measurements, and PDF analysis are in the Supporting Information.

3. RESULTS

3.1. Ex Situ XRD and PDF Analyses. To evaluate the local and long-range order of the lithiation intermediates, the Ba₈Ge₄₃ and α-Ge electrodes were electrochemically lithiated to different compositions and then subjected to ex situ synchrotron XRD and PDF measurements at room temperature. Scanning electron microscopy (SEM) of the electrodes showed that the Ba₈Ge₄₃ sample was composed of irregularly shaped, micrometer-sized particles (2–10 μm) with some larger shards (>20 μm) and the α-Ge sample was composed of similarly irregularly shaped, micrometer-sized particles (Figure...
Therefore, we assume that there are no nanosize effects on the structural or electrochemical observations made here. The voltage profiles and differential charge \( (dQ/dE) \) plots for the first lithiation of \( \text{Ba}_8\text{Ge}_{43} \) and \( \alpha-\text{Ge} \) are shown in Figure 2 with consistency with the literature, we have chosen to only compare our results to those reported by Jung et al.,

wherein X-ray PDF was also used for analysis of micrometer-sized \( \alpha-\text{Ge} \). Following a reaction of 1.75 equiv of Li per Ge atom, a nominal composition referred to as \( \text{Li}_{1.75}\text{Ge} \) hereafter, the XRD pattern shows reflections corresponding to \( \alpha-\text{Ge} \) and a lithium germanide phase we have tentatively identified as \( \text{Li}_2\text{Ge}_2 \) with \( \text{R}3\text{m} \) symmetry, indicating a two-phase reaction. This is supported by a Rietveld refinement analysis (Figure S2a and Table S2) fitting to the \( \text{Li}_2\text{Ge}_2 \) and \( \alpha-\text{Ge} \) structures with phase fractions of 83 and 17%, respectively. In the work by Jung et al., Li\(_2\)Ge\(_2\) (reported as having P3\(_2\)2\(_1\) symmetry but this is likely an error as there is no such space group and it is likely intended to be P3\(_2\)12) was identified as a major intermediate phase during lithiation of \( \alpha-\text{Ge} \) and first-principles calculations suggested the energetic feasibility of this phase. \(^\text{53} \) Li\(_2\)Ge\(_2\) and Li\(_4\)Ge\(_3\) have very similar structures where Ge–Ge dumbbells are arranged parallel to one another with slightly different amounts of Li surrounding them. As a result, the XRD and PDF patterns are nearly identical, making them difficult to differentiate. Our XRD results show that further lithiation of \( \alpha-\text{Ge} \) to an overall composition of \( \text{Li}_{1.75}\text{Ge} \) resulted in the almost complete disappearance of the \( \alpha-\text{Ge} \) phase as well as a decrease and broadening of the reflections attributed to \( \text{Li}_2\text{Ge}_2 \). A reflection at \( 2\theta = 5.4^\circ \) was also present in the diffraction pattern at this stage of the lithiation in the work by Jung et al.,

and therein attributed to a disordered Li-Ge\(_2\)-like phase. The XRD pattern of \( \text{Li}_{1.75}\text{Ge} \) shows reflections corresponding to crystalline \( \text{Li}_4\text{Ge}_4 \) and was fit well by Rietveld refinement analysis (Figure S2b and Table S3) with a lattice parameter of 10.7763(4) Å, consistent with previously reported results and the PDF pattern obtained here.

The details of the PDF refinements for the lithiation of the \( \alpha-\text{Ge} \) samples in Figure 2b are shown in Figure S3. The PDF of the pristine Ge particles could be refined with a good fit to the \( \alpha-\text{Ge} \) phase with \( R_w = 8.2% \) (Figure S3a). Lithiation to a composition of \( \text{Li}_{1.75}\text{Ge} \) and a voltage of 0.28 V resulted in a PDF pattern containing \( \alpha-\text{Ge} \) correlations with a decreased intensity and the emergence of new correlations indicative of the presence of another phase. Refinement of the PDF was attempted using the structures of \( \alpha-\text{Ge} \) and several highly lithiated Li–Ge compounds commonly referred to as “dumbbell phases” (e.g., Li\(_2\)Ge\(_3\), Li\(_4\)Ge\(_2\), Li\(_6\)Ge\(_4\), and Li\(_4\)Ge\(_3\)), \(^\text{31,56,57} \) wherein parallel Ge–Ge dumbbells are surrounded by slabs of Li atoms. Calculated PDF patterns and crystal structures for these phases are presented in Figures S4 and S5, respectively. The best fit for the PDF from \( \text{Li}_{1.75}\text{Ge} \) (\( R_w = 19.1% \)) was obtained with 9.4 mol % \( \alpha-\text{Ge} \) and 90.6 mol % \( \text{Li}_2\text{Ge}_2 \) (Figure S3b and Table S4). Fitting with Li\(_4\)Ge\(_3\) and Li\(_6\)Ge\(_4\) instead of Li\(_2\)Ge\(_2\) resulted in similar phase fractions and \( R_w \) values (19.7% for Li\(_2\)Ge\(_2\) and 22.9% for Li\(_3\)Ge\(_2\)), which is consistent with the nearly identical arrangement of Ge–Ge dumbbells in these phases (see Figure S5a–c). At a composition of \( \text{Li}_{1.75}\text{Ge} \) and a voltage of 0.17 V, the best fit attained was from a combination of Li\(_2\)Ge\(_2\) (64.3%) and Li\(_3\)Ge\(_2\) (35.7%) (Figure S3c and Table S5) similar to the results reported by Jung et al.,

wherein multiple combinations of Ge–Ge dumbbell phases resulted in comparable fits. We found that fitting to Li\(_4\)Ge\(_3\) and Li\(_6\)Ge\(_4\) also resulted in decent fits (Table S5), which suggests that the Ge–Ge dumbbells are the dominant local features present in the electrode at this point in the lithiation process. The fact that the PDF for \( \text{Li}_{1.75}\text{Ge} \) can be fit comparatively to multiple phases, as well as the broadness of the reflections in the XRD

![Figure 2. Voltage profile and corresponding \( dQ/dE \) plot of the lithiation of \( \text{Ba}_8\text{Ge}_{43} \) and \( \alpha-\text{Ge} \) at 25 m\( \text{A} \)/g (corresponding to C-rates of C/41 for \( \text{Ba}_8\text{Ge}_{43} \) and C/55 for \( \alpha-\text{Ge} \)) with a voltage cutoff of 10 mV vs Li/Li\(^+\). The blue, orange, and green circles represent the compositions at which cells were disassembled for \textit{ex situ} PDF and XRD measurements.](https://dx.doi.org/10.1021/acs.chemmater.0c03641)
pattern, suggests that the structure is disordered but maintains a local structural motif of Ge–Ge dumbbells and isolated Ge atoms. At a composition of Li$_{3.75}$Ge, the PDF could be fitted to Li$_{15}$Ge$_4$ with $R_w = 22.9\%$ (Table S6), the structure of which consists of isolated Ge atoms surrounded by Li. The addition of a Li–Ge dumbbell phase resulted in a better fit ($R_w = 11.8\%$) with 85.7 mol $\%$ Li$_{15}$Ge$_4$ and 14.3 mol $\%$ Li$_7$Ge$_3$ (Figure S3d and Table S6). The modest improvement in the fitting suggests that the Li–Ge dumbbell phases, the primary structural motifs identified prior to this point, have been mostly consumed by the addition of more Li atoms and breaking of the Ge–Ge bonds in the structure. The observation of a dumbbell phase in the PDF of the fully lithiated Ge is consistent with the results from Jung et al.,$^4$ wherein it was suggested that Li$_{15}$Ge$_4$ could decompose after formation. Alternatively, there still could be residual Ge–Ge bonding in the material. A similar observation was made after lithiation of $\alpha$-Si,$^{40}$ where Li$_{15}$Si$_4$ was found to have crystallized after full lithiation but features from Si–Si dumbbells were still observed in the PDF.

The synchrotron XRD patterns of the Ba$_8$Ge$_{43}$ samples are shown in Figure 3c with reference patterns for Li$_{15}$Ge$_4$ and Ba$_8$Ge$_{43}$. The XRD pattern for the as-synthesized Ba$_8$Ge$_{43}$ clathrate shows a small amount of $\alpha$-Ge as the secondary phase, possibly resulting from Ba loss via evaporation during the clathrate synthesis. After addition of 1.75 Li per Ge atom (i.e., to a composition of Li$_{1.75}$Ba$_{0.19}$Ge and a voltage of 0.175 V versus Li/Li$^+$), the reflections corresponding to the Ba$_8$Ge$_{43}$ phase decrease in intensity without any new reflections appearing, confirming that the Ba$_8$Ge$_{43}$ converts to an amorphous phase upon lithium insertion, consistent with our previous observations by laboratory XRD.$^{25}$ Subsequent lithiation to a composition of Li$_{2.75}$Ba$_{0.19}$Ge results in a further decrease in the Ba$_8$Ge$_{43}$ reflections and the appearance of reflections corresponding to Li$_{15}$Ge$_4$. At this point in the reaction, the cell has reached a voltage of 0.11 V versus Li/Li$^+$ (Table S1), which is below the potential where $\alpha$-Ge can be converted to Li$_{15}$Ge$_4$.$^4$ Therefore, we attribute the origin of Li$_{15}$Ge$_4$ to the reaction of Li with the $\alpha$-Ge impurity phase, not the clathrate phase. Upon further lithiation to Li$_{3.75}$Ba$_{0.19}$Ge, the XRD pattern only shows reflections attributed to Li$_{15}$Ge$_4$ formed from the impurity phase reaction, confirming that the lithiated clathrate phase is amorphous.

The corresponding PDF patterns for Ba$_8$Ge$_{43}$ at different degrees of lithiation are shown in Figure 3d. The X-ray PDF measurement is sensitive to the atomic scale correlations between pairs of atoms, giving insight into the local structuring of Ge, Li, and Ba atoms. The intensity of the correlations is

![Figure 3. (a, c) Synchrotron XRD ($\lambda = 0.20733$ Å) and (b, d) PDF ($\lambda = 0.161669$ Å) results for (a, b) pristine $\alpha$-Ge (PDF only), Li$_{1.75}$Ge, Li$_{2.75}$Ge, and Li$_{3.75}$Ge and (c, d) pristine Ba$_8$Ge$_{43}$, Li$_{1.75}$Ba$_{0.19}$Ge, Li$_{2.75}$Ba$_{0.19}$Ge, and Li$_{3.75}$Ba$_{0.19}$Ge.](https://dx.doi.org/10.1021/acs.chemmater.0c03641)
dependent on the atomic number and concentration of the elements, meaning that Ge correlations (Ge–Ge, Ge–Li, and Ge–Ba) are expected to contribute the most to the observed patterns in the clathrate. Refinement of the PDF for the pristine clathrate showed that there was a minimal amount (4.4 mol %) of α-Ge as a secondary phase (Figure S6a and Table S7), confirming the XRD results. In the low ρ region, the PDF shows correlations at ca. 2.51, 3.50, 3.96, and 5.92 Å (Figure 3d). Inspection of the simulated partial PDFs (Figure S4a) shows that these correlations correspond to direct Ge–Ge bonding, Ba–Ge correlations, next nearest neighbor Ge–Ge distances, and third nearest neighbor Ge–Ge distances, with minimal contributions from Ba–Ba correlations due to the large separation distance of the Ba atoms (~6 Å) in the clathrate structure (Figure S4a).

By observing how these correlations change with increasing amounts of lithium addition to Ba$_8$Ge$_{43}$, the average local structure of the lithiated intermediate phases can be determined. After addition of 1.75 Li per Ge, the PDF shows that the correlations decrease in the intensity relative to the pristine sample. Significant changes are seen at low ρ values, while the pattern at high ρ values (10–30 Å) resembles that for the pristine clathrate. Refinement of the pattern to the Ba$_8$Ge$_{43}$ structure from 10 < ρ < 30 Å confirms that the high ρ correlations match reasonably well with those for the pristine clathrate (Figure S6b and Table S7). The difference curve of the refinement from 2 < ρ < 30 Å reveals correlations at 2.62, 3.42, and 4.50 Å (Figure S6c) but no other features at ρ > 10 Å, suggesting that these low ρ correlations arise from an amorphous, lithium-containing phase that coexists with the pristine clathrate.

Upon addition of lithium to reach the composition of Li$_{2.75}$Ba$_{0.19}$Ge (at 0.11 V vs Li/Li$^+$), it is apparent that the Ba$_8$Ge$_{43}$ starting material has been completely reacted and the PDF lacks noticeable features at ρ > 10 Å, indicating the absence of long-range order. The PDF for Li$_{2.75}$Ba$_{0.19}$Ge (Figure 3d) shows features similar to those in the pristine clathrate, crystalline Ba$_8$Ge$_{43}$ and the amorphous Ba$_8$Ge$_{43}$ after delithiation (Figure S7d) show features with similar peak positions, implying that they have very similar local structures. This suggests that although the clathrate structure undergoes an amorphous phase transformation after addition of lithium, the local structure of the subsequent amorphous phase after lithium is removed resembles that seen in the original crystalline structure. In other words, despite the crystalline-to-amorphous transition, the local structural features of the clathrate are retained after one cycle. The Al-substituted clathrate, Ba$_8$Al$_{16}$Ge$_{30}$, was also subjected to PDF analysis after full lithiation to an amount of 1.9 Li per (Al + Ge) atom. The voltage profile and corresponding dQ/dE plot are presented in Figure S8 along with the PDF refinement (Table S8) of the pristine Ba$_8$Al$_{16}$Ge$_{30}$ and PDF after the reaction with 1.9 Li to a total composition of Li$_{0.9}$Ba$_{0.1}$Al$_{0.35}$Ge$_{0.65}$. Consistent with our previous work, the Al-substituted clathrate reacted at a lower voltage of 0.06 V versus Li/Li$^+$ compared to 0.2 V of Ba$_8$Ge$_{43}$ but displayed a lower capacity than that for Ba$_8$Ge$_{43}$. The PDF plot for the most lithiated composition (Figure S8c) showed that a significant amount of crystalline fraction was present, which could be fit well to the pristine Ba$_8$Al$_{16}$Ge$_{30}$ structure, meaning that the original clathrate phase was not fully reacted. Similar to the refinement for Li$_{2.75}$Ba$_{0.19}$Ge (Figure S6c), the difference pattern of the refinement for Li$_{1.8}$Ba$_{1.7}$Al$_{0.35}$Ge$_{0.65}$ revealed an amorphous phase with correlations at 2.64, 3.45, and 4.57 Å, suggesting the formation of a similar amorphous phase as that seen in the lithiation of Ba$_8$Ge$_{43}$. This suggests that the lithiation of Ba$_8$Al$_{16}$Ge$_{30}$ proceeds in a similar manner to Ba$_8$Ge$_{43}$; however, the presence of Al in the amorphous phase results in a lower reaction voltage and capacity compared to Ba$_8$Ge$_{43}$.

3.2. In Situ Heating PDF Studies. As described in the previous section, visual comparison of the PDFs for Ba$_8$Ge$_{43}$ and α-Ge after delithiation shows similarities in peak positions at low ρ values (~5 Å), suggesting similar local structures for the Li and Ge atoms. However, the assignment of the broad peaks from 6 to 10 Å in the lithiated clathrate samples is less obvious...
and could originate from Ge–Ge, Ba–Ge, and Li–Ge correlations. To identify the origin of these correlations, variable-temperature PDF measurements were conducted to evaluate the lithiated Ba$_8$Ge$_{43}$ structures upon moderate heating and their relationship to the original amorphous structure. Figure 4a,b shows PDFs of Ba$_8$Ge$_{43}$ lithiated to compositions of Li$_{2.75}$Ba$_{0.19}$Ge and Li$_{3.75}$Ba$_{0.19}$Ge acquired during in situ heating from room temperature to 450 and 420 K, respectively. The corresponding false colormaps are shown underneath in Figure 4c,d, where the light blue and dark blue shadings indicate regions of higher and lower intensities, respectively. For Li$_{2.75}$Ba$_{0.19}$Ge (Figure 4a,c), there is little change in the PDF pattern until reaching a temperature of 410 K, where the broad peaks from 6 to 10 Å begin to sharpen and noticeable long-range correlations begin to appear out to 30 Å, indicating that crystallization is occurring. After heating to 450 K, the peaks sharpen further, suggesting a higher degree of ordering. In the case of Li$_{3.75}$Ba$_{0.19}$Ge (Figure 4b,d), crystallization occurred at a lower temperature of 350 K, as seen by the appearance of correlations at $r > 10$ Å. A similar phenomenon was observed in the in situ PDFs obtained during lithiation of Ge nanoparticles, wherein a single broad peak around 4.5–4.6 Å was observed as opposed to the split peak seen in the PDF of dumbbell phases. The broad correlations from 6 to 10 Å in the amorphous sample become sharper and more intense after the heat treatment, suggesting that these interatomic distances become more ordered upon annealing. Refinement of the pattern obtained

![Figure 4](https://dx.doi.org/10.1021/acs.chemmater.0c03641)

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after heating to the structure of Li7Ge2 resulted in a fit with $R_w = 55\%$, which was improved to $R_w = 28.6\%$ by restricting the fit range to 6–30 Å to exclude the Ba−Ge correlation at 3.44 Å (Figure S11a,b and Table S9). The fairly good fit at higher $r$ values suggests that the long-range order in the Li2.75Ba0.19Ge phase after heating to 450 K is similar to that found in Li7Ge2, implying the presence of dumbbells and isolated Ge atoms. The largest discrepancy in the pattern was at low $r$ values (2–6 Å), suggesting the presence of an amorphous phase probably related to the Ba present in the sample. The correlations around 6–10 Å are fit well by the Li5Ge2 refinement, meaning that the broad peaks in the lithiated sample prior to heating are related to the correlations in the crystalline phase formed after heating. In the Li5Ge2 PDF pattern, the correlations from 6 to 10 Å represent the next nearest neighbor Ge−Ge correlations (either between single atoms or dumbbells), as illustrated in Figure S10b. Since major correlations die out past 10 Å in the unheated Li2.75Ba0.19Ge sample, it can be presumed that a similar, albeit disordered, structuring of Ge atoms is present in the amorphous sample.

Figure 5. (a) Comparison of PDFs of Li2.75Ba0.19Ge: unheated (blue), heated to 450 K (pink), and lithiated and unheated α-Ge (light blue). (b) Comparison of PDFs of Li3.75Ba0.19Ge: unheated (blue), heated to 420 K (pink), and lithiated and unheated α-Ge (light blue). Enlarged regions of $2 < r < 10$ Å are shown below. Patterns are y-offset for clarity.

Figure 6. (a, b) Synchrotron XRD results obtained during in situ heating XRD patterns (top) and false colormap (bottom) obtained during heating ramp to 480 K for (a) fully lithiated Ba8Ge43 (Li5.75Ba0.19Ge) and (b) fully lithiated α-Ge (Li5.75Ge). (c) XRD pattern (top) and false colormap (bottom) of Li3.75Ba0.19Ge during extended heating at 480 K.
In the PDFs of the fully lithiated samples shown in Figure 5b, the correlations from 2 to 5 Å in the clathrate-derived samples have three main correlations, while there are only two in the Li15−xGe sample (Figure 5b) due to the absence of Ba–Ge bonding. The broad correlations from 6 to 15 Å in Li1.75Ba0.19Ge become sharper after heating, an indication of increased ordering, suggesting that the amorphous and crystalline structures are related. On the other hand, in situ PDF measurements during heating from 310 to 420 K for the fully lithiated α-Ge sample (composed predominantly of Li1.5Ge) were also conducted; however, the pattern showed little change, indicating temperature stability over this range (Figure S12).

Refinement of the PDF from Li1.75Ba0.19Ge after heating to 420 K showed that the high r features of the PDF could be reasonably captured by the Li1.5Ge phase (Figure S11c and Table S9), suggesting that the long-range order present is from Li1.5Ge correlations. All of the PDFs display a peak around 4.72 Å, which is attributed to the combination of nonbonded Ge–Ge correlations (centered at 4.68 Å) and Li–Ge correlations (shoulder at ∼5 Å) found in the crystalline Li1.5Ge phase (see calculated PDF in Figure S10c). The significant discrepancy in the difference curve of the refinement for the heated sample (Figure S11c) suggests the presence of another phase. Due to the decrease in the intensity of the Ba–Ge peak at 3.44 Å after heating, the other phase is likely a Ba-containing amorphous phase. Similar to the Li1.75Ba0.19Ge sample, the fact that the features from 6 to 10 Å in the PDF of the heated Li1.75Ba0.19Ge sample can be connected to correlations from the Li1.5Ge crystalline phase suggests that the original features in the unheated sample can be assigned to similar structural features as those found in the crystalline phase.

3.3. Thermal Stability and Crystalline Phase Evolution during Heating. To probe the thermal stability and phase evolution of the amorphous phases formed during electrochemical lithiation of the Ba6Ge4 clathrate, in situ XRD heating experiments were conducted. A heating ramp from 300 to 480 K was performed in 20 K intervals with a 6 min hold at each temperature and scans taken every 2 min. While heating the amorphous Li1.75Ba0.19Ge sample (Figure 6a), no changes to the pattern were seen until reaching 380 K, at which point reflections corresponding to Li1.5Ge4 started to appear, consistent with the PDF in situ heating results. There were few additional changes to the XRD pattern with continuous heating up to 480 K. Rietveld refinement analysis showed that the reflections after heating fit well to the Li1.5Ge4 structure model (Figure S13) and showed a linear increase in a lattice parameter from 10.8119(13) at 360 K to 10.8350(5) at 480 K. In contrast, when performing a similar heat treatment for the Li1.75−xGe derived from α-Ge, the XRD pattern transformed from Li1.5Ge4 into a series of different reflections between 420 and 440 K (Figure 6b).

To further probe the phase transformations in Li1.75−xBa0.19Ge, the sample was held at 480 K and XRD scans were collected every 2 min. As shown in Figure 6c, many small reflections and a major reflection at 2θ = 3.9° started to appear with further heating as the Li1.5Ge4 reflections decreased in intensity. Figure 7 compares the XRD patterns for Li1.75−xGe and Li1.75Ba0.19Ge after heating at 480 K for 6 and 396 min (6.6 h), respectively, with identification of the reflections from crystalline phases from literature. In the Li1.75Ba0.19Ge sample, the Li1.5Ge4 transformed to numerous crystalline Li–Ge phases and a

Figure 7. Synchrotron XRD patterns of Li1.75Ba0.19Ge after heating at 480 K for 6.6 h and Li1.75Ge after heating ramp to 480 K.

Li–Ba–Ge phase with extended heating at 480 K. The phases identified include LiGe, Li7Ge2, Li7Ge3, Li9Ge4, Li15Ge4, and Ba3LiGe7. A plot with the reference patterns of the identified compounds is presented in Figure S14. The main reflection for Ba3LiGe7 (at 2θ = 3.9°) appeared after around 2 h and continued to grow during the 6.6 h hold time, while the reflections from Li1.5Ge4 transformed completely into the Li–Ge phases after 4 h. In contrast to the Ba-containing sample, the Li1.75−xGe sample needed less heating to transform to a similar set of Li–Ge phases. From comparison to the reference patterns (Figure S14), the Li1.75−xGe sample (which showed Li1.5Ge4 reflections at room temperature) appeared to transform into LiGe, Li7Ge2, Li7Ge3, Li9Ge4, and Li15Ge4 after 1 h heating ramp from 300 to 480 K. Notably, no reflections from Ba3LiGe7 were present, consistent with the presumed composition of the sample. The similar reaction products observed in both heating experiments suggest that Li1.5Ge4 decomposition underwent a similar pathway in both Li1.75−xBa0.19Ge and Li1.75−xGe samples; however, the time needed to achieve the decomposition of Li1.5Ge4 was longer for the sample derived from lithiation of the Ba6Ge4 clathrate, suggesting a difference in the reaction kinetics.

The thermal decomposition of Li1.5Ge4 is unexpected as it is a thermodynamically stable phase and melts congruently at 750 °C. Our results show that Li1.5Ge4 decomposed into Li–Ge dumbbell phases at 150 °C, implying that the Li content decreased to the extent that Li1.5Ge4 was not the preferred phase. Previously, heating studies on electrochemically synthesized Li15Si4, which is metastable, showed that Li15Si4 decomposed to Li2Si and Li7Si6 instead of Li4Si6 and Li9Si6 as expected based on the phase diagram. The authors hypothesized that reactions between Li and the solid electrolyte interphase (SEI) at the electrode/electrolyte interface or with the electrode binder could reduce the overall Li available in the system to react with Si. This is supported by a study showing that Li4Si6 synthesized via ball milling (i.e., no SEI present) decomposed into the expected products suggesting that the residual electrolyte and SEI play an important role in the thermal stability of the material. In this work, the in situ heating experiments were conducted in sealed capillaries made of borosilicate, which could also react with Li. However, conducting the same heat treatment using a Ta boat under argon resulted in similar XRD patterns (Figure S15), suggesting that this was not a factor. We conclude that the thermal decomposition of Li1.5Ge4 at 150 °C is likely related to reactions with the SEI, binder, or residual electrolyte,
causing a decrease in the net Li content and leading to the formation of Li–Ge dumbbell phases. Interestingly, the decomposition of Li$_{15}$Ge$_4$ in the clathrate-derived Ba-containing phase takes place over a longer period of time than the decomposition of Li$_{13}$Ge$_4$ derived from lithiation of α-Ge, implying that the presence of Ba slows these Li–Ge phase transformations.

Considering the final state of the system after the heat treatment, the presence and crystallization of Ba$_2$LiGe$_3$ from the Li$_{15}$Ge$_4$ sample indicate that the initial system was far from equilibrium. There are few reported crystalline phases in the Li–Ba–Ge system; thus, when Ba is evenly dispersed between Li and Ge atoms in the amorphous phase, the kinetic barrier to form the set of crystalline phases with the lowest energy is high as this requires a large degree of Ba migration. In addition, the Ba$_2$LiGe$_3$ phase features hexagonal Ge rings (Figure S5f) that would require Ge–Ge bond formation, which is expected to have a higher energy barrier than solely Li rearrangements. Only after 2–3 h of heating at 480 K does Ba and Ge have enough time to coalesce to form Ba$_2$LiGe$_3$, the presumed Ba-containing equilibrium phase at this composition.

Based on the results from the PDF, XRD, and in situ heating experiments, the lithiation of Ba$_8$Ge$_{43}$ appears to be heavily influenced by the presence of Ba in the reaction intermediates. In contrast to the crystalline phase transformations for α-Ge, the clathrate proceeds through lithiation by formation of amorphous intermediates with local structures similar to those in Li–Ge crystalline phases. The PDF heating experiments demonstrate that the amorphous phases that form initially after lithiation have structural relationships to the Li–Ge crystalline phases, evidenced by the ease in which they undergo crystallization at low temperatures. In situ XRD heating experiments for the Li$_{13}$Ba$_{0.19}$Ge and Li$_{15}$Ge$_4$ samples show that the Li$_{15}$Ge$_4$ phase, which is formed either electrochemically or by heating the amorphous Ba-containing phase, is unstable at 480 K and decomposes to other Li–Ge phases.

4. DISCUSSION

4.1. Lithiation Mechanism of Ba$_8$Ge$_{43}$. Overall, the lithiation of Ba$_8$Ge$_{43}$ is influenced by the presence of Ba in the reaction intermediates and results in an amorphous lithiation pathway. From the PDF analysis and in situ heating experiments, we determine that the amorphous reaction intermediates of Ba$_8$Ge$_{43}$ share a local structure like that of the Li–Ge crystalline phases. Therefore, we propose that the Ba atoms act as “pillars” to prevent the bulk nucleation and growth of Li–Ge crystalline phases during lithiation by physically separating smaller “pockets” of Li–Ge atoms that have a local structure similar to that in the Li–Ge phases.

Figure 8 illustrates the proposed lithiation pathway for the Ba$_8$Ge$_{43}$ clathrate. Initially, the pristine clathrate has Ba atoms distributed evenly throughout the Ge cage matrix (Figure 8a). As Li enters the system, a two-phase reaction begins with nucleation of an amorphous phase, which is presumed to have similar composition and structure as those seen in the crystalline Li–Ge dumbbell phases. However, the long-range parallel alignment of the Ge–Ge dumbbells (see, e.g., Figure S5a–c) is prevented due to the presence of the Ba atoms.

Therefore, the amorphous phase is proposed to consist of Ge–Ge dumbbells surrounded by Li atoms and located in between Ba atoms. This is depicted in Figure 8b, which shows a two-phase interface between an amorphous phase (with randomly oriented Ge–Ge dumbbells) and the pristine Ba$_8$Ge$_{43}$. As more Li atoms enter the system, the pristine clathrate continues to be consumed and is eventually completely converted to a Li–Ba–Ge amorphous phase. The exact composition is not known, but our results suggest that the conversion is complete by the time the total composition reaches Li$_{13}$Ba$_{0.19}$Ge. As seen in the PDF plot of Li$_{13}$Ba$_{0.19}$Ge (Figure 3d), the local order extends to ~10 Å, suggesting that the regions of Li–Ge order (indicated by the circled region in Figure 8c) are on this length scale. Considering that the Li$_{15}$Ba$_{0.19}$Ge sample crystallized into a structure resembling Li$_2$Ge$_2$ during the in situ heating measurement (Figure 4a), we expect that both dumbbells and isolated Ge atoms are present at this point in the lithiation.

With the incorporation of more Li atoms, Ge–Ge dumbbells are broken up in favor of isolated Ge atoms surrounded by Li, as depicted in Figure 8d for the composition Li$_{15}$Ba$_{0.19}$Ge. At this composition, the local structuring extends further to ~15 Å based on the PDF analysis. This increase suggests the growth of the Li–Ge pocket of local order, which is consistent with the expected volume expansion as more Li atoms enter the system. At this stage, the local structure is similar to that in the Li$_{15}$Ge$_4$ phase, which is supported by the crystallization of the amorphous phase to Li$_{15}$Ge$_4$ at 350 K. We note that more detailed modeling of the amorphous phases presented here would require the reverse Monte Carlo method and/or density functional theory calculations and will be reserved for future work.
We conclude that the lithiation pathway for Ba₈Ge₄₃ follows an amorphous, metastable phase evolution because of the kinetic differences between the host atoms and the electroactive Li atoms. This is similar to the lithiation of α-Si, which goes through an amorphous pathway instead of crystallizing to the equilibrium Li–Si phases. Because the Si atoms have low mobility at room temperature, phases that rely on Li movement are kinetically favorable. Ge has higher mobility at room temperature compared to Si, which accounts for why Li–Ge crystalline phases are kinetically favored to form in some circumstances. In the case of Ba₈Ge₄₃, the mobility of Ba is limited at room temperature, which kinetically traps Ba in the amorphous phase and prevents the formation of a more thermodynamically favorable (i.e., crystalline) phase at these compositions. This conclusion is supported by the in situ XRD heating experiments showing the formation of Ba₃LiGe₄ after heating at 480 K for multiple hours. On the basis that the Ba₃LiGe₄ phase is more Ba dense than the Li–Ba–Ge amorphous phase formed after lithiation, a significant amount of Ba migration is needed for Ba₃LiGe₄ to form. Thus, the presence of Ba between the Li–Ge pockets kinetically frustrates the phase landscape at room temperature, resulting in the formation of amorphous phases.

The fact that Ba₈Ge₄₃ undergoes this amorphous lithiation pathway has several effects on its electrochemical profile when compared to that of α-Ge. Most notably, the voltage of the two-phase reaction for the clathrate is 0.1 V lower than that of the lithiation of α-Ge (Figure 2). It is well known that amorphous phases will have higher energies than crystalline phases at the same composition. Because of the dependence of the chemical potential on the energy of the system, the phase with a higher energy will have a lower voltage. Considering that the local environment around Li in the Li–Ba–Ge amorphous phase is similar to that in the Li–Ge crystalline phases, it is expected that the energy will be higher for the amorphous phase, which is consistent with the lower reaction voltage seen for Ba₈Ge₄₃. The presence of Ba in the amorphous phase is expected to further increase the energy of the system due to the donation of electrons from Ba to Ge and thus increasing the electron density on Ge. Ab initio calculations would be needed to understand the contributions of these two separate effects.

In addition to the lower voltage, the lithiation of Ba₈Ge₄₃ is characterized by a single voltage plateau in contrast to the two plateaus for α-Ge. Voltage plateaus originate from the presence of two phases with discrete Li compositions. However, due to the amorphous nature of the intermediates formed upon lithiation of Ba₈Ge₄₃, the crystalline Li–Ge phases typically seen during lithiation of α-Ge are no longer kinetically accessible, leading to a wider range of possible structures with variable Li content for the clathrate case. After complete conversion of Ba₈Ge₄₃ to a Li–Ba–Ge amorphous phase via a two-phase reaction, the Li content in the amorphous phase is allowed to vary continuously as evidenced by the sloped voltage profile, which is indicative of a solid solution mechanism. We liken the lithiation mechanism of Ba₈Ge₄₃ to be more similar to that in α-Si, which first shows a voltage plateau corresponding to a two-phase transformation between the diamond structure and a highly lithiated amorphous phase; after the full conversion of α-Si, it can be reversibly cycled between amorphous Si and amorphous Li–Si phases. However, in the case of Ba₈Ge₄₃, bulk Li₄Ge₄ is not formed at the end of lithiation due to the presence of the Ba atoms impeding the long-range order of the Li–Ge pockets.

The voltage profile and corresponding PDF of Li₁₅Ba₀.₁₉Ge after delithiation both suggest that the material remains amorphous after the lithium is removed (Figure S7). The voltage profile from delithiation of Li₁₅Ge₄ derived from micrometer-sized α-Ge is characterized by two plateaus attributed to discrete phase transformations between Li₁₅Ge₄ and Li₄Ge₃ at 0.41 V and Li₄Ge₃ to amorphous Ge at 0.62 V. In contrast, the delithiation of Li₁₅Ba₀.₁₉Ge shows a single broad peak at 0.3 V in the dQ/dE plot with a sloped profile, implying solid solution behavior rather than discrete phase transformations. The PDF of the fully delithiated Ba₈Ge₄₃ has similar peak positions to the PDF of the pristine clathrate phase (Figure S7d), suggesting that after the removal of Li, a cage-like structure is preserved in this amorphous phase. Future PDF measurements will be needed to further investigate the delithiation mechanism and how the structure evolves with further lithiation cycles.

**4.2. Implications for Li-Ion Battery Anodes.** Our results indicate several clear differences in fundamental electrochemical and structural properties for the Ba₈Ge₄₃ clathrate compared to α-Ge, which could have advantages in the context of potential use scenarios as anodes in lithium-ion batteries. It is important to note that the crystalline clathrate phase would serve as a precursor to an amorphous phase, which would remain amorphous in subsequent cycles (similar to the lithiation/delithiation of diamond Si). The first potential advantage is that lithiation of Ba₈Ge₄₃ proceeds through amorphous solid solutions as opposed to crystalline phase transformations, and bulk crystallization of the thermodynamically stable Li₁₅Ge₄ phase is inhibited due to the presence of Ba atoms. Generally, avoiding transformations between crystalline phases can be beneficial for cycling stability by decreasing the tendency for particle damage due to localized stresses, large volume changes, and/or crystallography-related anisotropy in the lithiation strain. Tetrel clathrates represent a wide design space where the materials can form with different guest atoms, frameworks, and framework substitutions. Herein, we demonstrate how the presence of the Ba atoms prevents the crystallization of Li–Ge phases during electrochemical lithiation. However, there are many more possible compositions of clathrates. For example, type I Ge clathrates have been reported to form with Na₆.
The reaction voltage and the suppressed crystallization of Li phases, although future work will need to be conducted to further understand if electrochemical amorphization is unique to the Ba-containing clathrates and which structural conditions result in amorphization.

5. CONCLUSIONS

The lithiation pathway of the type I clathrate Ba₈Ge₄₃ was investigated with synchrotron PDF and XRD analyses. Based on the PDF results, Ba₈Ge₄₃ proceeds through an amorphous phase transition without formation of any detectable crystalline phases, although future in situ electrochemical studies would be needed to confirm this. Analysis of the PDFs of Ba₈Ge₄₃ after lithiation shows that the local order extends to ∼10 to 15 Å with similar structural features as those in crystalline Li–Ge phases of analogous composition. This is supported by in situ heating experiments showing that the amorphous Li–Ba–Ge phases crystallized into Li–Ge crystalline phases of similar composition. PDF analysis of Ba₁₁₆Ge₃₀ after lithiation showed that the clathrate transformed to an amorphous phase similar to the one formed upon lithiation of Ba₈Ge₄₃, suggesting that the substitution of Ge with Al on the clathrate framework has little effect on the local structure changes during the reaction.

We propose that the amorphous pathway seen in these clathrates is caused by the presence of the Ba atoms, which act as “pillars” to prevent the crystallization of the Li–Ge domains. The Ba atoms have low mobility at room temperature and are unable to reorder to the more thermodynamically favorable crystalline phases, resulting in a metastable pathway where only significant Li migration is possible. The amorphous reaction mechanism results in a single-phase reaction with a decreased reaction voltage and the suppressed crystallization of Li–Ge phases, which could have beneficial effects on cell performance. Characterization of the clathrate electrodes after lithiation and delithiation shows that despite the crystalline-to-amorphous transition, the local structural features of the original clathrate structure are retained after cycling. Thus, tetrel clathrates have potential use as precursors to atomically mix elements that form an amorphous alloying phase with desirable electrochemical properties. The wide design space for clathrates provides opportunities for optimizing alloying anodes by modification of their initial structure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c03641.

Detailed experimental procedures for the synthesis of type I Ge clathrates, electrochemical measurements, sample preparation for synchrotron measurements, pair distribution function analysis, powder X-ray diffraction, and scanning electron microscopy; supporting tables with the measured voltages and capacity for each sample after electrochemical lithiation; Rietveld refinement parameters for lithiated α-Ge; PDFgui refinement parameters for pristine, lithiated, and heated samples; supporting figures with SEM images of electrodes; plots of PDF refinements for pristine, lithiated, and heated samples; calculated total and partial PDF patterns and crystal structures of reference structures; electrochemical data of Ba₈Ge₄₃ and α-Ge after one full cycle; electrochemical data and PDFs of Ba₁₁₆Ge₃₀ after lithiation; comparison of total scattering structure function for samples after lithiation and heating; assignment of Ge–Ge correlation distances found in the PDF to distances between Ge atoms in selected dumbbell phases for Li₁₅Ge₄ and Li₇Ge₃, and Li₁₅Ge₄; Rietveld refinements of XRD patterns for Li₁₅Ge₄Ba₉₀₅Ge from in situ heating measurements and temperature-dependent lattice parameter for the formed Li₁₅Ge₄; variable-temperature PDF during in situ heating from 310 to 420 K of Li₁₅Ge₄; XRD patterns of Li₁₅Ge₄Ba₉₀₅Ge and Li₁₅Ge₄ after heating to 480 K and phase identification; and comparison of ex situ laboratory powder XRD pattern of Li₁₅Ge₄Ba₉₀₅Ge after heating in Ta versus glass capillary (PDF).

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