

A Low-Temperature Growth Mechanism for Chalcogenide Perovskites

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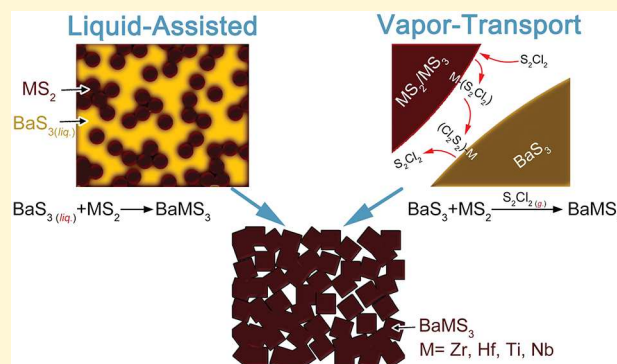


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ABSTRACT: Chalcogenide perovskites have attracted increasing research attention in recent years due to their promise of unique optoelectronic properties combined with stability. However, the synthesis and processing of these materials has been constrained by the need for high temperatures and/or long reaction times. In this work, we address the open question of a low-temperature growth mechanism for BaZrS₃. Ultimately, a liquid-assisted growth mechanism for BaZrS₃ using molten BaS₃ as a flux is demonstrated at temperatures ≥ 540 °C in as little as 5 min. The role of Zr-precursor reactivity and S_{2(g)} on the growth mechanism and the formation of Ba₃Zr₂S₇ is discussed, in addition to the purification of resulting products using a straightforward H₂O wash. The extension of this growth mechanism to other Ba-based chalcogenides is shown, including BaHfS₃, BaNbS₃, and BaTiS₃. In addition, an alternative vapor-transport growth mechanism is presented using S₂Cl₂ for the growth of BaZrS₃ at temperatures as low as 500 °C in at least 3 h. These results demonstrate the feasibility of scalable processing for the formation of chalcogenide perovskite thin-films.



1. INTRODUCTION

Chalcogenide perovskites have gained recent research attention due to their potential as Pb-free, inorganic perovskite semiconductors. Compared to hybrid halide perovskites, such as CH₃NH₃PbI₃, these chalcogenide perovskites have significantly improved structural stability.^{1–3} Compared to oxide perovskites, the inclusion of S or Se as anions reduces the band gap for applications with visible and NIR light. BaZrS₃ in particular has been a primary focus in recent research, possessing promising optoelectronic properties (primarily identified from theory) including band gap values relevant for photovoltaics, an extraordinarily high absorption coefficient, tolerance to deep defects, strong dielectric screening, favorable phonon properties, and desirable (isotropic) electron mobility for efficient charge transport.^{3–9} Additionally, BaZrS₃ is comprised of nontoxic and earth-abundant constituents.

However, the majority of reported syntheses require high temperatures and/or long reaction times.^{4,5} Such reactions have kinetic limitations—for example, due to solid-state growth techniques—and/or thermodynamic limitations—for example, using highly stable oxide precursors. BaZrS₃ powders were reported as early as 1957 by Hahn and Mutschke¹⁰ via annealing of binary sulfides (BaS, ZrS₂) at 900 °C for 2 weeks. Alternatively, Clearfield¹¹ reported the reaction of BaZrO₃ with CS₂ at 950–1200 °C in 1963. Similar reactions were reported over the following 60 years using mixtures of BaS, ZrS₂,

BaCO₃, ZrO₂, and BaZrO₃. Recent progress in the synthesis of BaZrS₃ thin films is summarized in the following reactions. Márquez et al.¹² and Wei et al.¹³ formed BaZrS₃ via pulsed laser deposition (PLD) using a Ba–Zr–O target followed by annealing in a reactive sulfur species at ca. 800–1050 °C. Alternatively, Yu et al.¹⁴ used a Ba–Zr–S target in PLD followed by an anneal with CS₂ at 900 °C, and Surendran et al.¹⁵ grew an epitaxial thin film of BaZrS₃ from a BaZrS₃ target using PLD in an H₂S environment at 700–850 °C. Comparotto et al.¹⁶ formed BaZrS₃ via cosputtering of Ba–Zr–S followed by sulfur-annealing from 650–900 °C. Sadeghi et al.¹⁷ reported BaZrS₃ grown via molecular beam epitaxy (MBE) at 900 °C. Gupta et al.¹⁸ reported BaZrS₃ via sulfurization of BaZrO₃ at 1050 °C. While high-quality films were obtained in all these reports, oxidation is commonly reported and many of the methods require specialized equipment. Practical fabrication of BaZrS₃ and other chalcogenide perovskites will require more moderate fabrication temperatures and shorter reaction times for cost-effective

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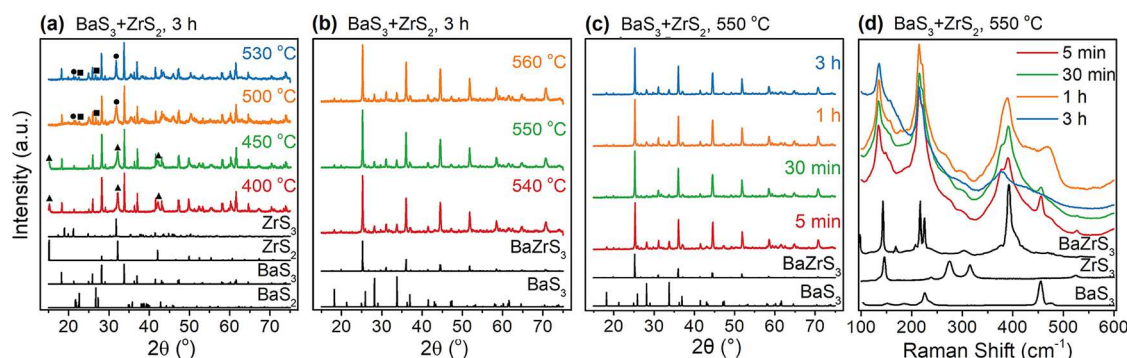


Figure 1. XRD patterns of samples from $\text{BaS}_3 + \text{ZrS}_2$ reactions (a) for 3 h at 400 °C, 450 °C, 500 °C, and 530 °C (triangles label ZrS_2 , circles label for ZrS_3 , and rectangles label BaS_3); (b) for 3 h at 540 °C, 550 °C, and 560 °C; and (c) at 550 °C for 5 min, 30 min, 1 h, and 3 h. (d) Raman spectra of samples from the reaction times in (c). Reference XRD patterns are shown in black labeled by compound (BaS_3 PDF 01-071-0377, BaS_3 PDF 01-073-1177, ZrS_2 PDF 01-089-4822, ZrS_3 PDF 01-080-0926, BaZrS_3 PDF 01-073-0847). Reference Raman spectrum for BaZrS_3 is from Gross et al. (measured at 14 K),¹⁹ while ZrS_3 and BaS_3 are measured on our synthesized precursors (see SI).

manufacturing and the use of traditional substrates, such as glass.

Preparation of BaZrS_3 at lower temperatures has drawn recent attention, though this research is still at an early stage. We recently reported the synthesis of BaZrS_3 nanoparticles at 330 °C,²⁰ with similar results reported by Zilevu et al.²¹ Such nanoparticles are yet to be processed into device-grade films. Turnley et al.²² reported the solution-based synthesis of BaZrS_3 via sulfurization of an organometallic Ba precursor and ZrH_2 at temperatures above 550 °C; however, continuous, dense films were not possible in this approach. While these experiments demonstrate the ability for BaZrS_3 to form at moderate temperatures, little is known about the low-temperature growth mechanism. For instance, Wang et al.²³ reported a reaction for BaZrS_3 powders at 600 °C (7 days) using very specific annealing conditions in a slight excess of sulfur vapor. This interesting reaction mechanism was not thoroughly considered until a recent review by Sopiha et al.⁴ where the importance of BaS_3 for the “fast formation” of BaZrS_3 was suggested. Thus, Comparotto et al.²⁴ reported a similarly inspired sulfur-anneal on a cosputtered Ba–Zr film for the formation of BaZrS_3 at 590 °C (using a SnS_2 capping layer to prevent oxidation). Wang et al.²³ also reported the synthesis of BaZrS_3 (7 days) at temperatures as low as 450 °C if a small amount of BaS is replaced with BaCl_2 , though the mechanism for this reaction was unknown. Niu et al.²⁵ also reported the synthesis of BaZrS_3 (and SrZrS_3) from BaS/SrS , Zr, and S at 600 °C with the inclusion of I_2 (60 h—though it is unclear if the reaction happens faster). We note that during the review stage of this work, Vincent et al.²⁶ reported a liquid flux-assisted growth mechanism for BaZrS_3 and BaHfS_3 whose results are complementary to that reported herein.

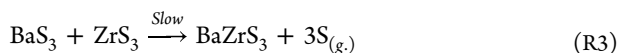
In this work, we address the open question of a low-temperature growth mechanism for BaZrS_3 . A systematic study of the reaction conditions (precursor composition, reaction time/temperature, precursor reactivity, and the use of halide catalysts) is reported. Ultimately, we achieve the rapid synthesis of BaZrS_3 via annealing of BaS_3 and ZrS_2 in as little as 5 min at 550 °C. A liquid-assisted grain growth mechanism in molten BaS_3 is responsible for the rapid, low-temperature growth. Alternatively, we demonstrate that the reaction temperature can be further reduced to 500 °C (below the melting point of BaS_3) via the addition of a chloride catalyst, albeit at a slower reaction rate. The reactivity of Zr precursors

decreases successively from ZrS_2 , $\text{Zr}(\text{S}_2\text{Cl}_2)$, ZrS_3 , to Zr-metal. The $\text{Ba}_3\text{Zr}_2\text{S}_7$ phase is obtained with low-reactivity Zr metal, while BaZrS_3 forms with the more reactive precursors. The resulting BaZrS_3 from liquid-assisted grain growth can be purified from residual BaS_3 -flux with a water wash. In contrast, $\text{Ba}_3\text{Zr}_2\text{S}_7$ is found to be unstable in water and converts to the BaZrS_3 phase. The formation conditions for unwanted binaries, such as ZrS_3 , BaS_2 , and BaS , are discussed. Finally, we extend the liquid-assisted growth mechanism to demonstrate similar results for BaHfS_3 , BaNbS_3 , and BaTiS_3 .

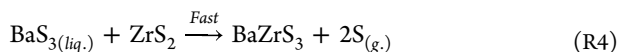
2. RESULTS AND DISCUSSION

2.1. Liquid (BaS_3) Assisted Growth of BaZrS_3 . To directly probe the role of BaS_3 in the low-temperature reaction mechanism for BaZrS_3 , we first mix ground powders of BaS_3 and ZrS_2 followed by vacuum sealing in a glass ampule. Samples were annealed for 3 h at varying temperatures from 400 to 560 °C. When annealed at lower temperatures (400 and 450 °C), no phase change occurs and the precursor BaS_3 and ZrS_2 powders remain unchanged, as identified in the X-ray diffraction (XRD) data shown in Figure 1a. As the temperature is increased to 500 and 530 °C, several reactions are initiated as evidenced by the XRD (Figure 1a), summarized by (R1)–(R3). [Note that throughout the reactions we refer to $\text{S}_{(\text{g})}$, though gaseous sulfur exists as a polysulfide whose length depends on temperature; $\text{S}_{(\text{g})}$ is shown for clarity in quantifying the amount of sulfur released and required by each reaction.] First, the slow decomposition of BaS_3 into BaS_2 is observed.²⁷ Second, the complete conversion of ZrS_2 into ZrS_3 is found. As the formation of ZrS_3 requires more sulfur than is released from the partial decomposition of BaS_3 , we also expect a slow reaction for the formation of BaZrS_3 , though no BaZrS_3 phase can be easily identified in the XRD (either due the amount formed or poor crystallinity due to the low reaction temperature). The complete conversion of ZrS_2 into ZrS_3 suggests ZrS_3 participates in the slow formation of BaZrS_3 at these temperatures, discussed in more detail when directly using ZrS_3 as a precursor in Section 2.3.





When the temperature is increased to 540 °C and higher, a dramatic change in the reaction occurs with virtually complete conversion of the precursors into BaZrS₃, with sharp, well-defined peaks in the XRD (Figure 1b). This change occurs close to the reported melting point of BaS₃ at 554 °C.²⁸ To better understand the reaction, BaS₃ was sealed individually in an ampule and annealed. During heating, yellow BaS₃ powder at room temperature gradually turned dark red and eventually into a black liquid droplet above 540 °C. This suggests the close relationship between the formation of the BaZrS₃ phase and liquid-phase BaS₃, described by (R4). Trace BaS₃ impurity peaks can also be found for all of the reactions at 540 °C and higher.



To illustrate the fast reaction rate of the BaS_{3(liq.)} growth mechanism in (R4), a series of reactions were performed at 550 °C (to ensure molten BaS₃) for various reaction times. XRD results for this time series are shown in Figure 1c, where phase formation and crystallinity of BaZrS₃ are virtually indistinguishable between the 5 min through 3 h reactions (see refined data in the SI).

The formation of BaZrS₃ was further confirmed by Raman spectroscopy, shown in Figure 1d for the same time series. This is primarily verified by the phonon modes for A_g⁴ (134.4 cm⁻¹), (B_{2g}⁴ + A_g⁵) (156.6 cm⁻¹), A_g⁶ (215.4 cm⁻¹), and B_{2g}⁶ (221.2 cm⁻¹); note that shifts in the reference Raman data reported from Gross et al.¹⁹ (measured at 14 K) are a result of the different measurement temperatures. Strong Raman scattering between 390 and 440 cm⁻¹ is attributed to resonant forbidden LO-phonon scattering in BaZrS₃;¹⁹ these features appear to broaden and weaken successively for the longer 1 and 3 h annealing times. In addition to BaZrS₃, the residual BaS₃ phase identified in XRD can also be seen in the Raman spectra (454.8 cm⁻¹). Furthermore, trace ZrS₃ (not observed in XRD) is identified by the small peak near 524 cm⁻¹ for the short reaction times, as ZrS₃ reacts slower than ZrS₂ (see Section 2.3).

Here we propose a reactive, liquid-assisted growth mechanism for BaZrS₃ in BaS_{3(liq.)} as a flux, as illustrated in Figure 2. Evidence for the liquid-assisted growth mechanism is primarily justified by the rapid crystallization of BaZrS₃ in as little as 5 min for temperatures coinciding with that greater

than the melting point of BaS₃. The benefits of liquid-assisted growth can be realized through enhanced mass transport to and from grain boundaries and is typically associated with significant grain growth during short processing times at low temperatures (as reported here) relative to solid-state processes.²⁹ The existence of trace BaS₃ is not unexpected since this reactive flux is mixed in stoichiometric proportion. Thus, as the reaction nears completion the continuous distribution of this critical liquid phase disappears, leaving behind isolated pockets of BaS₃. For bulk powder reactions, it may be advantageous to use excess BaS₃ (see (R7)) to maintain a continuous liquid flux throughout the process, as BaS₃ can be readily removed from the final product (see Section 2.2). However, a thin-film geometry may mitigate this issue.

To place our work in context with previously reported syntheses, annealing ZrS₂ and BaS is kinetically limited by mass transport during solid-state growth as no liquid flux is present (i.e., high temperatures and long reaction times are required). Alternatively, the inclusion of sulfur vapor during annealing (as in Wang et al.,²³ Comparotto et al.,²⁴ and Turnley et al.²²) allows for the formation of BaS₃ from amorphous Ba or BaS precursors—resulting in a similar growth mechanism as identified here at low temperature. Interestingly, if the partial pressure of S_(g) is too high during annealing, the growth of ZrS₃ is increasingly favored relative to the formation of BaZrS₃. To avoid this, we propose the direct use of BaS₃ as a barium precursor rather than annealing in excess sulfur vapor; however, excess sulfur vapor released by (R4) is still important to stabilize this reaction, discussed below in Section 2.3. Freund et al.³⁰ recently attempted to fabricate a BaZrS₃ thin film by reacting BaS₃ (from sulfurization of sputtered BaS) with Zr metal; however, this was unsuccessful due to a low annealing temperature (≤460 °C) and the low reactivity of Zr metal as a precursor (see Section 2.3). Finally, the use of oxide precursors is thermodynamically limited, particularly the favorable formation of ZrO₂, if any oxygen is present during annealing (i.e., high temperatures and long reaction times are required). This thermodynamic limitation is removed in our work by using oxygen-free precursors.

2.2. Product Purification. To recover a pure BaZrS₃ product, the resulting powders for reactions at 540 °C and higher can be rinsed in H₂O, in which BaS₃ is highly soluble. Accordingly, the product from the 550 °C reaction (3 h) was rinsed 3 times via a dispersion in ultrapure H₂O, which was subsequently recovered with centrifugation. This was followed by a similar ethanol wash 2 times to remove any residual H₂O and vacuum drying at room temperature. During the first round of rinsing in H₂O, the initial blackish powder turned to a dark red precipitate following centrifugation (see inset of Figure 3b for the purified BaZrS₃ powder), while the supernatant turned yellow, indicating the dissolution of BaS₃. Fitted XRD of the recovered pure BaZrS₃ product is shown in Figure 3a (also see Figure S9). Rietveld refinement yields lattice parameters of *a* = 7.062 Å, *b* = 9.981 Å, and *c* = 7.0171 Å, which are in good agreement with reported values.³¹ Similarly, the Raman spectrum of the purified powder in Figure 3b indicates the recovery of BaZrS₃.

Photoluminescence (PL), shown in Figure 3c, of the purified BaZrS₃ powder shows an emission peak near 698 nm (1.78 eV) which is in agreement with a range of previously reported values for BaZrS₃, shown by comparison in Figure S10. The PL emission is near the absorption edge measured via diffuse

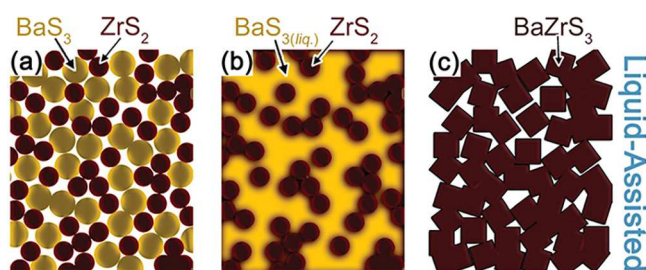


Figure 2. Schematic diagrams for three different stages in the liquid-assisted growth mechanism of BaZrS₃. (a) The initial mixture of BaS₃ and ZrS₂ powders at room temperature, (b) the initial formation of BaS₃ liquid at temperatures above ca. 540 °C, and (c) the recovered BaZrS₃ product.

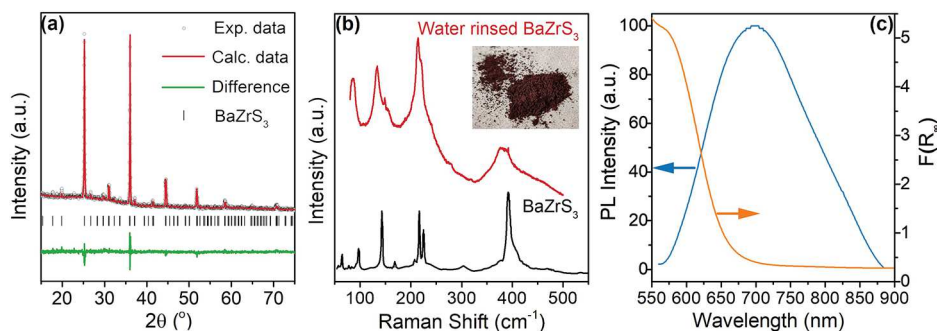


Figure 3. (a) XRD pattern with Rietveld refinement, (b) Raman spectrum, and (c) steady-state PL and absorption spectra for the water-washed BaZrS₃ product from the BaS₃ + ZrS₂ reaction at 550 °C for 3 h. Reference XRD shown in black labeled BaZrS₃ (PDF 01-073-0847). Reference Raman spectrum recorded at 14 K is from Gross et al.¹⁹

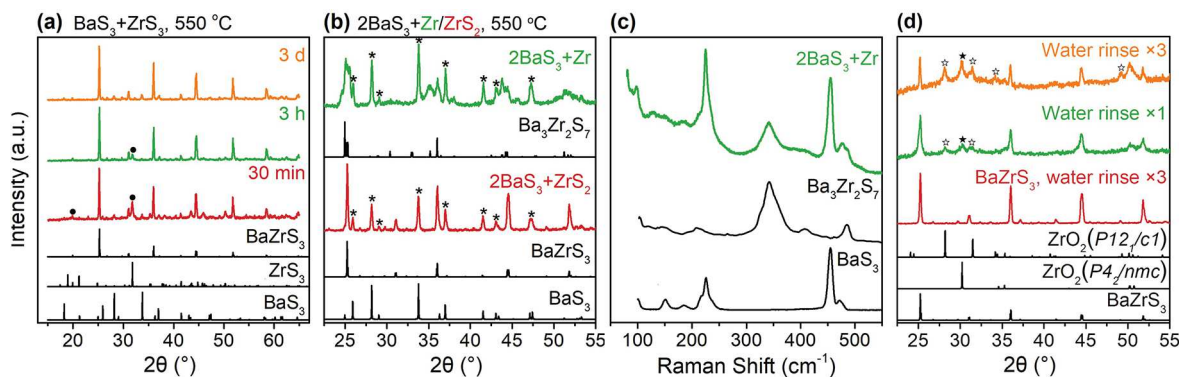


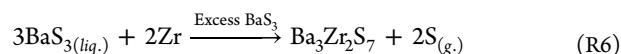
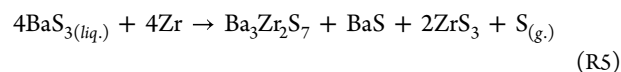
Figure 4. (a) XRD patterns of samples from reaction BaS₃ + ZrS₃ at 550 °C for various reaction times (circles label for ZrS₃). (b) XRD patterns of samples from BaS₃ + Zr-metal (green) and BaS₃ + ZrS₂ (red), both with excess BaS₃ (asterisks label for BaS₃) at 550 °C for 3 h. (c) Raman spectrum of the sample from BaS₃ + Zr-metal with excess BaS₃. Ba₃Zr₂S₇ reference is from Niu et al.¹ BaS₃ reference is measured Raman spectrum of BaS₃ precursor. (d) Powder XRD patterns of water-rinsed samples (orange and green for BaS₃ + Zr-metal and red for BaS₃ + ZrS₂) in (b) (filled stars label for ZrO₂ P4₂/nmc and hollow stars label for ZrO₂ P12₁/c1). Reference XRD patterns are shown in black labeled by compound (BaS₃ PDF 01-073-1177, ZrS₃ PDF 01-080-0926, BaZrS₃ PDF 01-073-0847, ZrO₂ P4₂/nmc PDF 01-079-1763, ZrO₂ P12₁/c1 PDF 01-072-1669).

reflectance (using the Kubelka–Munk transformation), also shown in Figure 3c. We refrain from extracting a band gap value from a Tauc plot of the transformed diffuse reflectance data based on the expected unusual nature of low energy transitions in the electronic structure of BaZrS₃.⁴ We expect the optoelectronic properties to be strongly impacted by anionic defects, as similarly reported for A-site alkali earth metal and B-site Group IVB oxide perovskites.³²

2.3. Zr Precursor Reactivity. It has been speculated that ZrS₃ can block the formation of BaZrS₃.⁴ Therefore, variations in the Zr precursor were considered to understand the role of Zr in the reaction pathway. Accordingly, the BaZrS₃ synthesis reaction at 550 °C was repeated for various reaction times; however, ZrS₂ was replaced with ZrS₃. XRD data, shown in Figure 4a, illustrates that BaZrS₃ can also form under these reaction conditions. However, the decreasing presence of ZrS₃ is identified for reactions at both 30 min and 3 h. The virtually complete reaction of ZrS₃ can be observed if the reaction time is extended to 3 days. In all cases, trace BaS₃ is observed, as similarly seen when using ZrS₂ as a precursor. These results illustrate the reduced reactivity of ZrS₃ relative to ZrS₂ in the formation of BaZrS₃, reflected in (R3) and (R4). Accordingly, the use of excess sulfur conditions should be avoided to prevent ZrS₃ formation for the rapid growth of BaZrS₃ at low-temperature. However, ZrS₃ does not block the growth of BaZrS₃. It can be noted that both Ba in BaS₃ and Zr in ZrS₂ remain in a 12-fold and 6-fold coordination state, respectively,

when transiting to BaZrS₃. In contrast, Zr is in an 8-fold coordination state in ZrS₃; the reduced coordination number of Zr in ZrS₂ may contribute to its increased reactivity.

The reactivity of Zr can be further reduced using elemental Zr-metal as a precursor. The stoichiometric reaction of BaS₃(liq.) and Zr at 550 °C (3 h) results in the formation of the (relatively Zr-poor) Ruddlesden–Popper phase Ba₃Zr₂S₇ (Figure S11), described by (R5). This is better illustrated when BaS₃ is included in excess, described by (R6), with XRD results shown in Figure 4b (Figure S12). Raman spectroscopy, shown in Figure 4c, further verifies the formation of Ba₃Zr₂S₇ in excess BaS₃. However, when excess BaS₃ is reacted with ZrS₂ rather than Zr-metal, the BaZrS₃ phase is still recovered following (R7), with XRD also shown in Figure 4b. Therefore, the formation of the (relatively Zr-poor) Ba₃Zr₂S₇ is a result of the reduced Zr reactivity rather than barium excess.



The appearance of BaS in (R5) is attributed to the relative reduction in excess sulfur vapor released by the reaction in comparison to (R4), (R6), and (R7). Low-temperature

annealing of BaS₃ in the absence of sulfur vapor results in the decomposition of BaS₃, as shown in Figure 1a (i.e., sulfur vapor stabilizes the BaS₃ phase). Therefore, a careful consideration of the sulfur vapor pressure is needed for the rapid reaction of pure-phase BaZrS₃ at low-temperature, even when elemental sulfur is not included as a precursor. For example, the reactor volume can make a significant contribution to the partial pressure of released S_(g).

An attempt was made to purify Ba₃Zr₂S₇ from the excess BaS₃ impurity with the H₂O rinse described in Section 2.2. However, we find Ba₃Zr₂S₇ is not stable in water. Figure 4d shows the XRD for the H₂O-rinsed Ba₃Zr₂S₇ product following 1× and 3× washing steps. In both cases, the Ba₃Zr₂S₇ phase has converted to BaZrS₃. Additionally, the formation of ZrO₂ (P12₁/c1 and P4₂/nmc) is observed. The ZrO₂ intensity increases with additional washing steps. Here we attribute the instability of the Ba₃Zr₂S₇ in water due to the intercalation of H₂O into the layered structure (Figure S13). The resulting exfoliated slabs retain a BaZrS₃ motif, with any resulting Ba(OH)₂ being soluble in the H₂O. The degradation of BaZrS₃ slabs into ZrO₂ may be a result of their small size, as they originate from an *n* = 2 Ruddlesden–Popper phase. We similarly find nanoscale BaZrS₃²⁰ is unstable to oxidation, which is also reported for BaZrS₃ with relatively reduced crystallinity.^{4,33} In contrast, bulk crystalline BaZrS₃ is found to be H₂O-stable here and elsewhere.^{18,33}

2.4. Vapor-Transport Growth of BaZrS₃ with Cl. The introduction of BaCl₂ into the solid-state syntheses of BaZrS₃ to lower the reaction temperature was first reported by Wang et al.²³ BaZrS₃ could be formed (in addition to BaS₃ and ZrO₂) at 450 °C over 7 days by reacting BaS with ZrS₂ in a specific excess of sulfur vapor, when 10% (molar) of the reactant BaS is replaced with BaCl₂. Little was reported regarding the mechanism of this low temperature synthesis. Similar results have been shown for (non-perovskite) PbTiS₃ and BaTiS₃.³⁴ We have previously shown (Section 2.1) that reaction temperatures lower than 540 °C cannot be used for the rapid reaction of BaS₃ with ZrS₂ into BaZrS₃. However, following Wang et al.,²³ if 10% (molar) BaS₃ is replaced with BaCl₂ we can achieve the formation of BaZrS₃ at 500 °C (3 h), with XRD of the resulting product shown in Figure 5.

In this chloride-containing reaction at 500 °C, liquid BaS₃ is no longer formed due to the low reaction temperature.

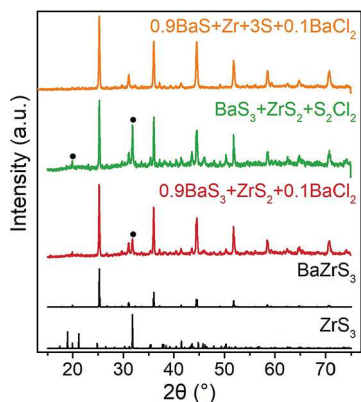
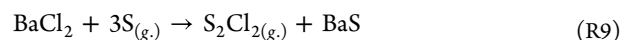
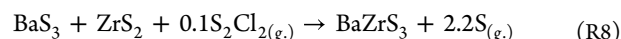
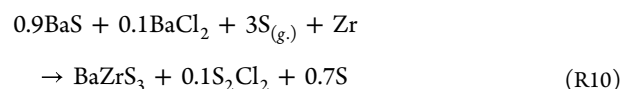


Figure 5. XRD patterns of reactions using Cl at 500 °C for 3 h (circles label ZrS₃). Reference XRD patterns are shown in black labeled by compound (ZrS₃ PDF 01-080-0926, BaZrS₃ PDF 01-073-0847).

However, the reaction rate is still relatively rapid as (primarily) BaZrS₃ forms in at least 3 h. Here we speculate a vapor-phase transport mechanism in the presence of chloride. Specifically, S₂Cl₂ can function as the vapor-phase transport agent, as described by (R8). S₂Cl₂ is commonly reported as a vapor-phase transport agent for the growth of single crystals, particularly for Group IVB transition metal chalcogenides.^{35,36} Furthermore, S₂Cl₂ can form from the reversible reaction of metal chlorides in excess sulfur,^{37,38} following (R9). S₂Cl₂ is a volatile (yellow) liquid at room temperature with a boiling point of 137 °C. Indeed, our work shows the reaction of BaCl₂ + S_(g) (500 °C, 3 h) forms a yellow liquid product when cooled to room temperature (though the instability of S₂Cl₂ in air makes further analysis challenging). Additionally, ZrS₂ can be readily dissolved in S₂Cl₂ to form a Zr-coordinated compound Zr-(S₂Cl₂). To demonstrate the S₂Cl₂ reaction mechanism, we also directly used S₂Cl₂ in the reaction rather than BaCl₂; XRD of the resulting product, Figure 5, shows similar results to the use of BaCl₂.



In the described chloride reactions, ZrS₃ forms as a secondary phase, following the now competitive reaction (R2), as sulfur is a product in the BaZrS₃ reaction (R8). However, a pure-phase BaZrS₃ product can be obtained (500 °C, 3 h) by reducing the amount of excess S following (R10); XRD for the product from this reaction is shown in Figure 5. The direct use of BaS₃ is not necessary at this reaction temperature since it occurs below the melting point of BaS₃, though is expected to form upon reaction with S. Note that in this reaction Zr metal was used, though no Ba₃Zr₂S₇ phase formed. This indicates a relatively balanced reactivity of BaS₃ and Zr-(S₂Cl₂) compared to Zr and ZrS₃ described in Section 2.3.



These results indicate that BaCl₂ acts as a halide source for S₂Cl₂ formation. This is in contrast to speculation that BaCl₂ is beneficial to reduce the S_(g) pressure below that required for ZrS₃ formation, or that BaCl₂ acts as a precursor for BaS₃.^{4,34} A proposed schematic for the vapor transport mechanism is depicted in Figure 6 in which accelerated mass transport of Zr via coordination with S₂Cl₂ allows for relatively rapid grain

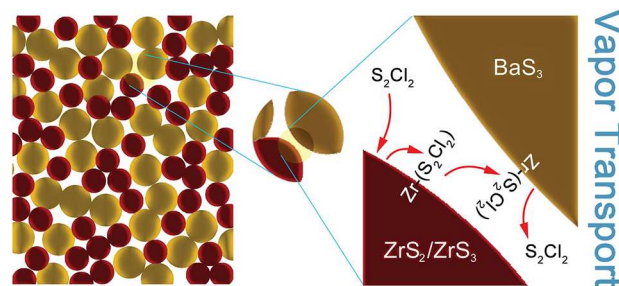


Figure 6. Schematic diagram of the vapor-transport growth mechanism. ZrS₂/ZrS₃ is shown in red and BaS₃ in yellow. A Zr-(S₂Cl₂) vapor-transport process is illustrated.

growth of BaZrS₃ (compared to the absence of S₂Cl₂ in which BaZrS₃ growth is limited for temperatures <540 °C).

2.5. Application of BaS₃-Flux for Additional ABS₃ Chalcogenides. Following the liquid-assisted growth mechanism described here-in (Section 2.1), BaS₃(_{liq.}) can similarly react with HfS₂, NbS₂, and TiS₂ at 550 °C (3 h) to readily form (chalcogenide perovskite) BaHfS₃, (hexagonal) BaNbS₃, and (hexagonal) BaTiS₃, respectively. XRD data are shown in Figure 7 following the water wash described in Section 2.2 (to

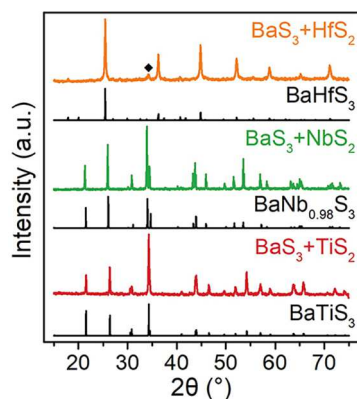


Figure 7. XRD patterns of samples from reaction of (BaS₃ + HfS₂), (BaS₃ + NbS₂), and (BaS₃ + TiS₂) at 550 °C for 3 h (diamond labels an unknown impurity peak in the BaHfS₃ product). Reference XRD patterns are shown in black labeled by compound (BaTiS₃ PDF 01-071-2000, BaNb_{0.98}S₃ PDF 01-083-0359, and BaHfS₃ from Lelieveld et al.³¹).

remove residual BaS₃). Diffuse reflectance data for BaHfS₃ (Figure S16) show a shift to higher energy compared to BaZrS₃, which is in agreement with its higher bandgap.³⁹ Images of the resulting powders as well as Rietveld refinement results can be found in the SI.

3. CONCLUSIONS

In this work, a low-temperature, liquid-assisted growth mechanism is demonstrated for Ba-based chalcogenide perovskites and related chalcogenides, including BaZrS₃, Ba₃Zr₂S₇, BaHfS₃, BaNbS₃, and BaTiS₃. The importance of liquid-BaS₃ is demonstrated for the rapid growth of these materials in as little as 5 min at temperature ≥540 °C. The reactivity of Zr is found to decrease from ZrS₂, Zr-(S₂Cl₂), to ZrS₃, ultimately resulting in the formation of the (relatively Zr-poor) Ruddlesden–Popper Ba₃Zr₂S₇ phase in the limit of elemental Zr-metal as a precursor. In this growth mechanism, we further demonstrate the role of S_(g) in the undesirable formation of ZrS₃ and in the stabilization of the desirable BaS₃ phase. The resulting BaZrS₃ from liquid-assisted grain growth can be purified from residual BaS₃-flux with a straightforward water wash. In contrast, Ba₃Zr₂S₇ is found to be unstable in water and converts to the BaZrS₃ phase, which oxidizes easily in water due to its small size. Lastly, in the absence of a liquid-phase, we also demonstrate a vapor-transport growth mechanism using S₂Cl₂ for the formation of BaZrS₃ at temperatures as low as 500 °C in at least 3 h.

BaZrS₃ is predicted to be thermodynamically stable relative to secondary binary phases, with the distorted perovskite phase as the ground state.⁴ Our results support this conclusion. Although ZrS₃ forms in excess S_(g), it will react to form BaZrS₃ given enough time (kinetically limited). On the other hand, it

has been proposed that BaZrS₃ may be unstable at S_(g) pressures where ZrS₃ forms;⁴ we find that this is not the case for similar reasons. In contrast, at low S_(g) pressures, the reaction is kinetically limited by diffusion in the absence of liquid-BaS₃.

These results demonstrate the feasibility of scalable processing for the formation of chalcogenide perovskite thin-films at suitable temperatures, and several approaches to their formation and purification are shown.

4. EXPERIMENTAL METHODS

4.1. Materials. Sulfuric acid (H₂SO₄, 6.0 N, cat. No. 8330-16), barium chloride (BaCl₂, ≥97%, cat. No. B31-500), elemental sulfur (S, 99.50%, cat. No. AA1078536), titanium powder (Ti, 99.5% metals basis, cat. No. AA4310522), zirconium powder (Zr, cat. No. AA0041814), and hafnium powder (Hf, 99.6% metals basis excluding Zr, cat. No. AA1020106) were purchased from Fisher Scientific. Sulfur monochloride (S₂Cl₂, 98%, cat. No. 157759) was purchased from Sigma-Aldrich. Sulfur and zirconium powder were dried in a vacuum oven at 75 °C for 2 days before use. All other materials were used as received.

4.2. Precursor Synthesis. BaS₃. First, Ba(OH)₂·8H₂O (32.546 g, 100 mmol) was dispersed in 200 mL of H₂O. The 6.0 N H₂SO₄ (33.3 mL, 100 mmol) was added slowly into the dispersion with vigorous agitation and an ice bath. The reaction was stopped at 5 h, and BaSO₄ was recovered by centrifugation. The product was washed with H₂O three more times before drying in the oven at 110 °C overnight. BaS was prepared by reduction of BaSO₄ with 4% hydrogen-balanced Ar in a tube furnace at 1000 °C for 12 h. The BaS product was a white powder. It was immediately taken into a N₂-filled glovebox and ground into fine white powder. BaS (5698 mg, 33.64 mmol) and elemental sulfur (2157 mg, 67.28 mmol) were mixed by grinding with an agate mortar and pestle in the glovebox. The mixture was then loaded into a dried borosilicate glass tube (OD 0.748 in, ID 0.606 in, length ca. 16 in) and flame-sealed under vacuum forming an ampule (length ca. 12 in). The ampule was heated in a muffle furnace from room temperature to 400 °C, with a ramp rate of 5 °C/min, and maintained for 12 h. The furnace was then turned off and allowed to slowly cool down to room temperature. The initial white BaS powder turned to lemon-yellow BaS₃ and was stored in the glovebox. Caution should be used when working with BaS₃ as barium polysulfides are water-soluble and known to be toxic upon ingestion, or can be an irritant upon skin exposure.

ZrS₂ and ZrS₃. Following the same mixing, evacuation, and sealing procedure of BaS₃ preparation, ZrS₃ was first made by reacting dried zirconium powder (Zr, 1095 mg, 12 mmol) and elemental sulfur (1154 mg, 36 mmol) in a dried borosilicate ampule (OD 0.748 in., ID 0.606 in., length ca. 12 in.). The mixture was heated in a muffle furnace to 300 °C, at 5 °C/min ramp rate, and maintained for 6 h. Next, it was heated in the same fashion to 400 °C, then 500 °C, at which point it was maintained 15 more hours. The furnace was then turned off and allowed to slowly cool down to room temperature. The initial dark gray mixture turned to a red powder of ZrS₃. For ZrS₂, the ZrS₃ powder was further decomposed in a tube furnace under ultrapure Ar. The tube furnace containing ZrS₃ was increased to 100 °C and maintained there for 30 min. The temperature was then increased to 800 °C within 1 h and maintained there for 2 h. The furnace was then turned off and allowed to slowly cool down to room temperature. The product ZrS₂ was a dark red powder and was stored in the glovebox.

HfS₂. Following the same mixing, evacuation, and sealing procedure of BaS₃ preparation, hafnium powder (1000 mg, 5.60 mmol) was mixed with elemental sulfur (359.2 mg, 11.20 mmol) into a dried quartz ampule (OD 0.55 in., ID 0.39 in., length ca. 13 in.). The mixture was heated in a muffle furnace to 750 °C from room temperature, at a 5 °C/min ramp rate, and maintained for 12 h. The furnace was then turned off and allowed to slowly cool down to room

temperature. A dark red/brown HfS_2 product formed and was stored in the glovebox.

TiS_2 . Following the same mixing, evacuation, and sealing procedure of BaS_3 preparation, TiS_2 was first made by reacting Ti powder (1107 mg, 23.10 mmol) and elemental sulfur (2222 mg, 69.30 mmol) into a dried borosilicate ampule (OD 0.748 in., ID 0.606 in., length ca. 12 in.). Heating and cooling followed the procedure described for ZrS_3 . The TiS_2 was then decomposed into TiS in the same way as ZrS_2 , though for 1.5 h instead of 2 h. The final product was greenish-yellow TiS_2 powder and was stored in the glovebox.

NbS_2 . Following the same mixing, evacuation, and sealing procedure of BaS_3 preparation, niobium powder (591.6 mg, 6.37 mmol) was mixed with elemental sulfur (408.3 mg, 12.74 mmol) into a dried quartz ampule (OD 0.55 in., ID 0.39 in., length ca. 13 in.). The mixture was heated in a muffle furnace to 850 °C from room temperature, at 5 °C/min, and maintained for 12 h. The furnace was then turned off and allowed to slowly cool down to room temperature. A black NbS_2 product formed and was stored in the glovebox.

4.3. Ternary ABS_3 and $\text{A}_3\text{B}_2\text{S}_7$ Chalcogenides. In a typical reaction, 1.5 mmol fine powder of both A site source precursor (BaS or BaS_3) and B site source precursor (ZrS_2 , ZrS_3 , Zr-metal powder, HfS_2 , NbS_2 , TiS_2) were measured in the glovebox and ground together with an agate mortar and pestle. The mixture was subsequently transferred into a borosilicate glass tube (OD 0.5 in., ID 0.38 in., length ca. 6 in.) and flame-sealed under vacuum forming an ampule (ca. 3 in long). The ampule was transferred into a preheated muffle furnace at the desired temperature (560 °C, 550 °C, 540 °C, 530 °C, 500 °C, 450 °C, 400 °C) for different times (3 h, 1 h, 30 min, 5 min). The ampule was taken directly out of the furnace and cooled in air at the end of the reaction. For BaS_3 excess and chloride-involved reactions, the Zr precursor remained 1.5 mmol, and BaS_3 was adjusted accordingly. For the S_2Cl_2 -involved reaction, S_2Cl_2 (12 μL) was first added to the end-sealed tube, followed by the addition of a stoichiometric mixture of BaS_3 and ZrS_2 on top. Extra caution should be used when working with corrosive S_2Cl_2 . It is highly sensitive to water/moisture and hydrolyzes to release HCl mist and SO_2 .

4.4. Ampule Sealing. Prior to sealing, all ampules were closed with a stopcock in the inert N_2 environment in the glovebox. Next, the closed tubes were taken out of the glovebox and directly attached to a roughing pump under vacuum for 10 min (S_2Cl_2 reactions were only pumped for 1 min). The ampules were then flame-sealed under vacuum (ca. 100–200 mTorr base pressure). Borosilicate tubes were sealed using a methylacetylene-propadiene propane (MAPP) torch while quartz tubes were sealed using an acetylene torch.

In the sulfurization reactions, sulfur quantities were as follows: (1) 38.0 mg/ cm^3 for BaS into BaS_3 , (2) 20.3 mg/ cm^3 for Zr into ZrS_3 , and (3) 19.5 mg/ cm^3 for Ti into TiS_3 , using borosilicate glass ampules with a 1.8 mm wall thickness. For the sulfurization reactions of (1) Hf into HfS_2 and (2) Nb into NbS_2 , 14.1 mg/ cm^3 and 16.0 mg/ cm^3 of sulfur were used, respectively, with quartz glass ampules of 2.0 mm wall thickness. Although no elemental sulfur was used for ABX_3 syntheses, the sulfur generated in the reactions is estimated to be ca. 17.3 mg/ cm^3 in borosilicate ampules with a 1.5 mm wall thickness by the end of the reactions. Under the conditions described, no ampule cracking was experienced. However, deviations from these values (e.g., increased sulfur amount, thinner wall thickness, or faster heating ramp rate) might increase the risk of pressure build-up and consequent ampule cracking.

4.5. Measurements. XRD measurements were performed with a PANalytical XPert Powder diffractometer using Cu $K\alpha$ radiation at 45 kV and 40 mA and a zero-background holder. For the purified BaZrS_3 , the XRD sample is a dropcast film. For all the other samples, powders were used for XRD measurements. Photoluminescence (PL), diffuse reflectance, and Raman measurements were performed on powder samples. PL was performed at 532 nm excitation. Diffuse reflectance measurements were performed with a white lamp and 99.9% diffuse reflectance standard. Both measurements utilized a NIREOS GEMINI interferometer and PicoQuant TimeHarp 260 time-correlated single photon counting system in “T2” mode to record interferograms, from

which PL or reflectance spectra were reconstructed by fast Fourier transform. Raman spectroscopy for water rinsed BaZrS_3 and $2\text{BaS}_3 + \text{Zr-metal}$ reaction was performed on a Horiba LabRAM ARAMIS with 785 nm wavelength excitation and a 10 $\times$ objective. Raman spectra of the other samples were recorded using a Renishaw inVia Reflex Raman Microscope in a backscattering geometry with different excitation wavelengths including 785, 633, and 532 nm with a 50 $\times$ objective. The measurement spot of each probed sample has been visually checked before and after measurement, indicating no laser damage. Furthermore, each laser has been calibrated by using a Si wafer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c00494>.

Additional XRD of precursors, BaZrS_3 , and $\text{Ba}_3\text{Zr}_2\text{S}_7$, Rietveld refinement for XRD presented here-in, comparison of PL data for BaZrS_3 , intercalation schematic for $\text{Ba}_3\text{Zr}_2\text{S}_7$, and diffuse reflectance data for BaHfS_3 (PDF)

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Notes

The authors declare no competing financial interest.

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