Synthesis of Sulfide Perovskites by Sulfurization with Boron Sulfides

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ABSTRACT: Chalcogenide perovskites (CPs), with the general composition ABX₃, where A and B are metals and X = S and Se, have recently emerged as promising materials for application in photovoltaics. However, the development of CPs and their applications has been hindered by the limitations of available preparation methods. Here we present a new approach for the synthesis of CPs, based on the sulfurization of ternary and binary oxides or carbonates with in situ formed boron sulfides. In contrast to the previously described approaches, the method presented here uses chemically stable starting materials and yields pure-phase crystalline CPs within several hours, under low hazard conditions. CP yields over 95% are obtained at temperatures as low as 600 °C. The generality of the approach is demonstrated by the preparation of CPs with compositions BaZrS₃, β-SrZrS₃, BaHfS₃, SrHfS₃, and EuHfS₃. Mechanistic insights about the formation of CPs are discussed.

A great level of interest in solid materials with perovskite crystalline structure in recent years has been stimulated primarily by the discovery that a subset of these materials, halide perovskites (HPs), possess a combination of properties excellent for exploitation in photovoltaics and, more broadly, optoelectronics. Integration of HPs into thin-film solar cells led to unprecedented performance enhancements. HPs were also shown to be very promising materials for the development of efficient light-emitting diodes, lasers, detectors, and other technologies. Despite the promise of HPs, their limited thermal and chemical stability and inclusion of toxic ions, such as lead, pose challenges for their commercial exploitation.

Chalcogenide perovskites (CPs), crystalline solids with the composition ABX₃, where A and B are metal cations and X = S and Se, have recently been suggested as a possible alternative to the structurally related HPs. Although more research is needed to fully assess their potential, theoretical and early experimental studies indicate that CPs have electronic properties similar to those of HPs, are comparable or better light absorbers, and have better chemical and thermal stability, and can be prepared without the use of toxic elements. Experimental studies of CPs have so far been limited, however, mainly because of challenges with their preparation. To date, all known CPs (all sulfides) were prepared by one of two solid-state, high-temperature (>600 °C) syntheses methods first described more than 60 years ago. In one method, the elements and/or binary sulfides are reacted in sealed, evacuated reaction tubes, according to eq 1:

A + B + 3S → ABS₃

AS + 2B → ABS₃

AS + BS₂ → ABS₃

In eqs 1 and 2, the typical examples of ion A are Ca²⁺, Sr²⁺, Ba²⁺, and Ln³⁺/⁴⁺ and those of ion B are Zr⁴⁺, Hf⁴⁺, Sc³⁺, and Ln³⁺/⁴⁺ (Ln = lanthanide). One drawback of both methods is long reaction time, with days to weeks often required for complete conversion. Another drawback of approach (1) is a high propensity of the starting materials A, B, AS, and BS₂ to oxidize even at ambient conditions (Figure S6). This often leads to product contamination with hard to separate oxides. In method (2), complete sulfurization is often difficult because of the limited thermal stability of H₂S and CS₂. Additional drawback is that both H₂S and CS₂ are toxic and form explosive mixtures with air.

In studies of binary oxides, Wu and Seo described a sulfurization approach based on a solid-state metathesis reaction with boron sulfides. The O → S metathesis reaction was shown to be very effective in the sulfurization of binary oxides of transition metals and lanthanides as well as actinides. The synthesis of α-EuZrS₃ from Eu₂O₃ and ZrO₂, in the presence of elemental boron and sulfur, was also recently reported. The approach has not yet been explored in the preparation of CPs.

In this work, we investigated a preparation of sulfide CPs by solid-state reactions of ternary and binary oxides and carbonates in the presence of boron and sulfur. The synthetic approach is schematically shown in the top part of Scheme 1. In a typical reaction, ternary oxide (a), binary oxides (b), and carbonates precursors with H₂S or CS₂ gas at temperatures of >1000 °C, according to eq 2:

ABO₃ + 3H₂S(1.5CS₂) → ABS₃ + 3H₂O(1.5CO₂)

ACO₃ + BO₂ + 3H₂S → ABS₃ + 3H₂O + CO₂

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element and binary oxide (c) or carbonate (d) were thoroughly mixed with a small (~10%) molar excess of elemental boron and a stoichiometric amount of sulfur and sealed under vacuum in a quartz reaction ampule. The ampule was heated in a high-temperature furnace at 500–1100 °C for several hours to several days. The full details of the syntheses are provided in the Supporting Information, SI.

High-Temperature Chemistry of Boron Sulfides. As described for the first time nearly 200 years ago,29 heating of a boron–sulfur mixture past the sulfur boiling point (444.6 °C) produces boron sulfides. More recent studies revealed that, in a vacuum, where sulfur sublimes below 120 °C, the reaction yields B$_2$S$_3$ and/or BS$_2$, depending on the B/S ratio in the starting mixture.30 B$_2$S$_3$ and BS$_2$ sublime at temperatures above 300 °C26 and form various oligomers and polymers.31 The high effectiveness of gaseous boron sulfides as sulfurizing agents for oxides is, in part, due to a large difference in the thermodynamic stability of the byproduct B$_2$O$_3$ (ΔG$_{298}$° = −1192.3 kJ/mol) and B$_2$S$_3$ (ΔG$_{298}$° = −247.6 kJ/mol) and BS$_2$ (ΔG$_{298}$° = −120 kJ/mol).35,33,26 Thus, boron sulfides serve not only as sources of sulfur but also as an effective “oxygen trap”.

As shown in the bottom part of Scheme 1, the high stability of B$_2$O$_3$ makes the sulfuration of metal oxides with boron sulfides thermodynamically more favorable than the sulfuration with H$_2$S [ΔG$_{298}$°(H$_2$S) = −228.6 kJ/mol and ΔG$_{298}$°(H$_2$O) = −33.3 kJ/mol]35 or CS$_2$ [ΔG$_{298}$°(CO$_2$) = −394.4 kJ/mol and ΔG$_{298}$°(CS$_2$) = 66.8 kJ/mol]35 or the direct reaction of binary sulfides. While the specific reaction mechanisms and kinetic barriers for reactions (a)–(d) are not known, a comparison of the reaction enthalpies calculated from the available experimental and theoretical data (Table TS7) suggests that they are highly thermodynamically favorable. This was one of the motivating factors for us to explore these processes experimentally.

Sulfurization of Ternary Oxides. The metathesis of ternary oxides was investigated for A = Ba$^{2+}$ and Sr$^{2+}$ and B = Zr$^{4+}$ and Hf$^{4+}$, according to reaction (3)(a in Scheme 1):

$$\text{ABO}_3 + n\text{B} + m\text{S} \rightarrow \text{ABS}_3 + \text{B}_2\text{O}_3$$

In the reaction, the italicized symbols A and B represent metal cations, and the nonitalic letter B represents boron. In the experiments the reaction mixtures were prepared with $n = 2.2$ and $m = 3$ and carried out at $T = 1000$ °C, with holding time $t = 36$ h. The X-ray diffraction (XRD) patterns of the reaction products are summarized in Figure 1. The peaks match the reference patterns of the corresponding CPs from the ICDD database.

Figure 1. Powder XRD patterns (blue traces) of the CPs prepared from the corresponding ABO$_3$ oxides and the reference literature patterns (orange traces) of the CPs obtained from the ICDD database. In all cases, $n = 2.2$ and $m = 3$, and the heating program (schematically shown by green traces) is as follows: ramp at 5 °C/min to 300 °C, hold 5 h, ramp at 5 °C/min to 600 °C, hold 5 h, ramp at 5 °C/min to 1000 °C, hold 36 h, and cool at 5 °C/min.
decreases to \( \sim 92\% \) (XRD trace shown in Figure 2). In both cases, traces of \( \text{ZrO}_2 \) were detected in the product mixture (Figure S2). Other possible side products were present in the amounts below our detection limit. To find the temperature required for full conversion, the samples heated at \( T = 600 \degree C \) for \( t = 5 \) h were subsequently exposed to temperatures of 650, 700, 800, 900, and 1000 \degree C, without any holding time at maximum temperature. The experiments revealed that complete conversion was achieved at 900 \degree C (Figure 2) or above. Interestingly, the full conversion to \( \text{BaZrS}_3 \) was also achieved by a simple temperature ramp to 900 \degree C (at 5 \degree C/min) without any preheating at lower temperatures (top trace in Figure 2). Notably, this reaction, including the cool down, was complete in less than 6 h (Table TS2).

The above analysis leads to several observations. Although partial conversion of \( \text{BaZrO}_3 \) to CP at \( T = 500 \degree C \) is encouraging, conditions for higher conversion rates and shorter reaction times have to be identified for the reaction at this temperature to be useful for applications. Increasing \( T \) to 600 \degree C leads to near-complete conversion in as little as 5 h. Surprisingly, extension of the reaction time does not lead to more complete conversion. This implies the presence of a kinetic barrier, which at this temperature is difficult to overcome. Our results show that a brief heating to 900 \degree C is sufficient to overcome the barrier and achieve full conversion.

To further investigate the possibility of complete \( \text{BaZrO}_3 \rightarrow \text{BaZrS}_3 \) conversion at \( T = 500−600 \degree C \), reaction (3) was carried out in the presence of excess sulfur (\( n = 5 \)). This was motivated by observations described previously in a report by Wang et al.,\(^{34}\) who showed that, in the reaction of BaS with \( \text{ZrS}_2 \) with excess sulfur and a small amount of \( \text{BaCl}_2 \), up to 90% conversion to \( \text{BaZrS}_3 \) can be achieved at \( T = 500 \degree C \) with \( t = 12 \) h and 96% conversion at \( T = 550 \degree C \) with \( t = 1 \) h. In our experiments with \( \text{BaZrO}_3 \) performed in the temperature range \( T = 500−600 \degree C \), with and without \( \text{BaCl}_2 \) added to the reaction mixture, we found the conversion to be more efficient without \( \text{BaCl}_2 \), with a maximum conversion rate of \( \sim 88\% \) at \( T = 600 \degree C \) and \( t = 1 \) h. At longer reaction times and lower temperatures, we observed lower conversion rates. Compared to stoichiometric reactions described above, the reactions with excess sulfur yielded higher fractions of \( \text{ZrO}_2 \), \( \text{ZrS}_3 \), and unreacted sulfur in the product mixtures.

Our results offer some mechanistic insights. Specifically, the presence of \( \text{ZrO}_2 \) and \( \text{ZrS}_3 \) in the product mixture indicates that at least a fraction of \( \text{BaZrO}_3 \) decomposes during the reaction. In addition, in several reactions carried out at 500–560 \degree C, we detected small amounts of barium sulfides \( \text{BaS}_n (n = 1−3) \). Because no binary compounds were identified in the product mixture upon a brief heating to \( \geq 900 \degree C \), we hypothesize that the detected binary compounds are reaction intermediates. Thus, under the studied conditions, one of the possible pathways for \( \text{BaZrO}_3 \rightarrow \text{BaZrS}_3 \) conversion involves the initial decomposition of the former, with \( \text{ZrO}_2 \) as one of the products. Upon \( \text{ZrO}_2 \) sulfurization, the CP is likely formed by the reaction of zirconium sulfide(s) with barium sulfides. The reaction is fast at \( \geq 900 \degree C \) but inefficient below 600 \degree C. Other reaction pathways may be contributing as well.

**Sulfurization of Binary Oxides and Carbonates.** The high efficiency of the sulfurization of ternary oxides prompted us to also explore similar reactions with the starting materials binary oxides and carbonates, according to reactions (4)–(6) (b)-(d) in Scheme 1):

\[
A_2\text{O}_3 + \text{BO}_2 + nB + mS \rightarrow A\text{BS}_3 + B_2\text{O}_3
\]  

\[
A + \text{BO}_2 + nB + mS \rightarrow A\text{BS}_3 + B_2\text{O}_3
\]  

\[
\text{ACO}_3 + \text{BO}_2 + nB + mS \rightarrow A\text{BS}_3 + \text{CO}_2 + B_2\text{O}_3
\]

The reactions were investigated for \( \text{ZrO}_2 \) and \( \text{SrS}_3 \) in the presence of boron sulfides in closed ampules. The method offers high conversion rates using chemically stable starting materials, significantly
Figure 3. Effect of the starting material on the sulfurization efficiency. Powder XRD patterns (blue traces) of β-SrZrS₃ CP prepared from the starting materials indicated in the legend by reaction with boron sulfides. In all cases, the heating program is as follows: ramp at 5 °C/min to 300 °C, hold 5 h, ramp at 5 °C/min to 600 °C, hold 5 h, ramp at 5 °C/min to 1000 °C, hold 36 h, and cool at 5 °C/min. Also shown are the reference literature patterns (orange traces) of β-SrZrS₃, ZrS₂, and ZrO₂ obtained from the ICDD database.

shorter reaction times, and improved safety over the previously reported methods. Optimization of the method for synthesis at more moderate temperatures and the preparation of new compositions are currently in progress.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c03200.

Synthesis details, characterization methods, reaction conditions and product composition for reactions with binary oxides and carbonates, SEM images, AES data, and selected thermodynamic data (PDF)

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Notes
The authors declare no competing financial interest.

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