Synthesis of Sulfide Perovskites by Sulfurization with Boron Sulfides

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Supporting Information Placeholder

ABSTRACT: Chalcogenide perovskites (CPs), with general composition ABX$_3$, where A and B are metals and X = S, Se, have recently emerged as promising materials for application in photovoltaics. However, the development of the CPs and their applications has been hindered by limitations of the available preparation methods. Here we present a new approach for synthesis of CPs, based on 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 preparation of CPs with compositions Ba-ZrS$_3$, β-SrZrS$_3$, BaHfS$_3$, SrHfS$_3$ and EuHfS$_3$. 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 a discovery that a subset of these materials, halide-perovskites (HPs), possess combination of properties excellent for exploitation in photovoltaics and more broadly optoelectronics.[1-2] Integration of HPs into thin-film solar cells led to unprecedented performance enhancements.[3] HPs were also shown to be very promising materials for development of efficient light emitting diodes, lasers, detectors and other technologies.[4-7] Despite the promise of HPs, their limited thermal and chemical stability and inclusion of toxic ions, such as lead, pose challenge for their commercial exploitation.
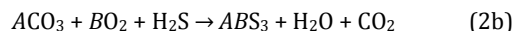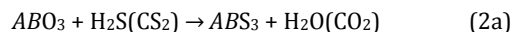
Chalcogenide perovskites (CPs), crystalline solids with the composition ABX$_3$, where A, B, are metal cations and X = S, Se, have been recently suggested as a possible alternative to the structurally related HPs.[8-11] Although more research is needed to fully assess their potential, theoretical[12-13] and early experimental[13-15] studies indicate that CPs have electronic properties similar to the HPs, are comparable or better light absorbers,[13,16] have better chemical and thermal stability[17-18] and can be prepared without the use of toxic elements. Experimental studies of the CPs have so far been limited, however, mainly due to the challenges with their preparation.

To date, all known CPs (all sulfides)[11] were prepared by one of two solid-state, high-temperature (>600 °C) syntheses methods, first described more than sixty years ago.[19-20] In one method, the elements and/or binary sulfides are reacted in sealed, evacuated reaction tubes, according to Eq. (1):

$$A + B + 3S \rightarrow AB S_3 \qquad (1a)$$
$$AS + B + 2S \rightarrow AB S_3 \qquad (1b)$$
$$AS + BS_2 \rightarrow AB S_3 \qquad (1c)$$

The second method is based on sulfurization of oxide or carbonate precursors with H$_2$S or CS$_2$ gas at temperatures >1000 °C, according to Eq. (2):

$$ABO_3 + H_2S(CS_2) \rightarrow ABS_3 + H_2O(CO_2) \qquad (2a)$$
$$ACO_3 + BO_2 + H_2S \rightarrow ABS_3 + H_2O + CO_2 \qquad (2b)$$

In equations (1) and (2), the typical examples of ion A are Ca^{2+}, Sr^{2+}, Ba^{2+}, Ln$^{2+/3+}$, and B are Zr^{4+}, Hf^{4+}, Sc^{3+}, Ln$^{3+/4+}$ (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, BS$_2$ to oxidation even at ambient conditions (see SI S6). This often leads to product contamination with hard to separate oxides. In method (2) complete sulfurization is often difficult due to the limited thermal stability of H$_2$S and CS$_2$.[21-22] Additional drawback is that both H$_2$S and CS$_2$ are toxic and form explosive mixtures with air.[23-24]

In studies of binary oxides, Wu and Seo described a sulfurization approach based on a solid-state metathesis reaction with boron sulfides.[25-26] The O→S metathesis reaction was shown to be very effective in the sulfurization of binary oxides of transition metals and lanthanides[25-26] as well as actinides.[27] Synthesis of α-EuZrS$_3$ from Eu$_2$O$_3$ and ZrO$_2$, in the presence of elemental boron and sulfur was also recently reported.[28] 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), element and binary oxide (c) or carbonate (d), were thoroughly mixed
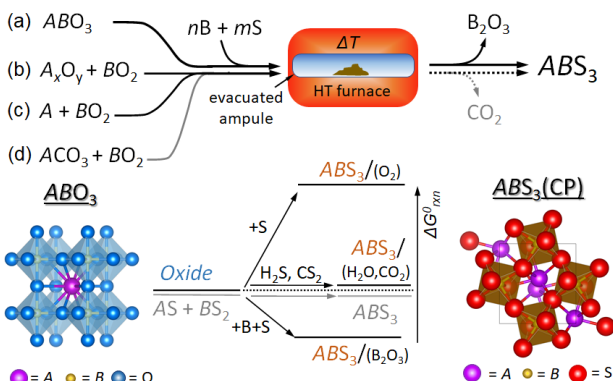
Scheme 1. Top: Diagram of the synthetic approach for preparation of CPs by sulfurization in the presence of boron. The italicized symbols A, B represent metal cations, nonitalic letter B represents boron. Bottom: Schematic energy diagram showing relative enthalpies of the sulfurization in the absence and presence of boron. Also shown are the crystal structures of a starting material ABO_3 (oxide) and the product ABS_3 (CP).

with a small (~10%) molar excess of elemental boron and 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 SI.

High-temperature chemistry of Boron Sulfides. As described for the first time nearly two hundred years ago,[29] heating of boron-sulfur mixture past the sulfur boiling point (444.6 °C) produces boron sulfides. More recent studies revealed that in vacuum, where sulfur sublimes below 120 °C, the reaction yields B_2S_3 and/or BS_2, depending on the B/S ratio in the starting mixture.[30] The B_2S_3 and BS_2 sublime at temperatures above 300 °C,[26] and form various oligomers and polymers.[31] The high effectivity 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_2O_3 ($\Delta G_f^{\circ,298}$ = -1192.3 kJ/mol) and B_2S_3 ($\Delta G_f^{\circ,298}$ = -247.6 kJ/mol) and BS_2 ($\Delta G_f^{\circ,298}$ = -120 kJ/mol).[32-33,26] Thus, boron sulfides serve not only as a source of sulfur but also as an effective "oxygen trap".

As shown in the bottom part of Scheme 1, the high stability of B_2O_3 makes the sulfurization of metal oxides with boron sulfides thermodynamically more favorable than the sulfurization with H_2S ($\Delta G_f^{\circ,298}(H_2O)$ = -228.6 kJ/mol, $\Delta G_f^{\circ,298}(H_2S)$ = -33.3 kJ/mol)[32] or CS_2 ($\Delta G_f^{\circ,298}(CO_2)$ = -394.4 kJ/mol, $\Delta G_f^{\circ,298}(CS_2)$ = 66.8 kJ/mol)[32] or direct reaction of binary sulfides. While the specific reaction mechanisms and kinetic barriers for reactions (a)-(d) are not known, comparison of reaction enthalpies calculated from available experimental and theoretical data (see SI TS7) suggests that they are highly thermodynamically favorable. This was one of the motivating factors for us to explore these processes experimentally.
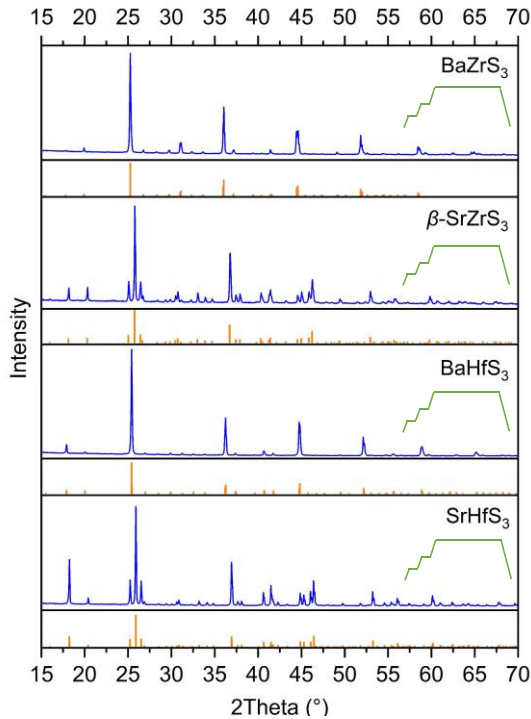

Figure 1. Powder x-ray diffraction patterns (blue traces) of the CPs prepared from the corresponding ABO₃ oxides and the reference literature patterns (orange traces) of the CPs obtained from the ICDD database. In all cases n = 2.2 and m = 3 and the heating program (schematically shown by green traces) was: ramp at 5 °C/min to 300 °C, hold 5 hrs., ramp at 5 °C/min to 600 °C, hold 5 hrs., ramp at 5 °C/min to 1000 °C, hold 36 hrs., cool down at 5 °C/min.

*(a) Sulfurization of ternary oxides AB*O₃. Metathesis of ternary oxides was investigated for A = Ba^{2+} and Sr^{2+} and B = Zr^{4+} and Hf^{4+}, according to reaction (3):

$$ABO_3 + nB + mS \rightarrow ABS_3 + B_2O_3 \tag{3}$$
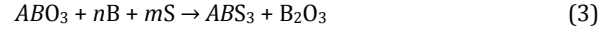
In the reaction the italicized symbols A, B represent metal cations, nonitalic letter B represents boron. In the experiments the reaction mixtures were prepared with n = 2.2 and m = 3 and carried out at T = 1000 °C, with holding time t = 36 hrs. The XRD patterns of the reaction products are summarized in Fig. 1. The peaks match the reference patterns of the corresponding CPs from the ICDD database. No Bragg reflections of any other phases were detected. The product lattice parameters are in good agreement with the literature values (see SI TS1), indicating the formation of pure phases. The sharpness of the diffraction peaks and flat background indicate high degree of crystallinity of the products.

Observation of high efficiency of the metathesis reaction at T = 1000 °C prompted us to investigate it at more moderate temperatures, T = 500-600 °C. This temperature range is an important threshold from the technological standpoint, as it represents an upper limit of thermal stability of the substrates typically used in the preparation of optoelectronic devices. The O→S metathesis of $BaZrO_3$ was performed according to (3), with n = 2.2 and m = 3 and temperatures and holding times systematically varied. The results are summarized in the bottom two panels of Fig. 2 and in Table TS2.

A Rietveld analysis of the XRD patterns of the reaction products for T = 500 °C shows that for t = 48 hrs. the conversion to $BaZrS_3$ was about ~48.5% complete and increased to ~63.8% at t = 168 hrs. (bottom XRD pattern in Fig. 2). The other
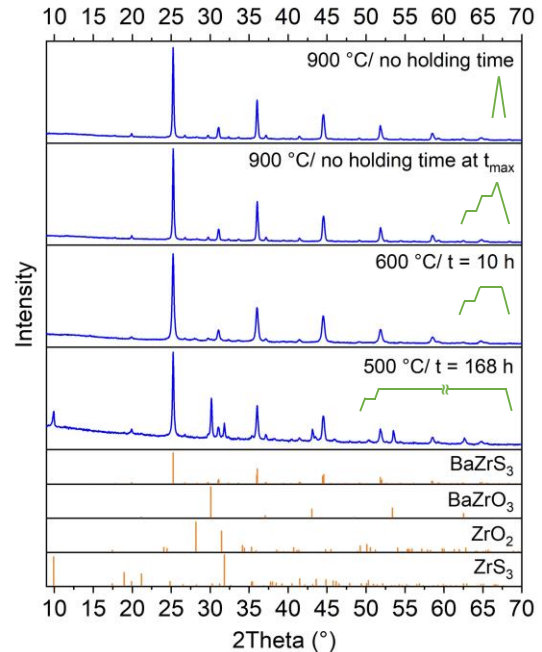

Figure 2. Sulfurization of $BaZrO_3$ at moderate temperatures. Powder XRD patterns (blue traces) of the reaction products as a function of reaction temperature T and holding time "t". In all cases n = 2.2 and m = 3. The heating programs are schematically shown by green traces. In the bottom three panels the heating program was: ramp at 5 °C/min to 300 °C, hold 5 hrs., ramp at 5 °C/min to T, hold "t" hrs., cool down to RT at 5 °C/min. In the top panel the heating program was: ramp at 5 °C/min to 300 °C, cool down to RT at 5 °C/min. Also shown are reference literature patterns (orange traces) of the $BaZrO_3$, $BaZrS_3$, ZrS_3 and ZrO_2 obtained from the ICDD database.

components of the product mixture were $BaZrO_3$ and ZrS_3. The analysis of the results for $T = 600$ °C shows that at t = 5 hrs. the product comprises ~97% of $BaZrS_3$. At t = 10 hrs. the yield decreases to ~92% (XRD trace shown in Fig. 2). In both cases traces of ZrO_2 were detected in the product mixture (see Fig. 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 $T = 600$ °C for t = 5 hrs. were subsequently exposed to temperatures 650, 700, 800, 900 and 1000 °C, without any holding time at maximum temperature. The experiments revealed that the complete conversion is achieved at 900 °C (Fig. 2), or above. Interestingly, the full conversion to $BaZrS_3$ was also achieved by a simple temperature ramp to 900 °C (at 5 °C/min) without any preheating at lower temperatures (top trace in Fig. 2). Notably, this reaction, including the cool down, was complete in less than six hours (see TS2).

The above analysis leads to several observations. Although the partial conversion of $BaZrO_3$ to CP at $T = 500$ °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 °C leads to near complete conversion in as little as 5 hrs. Surprisingly, extension of the reaction time does not lead to more complete conversion. This implies a presence of a kinetic barrier, which at this temperature is difficult to overcome. Our results show that a brief heating to 900 °C is sufficient to overcome the barrier and achieve the full conversion.

To further investigate the possibility of complete $BaZrO_3 \rightarrow BaZrS_3$ conversion at $T = 500\text{-}600$ °C, the reaction (3) was carried out in the presence of excess sulfur ($m = 5$). This was motivated by observations described previously in a report by Wang *et al.*,[34] who showed that in the reaction of BaS with ZrS_2 with excess sulfur and a small amount of $BaCl_2$ up to 90% conversion to $BaZrS_3$ can be achieved at $T = 500$ °C with t = 12 hrs. and 96% conversion at $T = 550$ °C with t = 1 hr. In our experiments with $BaZrO_3$, performed in the temperature range $T = 500\text{-}600$ °C, with and without $BaCl_2$ added to the reaction mixture, we found the conversion to be more efficient without $BaCl_2$, with maximum conversion rate of ~88% at $T = 600$ °C and t = 1 hr. At longer reaction times and lower temperatures, we observed lower conversion rates. Compared to the stoichiometric reactions described above, the reactions with excess sulfur yielded higher fractions of ZrO_2, ZrS_3 and unreacted sulfur in the product mixtures.

Our results offer some mechanistic insights. Specifically, the presence of ZrO_2 and ZrS_3 in the product mixture indicates that at least a fraction of the $BaZrO_3$ decomposes during the reaction. In addition, in several reactions carried out at 500-560 °C we detected small amounts of barium sulfides BaS_n (n = 1-3). Since no binary compounds were identified in the product mixture upon brief heating to ≥900 °C, we hypothesize the detected binary compounds are reaction intermediates. Thus, under the studied conditions one of the possible pathways for $BaZrO_3 \rightarrow BaZrS_3$ conversion involves initial decomposition of the former, with ZrO_2 as one of the products. Upon ZrO_2 sulfurization, the CP is likely formed by the reaction of zirconium sulfide(s) with barium sulfides. The reaction is fast at ≥900 °C, but inefficient below 600 °C. Other reaction pathways may be contributing as well.

(b-d) Sulfurizations with binary oxides and carbonates. The high efficiency of sulfurization of ternary oxides prompted us to also explore similar reactions with starting materials binary oxides and carbonates, according to reactions (4)-(6):
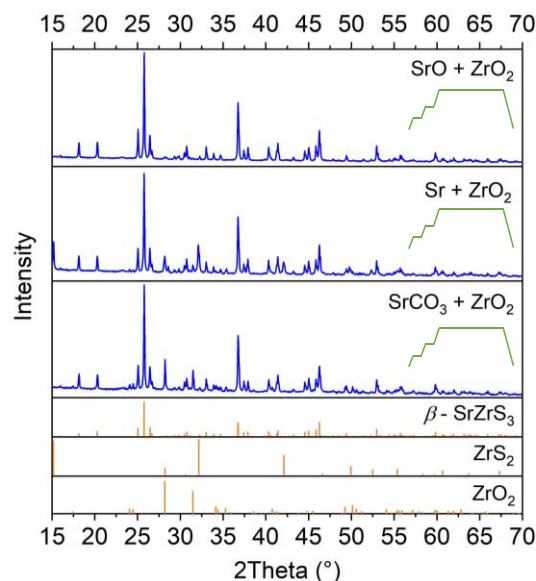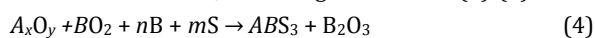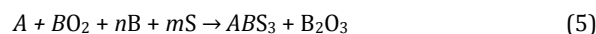
$$A_xO_y + BO_2 + nB + mS \rightarrow ABS_3 + B_2O_3 \qquad (4)$$

Figure 3. Effect of starting material on the sulfurization efficiency. Powder XRD patterns (blue traces) of β-$SrZrS_3$ CP prepared from starting materials indicated in the legends, by reaction with boron sulphides. In all cases, the heating program was: ramp at 5 °C/min to 300 °C, hold 5 hrs., ramp at 5 °C/min to 600 °C, hold 5 hrs., ramp at 5 °C/min to 1000 °C, hold 36 hrs., cool down at 5 °C/min. Also shown are reference literature patterns (orange traces) of the β-$SrZrS_3$, ZrS_2 and ZrO_2 obtained from the ICDD database.

$$A + BO_2 + nB + mS \rightarrow ABS_3 + B_2O_3 \qquad (5)$$

$$ACO_3 + BO_2 + nB + mS \rightarrow ABS_3 + CO_2 + B_2O_3 \qquad (6)$$

The reactions were investigated for $A = Ba^{2+}$, Sr^{2+} and Eu^{3+} and $B = Zr^{4+}$ and Hf^{4+}. The details of the reaction conditions and the product compositions are summarized in SI in Tables TS3-5. The highest conversion rates to CPs were in all three types of reactions observed for $A = Sr^{2+}$ and $B = Zr^{4+}$. The XRD patterns of the products of the three reactions, carried out at $T = 1000$ °C and t = 36 hrs., are shown in Fig. 3. The Rietveld analysis revealed that for reaction (4) the conversion rate to β-$SrZrS_3$ CP is ~99%, with about 1% of ZrO_2. For reaction (5) the CP yield was 74% with ~8% ZrO_2 and ~18% ZrS_2. As the reaction (5) is thermodynamically more favorable than (4) (see TS6), the lower conversion rate suggests a larger kinetic barrier for the former. In the case of rxn. (6) the conversion rate was 82% with ~18% ZrO_2 in the product mixture. The lower conversion rate compared to reactions (3) and (4) may be due to a lower thermodynamic favorability (see TS6) and/or a negative effect of CO_2 formed as a side product during the reaction.

Finally, we found that heating of partially oxidized binary sulfides in the presence of boron sulfides can also be used to effectively remove the oxide impurities. The details are provided in SI section 10.

In summary, we presented a new method for preparation of CPs, based on sulfurization of ternary oxides with boron sulfides in closed ampules. The method offers high conversion rates using chemically stable starting materials, significantly shorter reaction times and improved safety over the previously reported methods. Optimization of the method for synthesis at more moderate temperatures and preparation of new compositions are currently in progress.

ASSOCIATED CONTENT

Supporting Information

Synthesis details, characterization methods, reaction conditions and product composition for reactions with binary oxides and carbonates, SEM images, AES data, selected thermodynamic data. This material is available free of charge via the internet at http://pubs.acs.org.

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Author Contributions

R.B.: Conceptualization, materials synthesis, characterization, data analysis, visualization, manuscript editing. S.K.T.: Materials synthesis, visualization, manuscript editing. P.H. Materials characterization, data analysis, visualization, manuscript editing. L.V. Materials characterization, data analysis, manuscript editing. M.S. Conceptualization, funding acquisition, project administration, original manuscript writing, data analysis, visualization, editing.

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Synopsis. Chalcogenide perovskites with compositions $BaZrS_3$, β-$SrZrS_3$, $BaHfS_3$, $SrHfS_3$ and $EuHfS_3$ were synthesized from ternary oxides, binary oxides and carbonates in vacuum by reaction with in-situ formed boron sulfides. The new synthetic approach offers several advantages over previously reported methods, including the use of chemically stable starting materials, shorter reaction times, less hazardous preparation conditions. The effects of the of the reaction time, temperature and starting mixture composition and mechanistic insights about the reactions are discussed.

(a) ABO_3

(b) $A_xO_y + BO_2$

(c) $A + BO_2$

(d) $ACO_3 + BO_2$

$nB + mS$

ΔT

HT furnace

B_2O_3

ABS_3

CO_2

$\bullet$ = A $\circ$ = B $\bullet$ = O $\bullet$ = S