On the feasibility to form BaZrS₃ chalcogenide perovskite from sulfurized oxide precursors

Santhanu Panikar Ramanandan,¹ Andrea Giunto,¹ Elias Z. Stutz,¹ Benoit Xavier Marie Reyner,¹ Iléane Tiphaine Françoise Marie Lefevre,¹ Marin Rusu,² Susan Schorr,²,³ Thomas Unold,² Anna Fontcuberta i Morral,¹,⁴ José Márquez Prieto,²,⁵* Mirjana Dimitrievska,¹,⁶*

¹ - Laboratory of Semiconductor Materials, Institute of Materials, Faculty of Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.
² - Department of Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
³ – Institute of Geological Sciences, Freie Universitaet Berlin, Maltese St. 74-100, 12249 Berlin, Germany
⁴ - Institute of Physics, Faculty of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.
⁵ - Humboldt University of Berlin, Unter den Linden 6, 10117 Berlin, Germany.
⁶ - Transport at Nanoscale Interfaces Laboratory, Swiss Federal Laboratories for Material Science and Technology (EMPA) Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

§These authors have contributed equally to this work
*corresponding authors: jose.marquez@physik.hu-berlin.de; mirjana.dimitrievska@epfl.ch

Abstract

Barium zirconium sulfide (BaZrS₃) is an earth-abundant and environmentally friendly chalcogenide perovskite with promising properties for various energy conversion applications. Recently, strong focus has been put into exploring different synthesis pathways for efficient high-quality thin film growth. Among them, sulfurization of oxide precursors has been suggested as viable solution for effective synthesis, especially from perspective of circumventing the difficulty of handling alkali earth metals.

In this work, we explore in detail the mechanism and efficiency of BaZrS₃ formation from BaZrO₃ oxide precursors at various sulfurization temperatures. We propose a formation mechanism of BaZrS₃, which is based on a two-step reaction involving an intermediate amorphization step of the BaZrO₃ crystal phase. We show that the diffusion of S and the energetic barrier associated to BaZrS₃ crystallization are both rate-limiting steps of this reaction at lower sulfurization temperatures (< 800 °C). At higher sulfurization temperatures ≥800 °C, a larger rate of conversion from oxide to sulfide phase is observed. However, even with the increased conversion rate, only films sulfurized at 1000 °C have significantly large grains that make them suitable for optoelectronic devices. Finally, we observe formation of stoichiometric BaZrS₃ ([Ba] / [Zr] = 1) even under non-equilibrium conditions, such as Zr-rich oxide precursor, with the extra Zr forming ZrO₂ phase at the substrate-film interface. This marks BaZrS₃ quite unique among the other types of chalcogenides, such as chalcopyrites and kesterites, which can accommodate quite a large range of non-stoichiometric compositions.
Introduction

Extensive harvesting of solar energy is required to minimize the use of fossil fuels for energy generation and to reduce CO₂ emissions. From the materials research perspective, new solutions based on abundant and non-toxic resources need to be developed for sustainable future deployment of solar energy on a large scale. With this in mind, chalcogenide perovskites are recently explored as a new wide-bandgap alternative for thin film photovoltaic (PV) absorbers. Encouraging optoelectronic properties have been already demonstrated experimentally, including an extraordinarily high absorption coefficient, high luminescence efficiency, relatively large charge carrier mobilities, and the capability of being chemically doped to become both, n and p-type semiconductors. These materials are predicted to be “defect tolerant” by ab-initio calculations: Detrimental defects with energy levels in the middle of the bandgap have high formation energies, thus being unlikely to be present in high concentrations in the material.

From all the chalcogenide perovskites experimentally demonstrated, the most studied compound so far is BaZrS₃, which crystallizes in the perovskite GdFeO₃-type structure. BaZrS₃ has been reported to be a direct semiconductor with a bandgap value in the range of 1.8 to 2.0 eV, making this compound attractive for a top cell in a photovoltaic tandem with Si, or for solar water splitting applications. A variety of synthesis routes for thin films have recently appeared, all based on physical vacuum deposition (PVD) methods. Most of these reports rely on a two-stage process in which an amorphous precursor film of Ba-Zr-O or Ba-Zr-S is first deposited, and then BaZrS₃ is crystallized in a second annealing step, often in presence of a reactive atmosphere containing sulfur.

Some of the elements constituting chalcogenide perovskites in their metallic form and their sulfide binaries are extremely sensitive to air. This is for example the case of metallic Ba or for BaS₂. Using these materials as precursor films thus requires avoiding air exposure. Because of this inconvenience, many of the reported synthesis routes for BaZrS₃ use oxide precursor films. It has been suggested that this synthesis route has the additional advantage that the optoelectronic properties of the thin films can be controlled by the partial replacement of O by S in the film, ultimately allowing to tune the material bandgap. However, this remains to be understood considering that as noted by Clearfield in powder samples, and later verified by Marquez et al. in thin films, BaZr(S,O)₃ does not form a crystalline solid solution.

The main disadvantage of using oxides as precursors is that the replacement of O by S to form BaZrS₃ is an energetically expensive process, requiring synthesis temperatures exceeding 800 °C. This implies potential challenges for the future growth of these compounds in most of the commonly used conductive transparent substrates. At the moment, it is not clear whether the high-temperature requirement for crystallizing BaZrS₃ thin films is due to a limited diffusivity of the S atoms within the oxide precursor film, or limitations in the chemical reaction due to the formation of oxide intermediate compounds or secondary phases. Understanding the growth and formation mechanisms of chalcogenide perovskites will greatly accelerate the design of new synthesis routes for this new material class in thin films, enabling control of their composition and optoelectronic properties for their implementation in devices.

This work explores the formation mechanism involved in converting Ba-Zr-O precursor layers into BaZrS₃ by sulfurization at high temperatures between 700 °C and 1000 °C. Detailed morphological and compositional assessment of formed thin films was performed by (scanning) transmission electron microscopy (S/TEM) coupled with energy dispersive x-ray spectroscopy (EDX) and selective area electron diffraction (SAED) analysis on cross-sections of the thin films. Complementary phase identification was done using grazing incidence wide angle X-ray scattering (GIWAXS) and Raman spectroscopy. Based on these results, we explore and discuss the efficiency of the synthesis reaction
for converting Ba-Zr-oxides into Ba-Zr-sulfides, the possible limitation of S diffusion into the BaZrO₃ layers, and the preferential formation of secondary phases that could influence the formation of BaZrS₃.

**Experimental section**

**Material preparation**

We start by preparing a series of Ba-Zr-S-O thin films with different sulphur compositions. For this purpose, a thin amorphous layer of Ba-Zr-O with a thickness of 150 nm was deposited by Pulsed Laser Deposition (PLD) on a quartz substrate, and then annealed under a continuous flow of 5% H₂S(g) in argon at different temperatures ranging from 700 °C to 1000 °C for 30 minutes. A schematic illustration of the sulfurization process is shown in Figure 1. As shown in Figure 1c, this process resulted in a series of Ba-Zr-S-O thin films with a gradual colour change as a function of the sulfurization temperature, which correlates with the change in S composition. The film colour goes from a pale yellow for the S-poor sample sulfurized at 700 °C, to light and dark orange for samples with medium S composition, respectively sulfurized at 800 °C and 900 °C, to a dark red for the S-rich sample sulfurized at 1000 °C. The amorphous precursor film and sulfurized films are the same samples studied in Ref. [14], and more details on their composition and synthesis are reported there. In order to investigate the mechanism of S incorporation and formation of BaZrS₃ from BaZrO₃ we performed in-depth compositional, morphological and structural characterization of the prepared samples.

![Figure 1. Schematic illustration of the Ba-Zr-S-O thin film synthesis:](image)

(a) A series of ~150-nm-thick amorphous Ba-Zr-O films on quartz substrates are synthesized by pulsed laser deposition (PLD) and (b) subsequently annealed under a continuous flow of 5% H₂S(g) in argon at various temperatures from 700 °C to 1000 °C. (c) The obtained Ba-Zr-S-O thin films show a gradual color change due to the variation in S composition. The color change goes from a pale yellow for the S-poor sample sulfurized at 700 °C, to orange hues for samples with medium S compositions sulfurized at 800 °C and 900 °C, to finally dark red for S-rich sample sulfurized at 1000 °C.
Characterization methods

Grazing Incidence Wide Angle X-ray Scattering: GIWAXS measurements were performed on a Bruker Discover Plus equipped with a rotating anode and a Dectris Eiger2 500K detector operating in 2D mode. Collimating optics of 300 micron were used to select the beam shape. Grazing incident angles of 0.3°, 0.5°, 1°, 1.5° and 2° were used.

Raman spectroscopy: Raman measurements were performed complimentary to the GIWAXS characterization to identify formed phases, defects, inhomogeneities and crystallinity. Raman spectroscopy was implemented in backscattering configuration at 12 K. The 488 nm and 532 nm line of a Coherent sapphire optically pumped semiconductor lasers were used for excitation. The beam was focused on the sample with a microscope objective with a numerical aperture of 0.75, resulting in a 1 μm diameter spot, reaching a radiant power of the order of 500 μW. The backscattered light was analyzed using a TriVista triple spectrometer with 900 cm⁻¹, 900 cm⁻¹ and 1800 cm⁻¹ gratings in subtractive mode and a Princeton Instrument liquid nitrogen cooled multichannel CCD PyLoN camera. All spectra were calibrated based on the reference sulfur Raman spectrum.

Scanning electron microscopy (SEM): Morphological properties of the samples’ surface were characterized with a Zeiss Merlin SEM microscope operated at 3 kV and using in-lens detector.

(Scanning) Transmission electron microscopy and energy-dispersive x-ray spectroscopy: Cross-sections of the thin film samples were prepared with a dual-beam focused ion beam and scanning electron microscope (FIB-SEM, Zeiss Nvision 40). Annular dark field (ADF) STEM image and EDX elemental maps were collected using FEI Talos transmission electron microscope operating at 200 kV.

Results

Morphological and microstructural assessment of Ba-Zr-S-O thin films

First, we look at the surface morphology and film microstructure of the sulfurized Ba-Zr-O thin films, summarized in Figure 2. We report in Figure 2a-d SEM images of the thin film surface at increasing sulfurization temperatures. A strong dependency of the surface morphology on the sulfurization temperature is observed. The thin film sample sulfurized at 700 °C (Figure 2a) shows a rather smooth surface when compared to films annealed at higher temperatures. On the other hand, sulfurization at 800 °C (Figure 2b) leads to appearance of crystalline grains on the film surface. Further increasing of the sulfurization temperature to 900 °C (Figure 2c) promotes the growth of more crystalline domains, characterized by dimensions smaller than 250 nm. Finally, sulfurization at 1000 °C (Figure 2d) leads to the formation of large grains with dimensions up to 500 nm. To understand the origin and composition of these crystalline grains we turn to investigate the films structural properties using TEM.

Bright-field TEM (BF-TEM) images of the cross-sections of the thin film samples are reported in Figure 2e-h, while Figure 2i-l show the selected area electron diffraction (SAED) patterns respectively acquired from the film cross-sections in (e-h). Figure S1 in the Supporting Information labels the regions from which the SAED patterns were measured.

The BF-TEM image of the film sulfurized at 700 °C (Figure 2e) shows that the film surface has uniform contrast, while large grains are present in the bulk of the film, as indicated by red arrows. The associated SAED pattern in Figure 2i shows highly discontinuous diffraction rings with multiple bright diffraction spots indicating the presence of multiple randomly oriented crystal grains of BaZrO₃. No clear diffraction patterns from other phases is observed at this temperature, indicating that any sulphide phase present in the film (discussed later in Figure 3) is likely amorphous, and thus the grains observed in Figure 2e are BaZrO₃. Based on the BF-TEM image (Figure 2f), sulfurization at 800 °C leads to disappearance of the large BaZrO₃ grains from most of the film bulk, though BaZrO₃ grains remain
present at the interface with the quartz substrate. On the other hand, strongly diffracting regions characterised by dimensions <10 nm appear in the bulk, as indicated by green arrows. The relative SAED pattern in Figure 2j shows the appearance of new discontinuous diffractions rings, belonging to crystalline BaZrS$_3$ and ZrO$_2$, likely linked with the appearance of nano-grains in the bulk of the film. Few bright diffraction spots belonging to the BaZrO$_3$ phase suggest that the large grains at the substrate-film interface are what remains of the original BaZrO$_3$ phase. At 900 °C, in TEM Figure 2g we see a complete disappearance of large BaZrO$_3$ grains at the substrate-film interface, and the appearance of considerably larger diffracting grains in the bulk of the film, as indicated by green arrows. As a consequence, the relative SAED pattern in Figure 2k shows brighter diffraction spots belonging to the ZrO$_2$ and BaZrS$_3$ phases. In addition, a new diffraction ring belonging to BaZrO$_3$ appears, as shown in Figure 2k, which is probably originated from breaking down of the large BaZrO$_3$ grains at the substrate-film interface into smaller crystallites.

Finally, the TEM cross-section of the sample sulfurized at 1000 °C (Figure 2h) shows the presence of large regions without any diffraction contrast at the surface of the film. On the other hand, strongly diffracting smaller regions with an average size of about 20 nm appear towards the interface with the substrate. In the relative SAED pattern in Figure 2l the presence of many diffraction spots of crystals in arbitrary orientations can be observed. Intense diffraction spots were identified to belong to BaZrS$_3$ and ZrO$_2$ crystals. The absence of rings in this SAED pattern is owed to the low number of crystal grains due to extensive crystal growth enabled by the high sulfurization temperature.

To relate the surface morphology observed by SEM in Figure 2(a-d) to the film microstructure observed in TEM in Figure 2(e-h), and to determine the distribution of the crystal phases observed in the SAED patterns in Figure 2(i-l), we discuss next the compositional analysis of the films performed by STEM-EDX.
Figure 2. Morphological and structural assessment of Ba-Zr-S-O thin films sulfurized at various temperatures: (a-d) SEM top view images of the Ba-Zr-O films sulfurized at various temperatures and showing increase in the grain size with the increase in sulfurization temperature. (e-h) Cross-sectional TEM bright field images of the thin films showing changes in the microstructure. (i-l) TEM-SAED patterns obtained on the cross-sections of Ba-Zr-S-O films (avoiding diffraction from the quartz substrate) pointing to structural and phase changes with sulfurization temperature. Color labels in the SAED patterns indicate different phases: BaZrO$_3$ (orange), BaZrS$_3$ (red), ZrO$_2$ (blue). Full indexing of the diffraction planes, identification of phases and the exact selected area used for measurements of the SAED patterns is shown in Figure S1 in the Supporting Information.

Compositional assessment of Ba-Zr-S-O thin films

STEM-EDX elemental mapping was performed on the cross-sections of the sulfurized thin films in order to obtain information on their chemical composition, as summarized in Figure 3. Figure 3a presents the ADF-STEM images and compositional mapping of the thin film cross-sections for different sulfurization temperatures. The compositional maps are superpositions of elemental compositions of cations (Ba and Zr, middle panel in Figure 3(a)) and anions (S and O, bottom panel in Figure 3(a)). Individual elemental maps of each sample are presented in the Supporting Information (Figures S2-S5). Figures 3b and 3c show changes respectively in the cation ([Zr] / ([Zr] + [Ba])) and anion ([S] / ([S] + [O])) atomic composition as function of depth in the film, obtained from compositional line scans performed from the surface of the film towards the substrate.

Figure 3. Compositional assessment of Ba-Zr-S-O thin films sulfurized at various temperatures: (a) Annular dark-field STEM images and accompanying EDX elemental maps of thin film cross-sections showing variations in Zr-Ba and O-S compositions with sulfurization temperatures. Separation between Ba-rich and Zr-rich regions in correlation with S-rich and O-rich regions is observed at higher temperatures, pointing to formation of BaZrS$_3$ and ZrO$_2$ phases. Line scans of (b) [Zr]/([Zr] + [Ba]) and (c) [S]/([S] + [O]) show variations in cation and anion atomic compositions along the films thickness.
We first consider the average films composition as a function of depth in the film. We start by highlighting compositional line scans averaged over the film width in Figures 3b-c. Concerning the bulk of the films, Figure 3b shows that all sulfurized samples are Zr-rich and Ba-poor (([Zr] / ([Zr] + [Ba]) > 0.5) due to off-stoichiometric precursor amorphous Ba-Zr-O films.23 Regarding the anion composition, Figure 3c shows that, as a result of S diffusion during annealing, the S concentration is highest near the surface, and decreases towards the film-substrate interface. As expected from the increase in diffusion coefficients with temperature, the total S concentration in the films increases as the sulfurization temperature is increased.

However, it is interesting to note that the first 25 nm from the surface of the films shows a slightly different trend. Based on the EDX elemental maps and compositional line scans presented in Figure 3, we can observe Ba and S rich layer in the first few nanometers from the surface in all thin films. Below this, there is an O-rich layer with similar thickness. This most probably indicates a formation of Ba-S-O secondary phases in the top surface layers of the films. Further characterization with XRD and Raman spectroscopy could not reveal the exact nature of the phases present in this layer, which is probably due to the very low quantity present in the film.

Next, we discuss the spatial distribution of cations and anions across the width and thickness of the films as shown in Figure 3a. In the film sulfurized at 700 °C, while the bulk cation composition looks fairly homogeneous, phase separation in anion composition is observed: spatial inhomogeneity indicates that separate S-rich and O-rich phases are present. This confirms the conclusions obtained from TEM analysis of this sample, which suggested the presence of an amorphous phase of Ba-Zr-O, and large crystal grains of BaZrO3. On the other hand, the film sulfurized at 800 °C shows nano-phase separation of both cations and anions in correspondence with nanocrystallites seen previously in the TEM image in Figure 2f, and now also visible in the ADF image. These nanocrystallites correspond to a Zr- and O-rich phase, indication of the crystalline ZrO2 phase observed by TEM in SAED Figure 2j. Given the dim SAED spots belonging to BaZrS3 in Figure 2j and the compositional STEM EDX contrast seen in Figure 3a, we believe the ZrO2 crystallites are immersed in a matrix of nanocrystalline BaZrS3 with possibly an amorphous component of Ba-Zr-S(-O). At the substrate-film interface, the film sulfurized at 800 °C is still strongly rich in O, confirming that the large grains observed also in Figure 2f are likely unreacted crystals of BaZrO3. Increasing the sulfurization temperature to 900 °C leads to complete decomposition of BaZrO3 grains, and to increased phase separation into O- and S-rich phases in the bulk of the film. This is in agreement with crystal growth observed from brighter spots in the SAED pattern of Figure 2k. On the other hand, the surface protrusion and first 50 nm of the film near the surface show a homogeneous distribution of Ba, Zr, and S, pointing to probable formation of larger grains of BaZrS3. This indicates that the surface protrusions observed by SEM in Figure 2c are the result of formation of BaZrS3 crystals. Further increasing the sulfurization temperature to 1000 °C, the STEM-EDX contrast in Figure 3a indicates that the sub-surface region is uniformly constituted of BaZrS3, suggesting that the 500-nm-sized grains observed by SEM in Figure 2d are BaZrS3 grains, in agreement with the bright TEM SAED spots of BaZrS3 in Figure 2f. The size of the Zr- and O-rich phase grains also increases at this sulfurization temperature, as expected from the SAED pattern of Figure 2f.

Phase identification in Ba-Zr-S-O thin films
To confirm the presence of phases identified with TEM analysis in the sulfurized Ba-Zr-O thin films, we performed GIWAXS (Figure 4) and Raman spectroscopy (Figure S6 in the Supporting Information).

Figure 4a presents representative GIWAXS patterns of sulfurized BaZrO3 samples measured with grazing incidence (GI) angles (αi) of 0.3, 0.5 and 2.0°, while complementary measurements with 1.0 and 1.5° are shown in Figure S7a in the Supporting Information. Bottom panel in Figure 4a shows the reference patterns of BaZrO3,23 BaZrS3,23 and ZrO2,31 phases, whose structures are illustrated in Figure
4b. In the GIWAXS configuration, X-ray penetration depth is controlled by the GI angle and can be calculated based on the incident angle and material parameters as shown in Ref. [32]. Based on these calculations we have reported in Figure 4c and Figure S7c the average penetration depths of X-rays for various GI angles in the case of sulfurized BaZrO$_3$ samples. Low GI angles (0.3° and 0.5°) have an estimated penetration depth of less than 50 nm, while the higher GI angles (2°) penetrate the entire bulk of the film (> 200 nm). This means that the information obtained from GIWAXS measurements with lower GI angles is indicative mostly of the phases present near the surface of the films, while in our case at $\alpha_i = 2^\circ$ we probe the entirety of the films.

The Bragg reflections observed in the GIWAXS patterns for sample sulfurized at 700 °C match well the reference positions of cubic perovskite-type BaZrO$_3$ (space group Pm-3m) for measurements with both low and high GI angles. This indicates that crystalline BaZrO$_3$ phase is a major phase present throughout the film, as observed by TEM. Furthermore, a low intensity peak at around $2\theta = 25.3^\circ$ is observed in the GIWAXS pattern measured with 0.3° and 0.5° GI angles. This reflection corresponds to the orthorhombic perovskite-type BaZrS$_3$ (space group Pnma), and indicates formation of a small amount of crystalline BaZrS$_3$ in the surface region of the films, undetected by TEM SAED in Figure 2i.

**Figure 4.** Phase identification of Ba-Zr-S-O thin films sulfurized at various temperatures: (a) Representative GIWAXS patterns of Ba-Zr-S-O films synthesized at different temperatures. The measurements were performed with grazing incidence angles ($\alpha_i$) of 0.3°, 0.5° and 2°, allowing microstructural assessment of the surface ($\alpha_i \leq 0.5^\circ$) and bulk ($\alpha_i = 2.0^\circ$) regions of the thin films. Based on the positions of reflections in the patterns, three phases were identified: BaZrS$_{323}$, BaZrO$_{323}$ and ZrO$_{231}$. Reference patterns of these phases are reported on the x-axis of the GIWAXS scans. (b) Crystal structure representations of BaZrS$_3$ and BaZrO$_3$. (c) Estimated penetration depth of X-rays for different grazing incidence angles used in this study.
The samples sulfurized at 800 °C and 900 °C show less intense reflections belonging to the cubic perovskite-type BaZrO$_3$ phase, and progressively more pronounced reflections attributed to the orthorhombic perovskite-type BaZrS$_3$. Additionally, new peaks are observed at 2θ angles of 35.3° and 50.6°, which point to formation of the ZrO$_2$ phase. The reflections belonging to the ZrO$_2$ phase could be identified with either cubic (space group $Fm\overline{3}m$) or tetragonal structure (space group $P4_2/nmc$). Differentiation between the two from the XRD measurements is difficult as XRD patterns from both structures are very similar. Usually, the tetragonal structure can be distinguished by the characteristic splitting of the diffraction peaks, absent in the patterns of the cubic phase. However, this task was impossible in our mixed system, with Bragg peak broadening due to small GI angles and nano-size of ZrO$_2$ crystallites. Therefore, in our case we will refer to this phase as only ZrO$_2$.

Interestingly, we can observe that both at 800 °C and 900 °C the ratio of BaZrS$_3$ peak at 2θ = 25.3° to the oxide peak (BaZrO$_3$ or ZrO$_2$) at 2θ = 30.2° decreases towards larger GI angles, indicating that the BaZrS$_3$ phase is mainly present at the surface, as expected from the STEM analysis. Lastly, the Bragg peak corresponding to BaZrO$_3$ (2θ = 43.4°) seems to disappear in the film sulfurized at 900 °C, despite the diffused diffraction ring observed in SAED in Figure 2k. On the other hand, the Bragg peak of ZrO$_2$ (2θ = 50.6°) slightly increases at 900 °C compared to 800 °C, suggesting the ZrO$_2$ phase grows at the expenses of BaZrO$_3$.

As the sulfurization temperature further increases to 1000 °C, the Bragg peaks corresponding to the BaZrS$_3$ phase become more intense for all GI angles suggesting that the fraction of crystalline BaZrS$_3$ in the film increases at 1000 °C. Furthermore, at GI angle of 2°, Bragg peaks of orthorhombic perovskite-type BaZrS$_3$ are considerably sharper compared to other sulfurization temperatures, indicating more extensive BaZrS$_3$ grain growth at 1000 °C in accordance with the TEM image of Figure 2h. Concerning the oxide phase peaks, low-intensity peaks corresponding to the ZrO$_2$ phase are observed (mostly at 2θ = 30.2°), with slightly higher intensity at high GI angles of 2°. This indicates that the ZrO$_2$ phase is located mostly towards the substrate-film interface, in agreement with the STEM image in Figure 3a. The absence of peaks corresponding to BaZrO$_3$ suggests a complete conversion of this phase into BaZrS$_3$ at the sulfurization temperature of 1000 °C.

On a final note, we performed Raman spectroscopy characterization, reported in Figure S6, to confirm the presence of the observed crystal and amorphous phases. Detailed analysis of the Raman spectra is presented in the Supporting Information. Here, we briefly mention that Raman yields significantly broad peaks for the film sulfurized at 700 °C, confirming the presence of the Ba-Zr-S-O amorphous phase. For increasing sulfurization temperatures, Raman confirms the trends observed with GIWAXS and TEM SAED, with BaZrS$_3$ crystal growth at increasing temperatures at the expenses of BaZrO$_3$, and the appearance of a ZrO$_2$ phase starting at 800 °C.

**Discussion**

Before discussing the sulfurization reaction mechanisms, we highlight that sulfurization of Ba-Zr-O at different temperatures does not lead to formation of crystalline solid-solution BaZr(O$_{x}$S$_{1-x}$)$_3$, confirming the results from Ref. [17]. This is shown by both Raman spectroscopy and GIWAXS, as the measured peaks are always centered at the expected positions of either the oxygen-pure BaZrO$_3$ phase or the sulfur-pure BaZrS$_3$ phase. This means that the synthesized layers present a mixture of crystalline domains corresponding to either cubic BaZrO$_3$, orthorhombic BaZrS$_3$, or other secondary phases, while no domains are present where S and O are statistically intermixed within a crystalline single phase. This agrees with recent density functional theory calculations on intrinsic defects in BaZrS$_3$, which showed that BaZrS$_3$ is sufficiently defect-tolerant due to high formation energies of compositional defects. This is in difference to other chalcogenide systems, such as chalcopyrite (Cu(In, Ga)Se$_2$) or kesterites (Cu$_2$ZnSn(S,Se)$_4$) which tend to accommodate quite a wide range of off-stoichiometric...
compositions.\textsuperscript{27,29} While on one side the stoichiometric compositional growth of BaZrS\textsubscript{3} under non-equilibrium conditions can be beneficial due to avoidance of detrimental compositional defects, it can also lead to limitations in the tunability of properties which could be achieved by changes in the composition.

We now propose the following formation mechanism of the sulfide perovskite phase from amorphous Ba-Zr-O precursors, based on the morphological and microstructural characterization of the films sulfurized at different temperatures: During heating, the amorphous precursor Ba-Zr-O film crystallizes in the cubic perovskite-type BaZrO\textsubscript{3} crystal phase at temperatures below 700 °C.\textsuperscript{35,36} As the film is exposed in H\textsubscript{2}S atmosphere for 30 minutes at 700 °C, BaZrO\textsubscript{3} grains grow further, while S species diffuse into the film. Judging from the S-rich and O-rich phase separation observed by STEM in Figure 3a, we speculate S diffuses through the BaZrO\textsubscript{3} grain boundaries, reacting at the grain surfaces, and forming an amorphous Ba-Zr-S-O phase. At 700 °C, BaZrO\textsubscript{3} grains are almost completely amorphized on the film surface, where S is present in considerably higher concentrations with respect to the bulk. GIWAXS measurements also point at initial BaZrS\textsubscript{3} crystal growth at surface, but this is not detected by TEM SAED, indicating extremely small crystallite size. At 800 °C, S diffusion occurs more rapidly, and the total concentration of S in the film increases. As a consequence, the BaZrO\textsubscript{3} crystal phase is amorphized more strongly than at 700 °C, and large BaZrO\textsubscript{3} grains remain only at the substrate-film interface, as seen in Figure 2f. At this higher sulfurization temperature, signatures of BaZrS\textsubscript{3} crystal phase are present from the entire film in both GIWAXS and TEM SAED. In addition, at 800 °C a new nanocrystalline phase of ZrO\textsubscript{2} forms in the bulk of the film, evidenced by GIWAXS, STEM and TEM SAED. Because the initial amorphous Ba-Zr-O precursor film was rich in Zr, as shown in the compositional analysis of Figure 3b, the formation of the ZrO\textsubscript{2} may be attributed to capturing of out-diffusing O from the extra, off-stoichiometric Zr present in the film. Zr would capture preferentially O rather than S because ZrS\textsubscript{2} has higher formation energy (-1.956 eV/atom)\textsuperscript{37} than ZrO\textsubscript{2} (-3.755 eV/atom).\textsuperscript{38} At 900 °C, the BaZrO\textsubscript{3} phase is almost disappeared, and is present only in the form of nanocrystallites, visible in the TEM SAED pattern of Figure 2k. At this temperature, XRD and TEM SAED point at more extensive grain growth of both the BaZrS\textsubscript{3} and ZrO\textsubscript{2} phases. Finally, at 1000 °C the BaZrO\textsubscript{3} phase is absent, while crystal grains of both ZrO\textsubscript{2} and BaZrS\textsubscript{3} grow substantially larger compared to the lower sulfurization temperatures, yielding sharper peaks in both GIWAXS and Raman spectroscopy. BaZrS\textsubscript{3} grains grow within the film bulk and out of the film surface, as seen by both SEM and TEM in Figure 2. BaZrS\textsubscript{3} grains outgrow from the surface because of the lower atomic density of its orthorhombic perovskite-type crystal structure compared to the cubic BaZrO\textsubscript{3}. Judging from the final concentration of S in the film in Figure 3c, and the absence of amorphous phases at 1000 °C, we can infer most of the initial O present in the film has diffused out during sulfurization.

Considering the reactions occurring during sulfurization at different temperatures, we discuss the rate-limiting factors the formation of BaZrS\textsubscript{3} by sulfurization of BaZrO\textsubscript{3}. Several factors influence, and can possibly limit this reaction: (i) the reaction energetic barrier involved in converting oxides to sulfides, (ii) the diffusion of S atoms in BaZrO\textsubscript{3} layers and (iii) the preferential formation of secondary phases. In perfectly stoichiometric compositional conditions, BaZrS\textsubscript{3} is expected to form following the reaction

\[
\text{BaZrO}_3(s) + 3\text{H}_2\text{S}(g) \rightarrow \text{BaZrS}_3(s) + 3\text{H}_2\text{O}(g)
\]  

(1)

Based on our experimental results, we observe that this reaction goes in fact through an intermediate amorphization step of the BaZrO\textsubscript{3} crystal phase. Reaction (1) can thus be expressed as a 2-step reaction (considering the case of stoichiometric cation (Ba and Zr) compositions):

\[
c\text{BaZrO}_3(s) + 3\text{H}_2\text{S}(g) \rightarrow a\text{BaZrS}_3(s) + 3\text{H}_2\text{O}(g)
\]  

(2)

\[
a\text{BaZrS}_3(s) \rightarrow c\text{BaZrS}_3(s)
\]  

(3)
From Figure 3a, we can observe that already at 700 °C no large BaZrO3 crystal grains are present at the surface, where the S concentration is high, indicating that S completely amorphized the BaZrO3 crystal phase here. On the other hand, in the bulk of the film, where only a small amount of S could diffuse, we can observe large BaZrO3 grains. From this, we can infer that reaction (2) can easily occur already at 700 °C, and thus the diffusion of S is the rate-limiting step. On the other hand, the newly formed amorphous Ba-Zr-S phase does not seem to significantly crystallize to BaZrS3 at 700 °C, despite the high S concentration at the film surface. This indicates that the crystallization of BaZrS3 (3) is the rate-limiting step of this reaction. The energetic barrier associated to BaZrS3 crystallization can be more easily overcome by increasing the sulfurization temperature. Indeed, the BaZrS3 crystal phase appears in the form of nanocrystallites at 800 °C, growing in volume as the sulfurization temperature is increased. Finally, while we do observe the formation of a ZrO2 secondary phase, we see no indication that this phase is a rate-limiting factor of reaction (1). However, to confirm this, sulfurization of Zr-poor precursor films should be investigated. Absence of ZrO2 formation in these conditions would confirm that ZrO2 forms as a result of O capture from extra, off-stoichiometric Zr. On the other hand, presence of ZrO2 in a sulfurized Zr-poor Ba-Zr-O film would indicate that the out-diffusing O is partly capturing Zr from the film to form ZrO2. In the latter case, this step would be a limiting factor of reaction (1).

As a final comment on the sulfurization of oxide precursor films as a synthesis method of BaZrS3 for optoelectronic applications, it is evident that sulfurizing at 700 °C is not enough, as S diffusion is slow, and BaZrS3 crystallization does not occur. The situation improves at higher sulfurization temperatures ≥800 °C, where larger rate of conversion from oxide to sulfide phase is observed. However, even with the increased conversion rate, only films grown at 1000 °C have large enough grains that would allow their use in optoelectronic devices.

Conclusions
We have prepared a series of BaZrO3 thin films sulfurized at temperatures ranging from 700 °C to 1000 °C. We used STEM-EDX, TEM SAED and GIWAXS to investigate in detail the effect of sulfurization on the morphological, compositional and structural properties of the formed layers. We propose a formation mechanism of BaZrS3, which is based on a two-step reaction involving an intermediate amorphization step of the BaZrO3 crystal phase. We show that the diffusion of S and the energetic barrier associated to BaZrS3 crystallization are both rate-limiting steps of this reaction at lower sulfurization temperatures (< 800 °C). At higher sulfurization temperatures ≥800 °C, a larger rate of conversion from oxide to sulfide phase is observed. However, only films grown at 1000 °C have large enough grains that would make them suitable for device fabrication. These results suggest that this slow reaction dynamics might prove to be undesirable in the long run for formation of thin films for PV applications.

Supporting Information
Supporting Information is available free of charge at XXXX.

STEM-EDX elemental maps, GIWAXS patterns, Raman measurements, SAED-TEM patterns

Competing Interests
The authors declare that they have no competing financial interests.
Authors contributions
M.D. and J.M.P. conceived the research idea and supervised the work, with the help from A.F.M. and T.U. J.M.P. and M.R. prepared the samples. S.R.P. and A.G. prepared the thin film lamellas, and preformed the STEM-EDX analysis. E.S., B.X.M.R., and I.T.F.M.L. performed Raman measurements and analysis. M.D. and S.S. did GIWAXS experiments and analysis. M.D., A.G., S.R.P., and J.M.P. wrote the manuscript with the inputs from all authors.

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References
(1) Sopiha, K. V.; Comparotto, C.; Márquez, J. A.; Scragg, J. J. S. Chalcogenide Perovskites: Tantalizing Prospects, Challenging Materials. *Advanced Optical Materials* 2022, 10 (3), 2101704. https://doi.org/10.1002/adom.202101704.
(2) Tiwari, D.; Hutter, O. S.; Longo, G. Chalcogenide Perovskites for Photovoltaics: Current Status and Prospects. *J. Phys. Energy* 2021, 3 (3), 034010. https://doi.org/10.1088/2515-7655/abf41c.
(3) Adjogri, S. J.; Meyer, E. L. Chalcogenide Perovskites and Perovskite-Based Chalcohalide as Photoabsorbers: A Study of Their Properties, and Potential Photovoltaic Applications. *Materials (Basel)* 2021, 14 (24), 7857. https://doi.org/10.3390/ma14247857.
(4) Niu, S.; Milam-Guerrero, J.; Zhou, Y.; Ye, K.; Zhao, B.; Melot, B. C.; Ravichandran, J. Thermal Stability Study of Transition Metal Perovskite Sulfides. *Journal of Materials Research* 2018, 33 (24), 4135–4143. https://doi.org/10.1557/jmr.2018.419.
(5) Nishigaki, Y.; Nagai, T.; Nishiwaki, M.; Aizawa, T.; Kozawa, M.; Hanzawa, K.; Kato, Y.; Sai, H.; Hiramatsu, H.; Hosono, H.; Fujiwara, H. Extraordinary Strong Band-Edge Absorption in Distorted Chalcogenide Perovskites. *Solar RRL* 2020, 4 (5), 1900555. https://doi.org/10.1002/solr.201900555.
(6) Meng, W.; Saparov, B.; Hong, F.; Wang, J.; Mitzi, D. B.; Yan, Y. Alloying and Defect Control within Chalcogenide Perovskites for Optimized Photovoltaic Application. *Chemistry of Materials* 2016, 28 (3), 821–829. https://doi.org/10.1021/acs.chemmater.5b04213.
(7) Hanzawa, K.; Imura, S.; Hiramatsu, H.; Hosono, H. Material Design of Green-Light-Emitting Semiconductors: Perovskite-Type Sulfide SrHFS3. *Journal of the American Chemical Society* 2019, 141 (13), 5343–5349. https://doi.org/10.1021/jacs.8b13622.
(8) Niu, S.; Huyan, H.; Liu, Y.; Yeung, M.; Ye, K.; Blankemeier, L.; Orvis, T.; Sarkar, D.; Singh, D. J.; Kapadia, R.; Ravichandran, J. Bandgap Control via Structural and Chemical Tuning of Transition Metal Perovskite Chalcogenides. *Advanced Materials* 2017, 29 (9), 1604733. https://doi.org/10.1002/adma.201604733.
(9) Yang, R.; Jess, A. D.; Fai, C.; Hages, C. J. Low-Temperature, Solution-Based Synthesis of Luminescent Chalcogenide Perovskite BaZrS3 Nanoparticles. *J. Am. Chem. Soc.* 2022, 144 (35), 15928–15931. https://doi.org/10.1021/jacs.2c06168.
(10) Ye, K.; Zhao, B.; Diroll, B.; Ravichandran, J.; Jaramillo, R. Time-Resolved Photoluminescence Studies of Perovskite Chalcogenides. *Faraday Discussions* 2022. https://doi.org/10.1039/D2FD00047D.
(11) Yu, Z. Chalcogenide Perovskite BaZrS3 Thin-Film Electronic and Optoelectronic Devices by Low Temperature Processing. *Nano Energy* 105959. https://doi.org/10.1016/j.nanoen.2021.105959.
(12) Okai, B.; Takahashi, K.; Saeki, M.; Yoshimoto, J. Preparation and Crystal Structures of Some Complex Sulphides at High Pressures. *Materials Research Bulletin* **1988**, *23*(11), 1575–1584. https://doi.org/10.1016/0025-5408(88)90245-0.

(13) Lelieveld, R.; IJdo, D. J. W. Sulphides with the GdFeO 3 Structure. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry* **1980**, *36*(10), 2223–2226. https://doi.org/10.1107/s056774088000845x.

(14) Clearfield, A. The Synthesis and Crystal Structures of Some Alkaline Earth Titanium and Zirconium Sulphides. *Acta Crystallographica* **1963**, *16*(2), 135–142. https://doi.org/10.1107/s0365110x6300030x.

(15) Xu, M.; Sadeghi, I.; Ye, K.; Jaramillo, R.; LeBeau, J. M. Investigation of Chalcogenide Perovskite Thin Films Using Scanning Transmission Electron Microscopy (STEM). *Microscopy and Microanalysis* **2022**, *28*(S1), 2548–2549. https://doi.org/10.1017/S1431927622009722.

(16) Márquez, J. A.; Rusu, M.; Hempel, H.; Ahmet, I. Y.; Kölbach, M.; Simsek, I.; Choubrac, L.; Gurieva, G.; Gunder, R.; Schorr, S. BaZrS3 Chalcogenide Perovskite Thin Films by H2S Sulfurization of Oxide Precursors. *The journal of physical chemistry letters* **2021**, *12*, 2148–2153.

(17) Bennett, J. W.; Grinberg, I.; Rappe, A. M. Effect of Substituting of S for O: The Sulfide Perovskite BaZrS3 Investigated with Density Functional Theory. *Phys. Rev. B* **2009**, *79*(23), 235115. https://doi.org/10.1103/PhysRevB.79.235115.

(18) Bruna, M.; Ott, A. K.; Ijás, M.; Yoon, D.; Sassi, U.; Ferrari, A. C. Doping Dependence of the Raman Spectrum of Defected Graphene. *ACS Nano* **2014**, *8*(7), 7432–7441. https://doi.org/10.1021/nn405267g.

(19) Dimitrievska, M.; Oliva, F.; Guc, M.; Giraldo, S.; Saucedo, E.; Pérez-Rodríguez, A.; Izquierdo-Roca, V. Defect Characterisation in Cu2ZnSnSe4 Kesterites via Resonance Raman Spectroscopy and the Impact on Optoelectronic Solar Cell Properties. *J. Mater. Chem. A* **2019**, *7*(21), 13293–13304. https://doi.org/10.1039/C9TA03625C.
(28) Dimitrievska, M.; Fairbrother, A.; Saucedo, E.; Pérez-Rodríguez, A.; Izquierdo-Roca, V. Influence of Compositionally Induced Defects on the Vibrational Properties of Device Grade Cu2ZnSnSe4 Absorbers for Kesterite Based Solar Cells. *Appl. Phys. Lett.* **2015**, *106* (7), 073903. https://doi.org/10.1063/1.4913262.

(29) Dimitrievska, M.; Fairbrother, A.; Saucedo, E.; Pérez-Rodríguez, A.; Izquierdo-Roca, V. Secondary Phase and Cu Substitutional Defect Dynamics in Kesterite Solar Cells: Impact on Optoelectronic Properties. *Solar Energy Materials and Solar Cells* **2016**, *149*, 304–309. https://doi.org/10.1016/j.solmat.2016.01.029.

(30) Dimitrievska, M.; Fairbrother, A.; Pérez-Rodríguez, A.; Saucedo, E.; Izquierdo-Roca, V. Raman Scattering Crystalline Assessment of Polycrystalline Cu2ZnSnS4 Thin Films for Sustainable Photovoltaic Technologies: Phonon Confinement Model. *Acta Materialia* **2014**, *70*, 272–280. https://doi.org/10.1016/j.actamat.2014.02.035.

(31) Martin, U.; Boysen, H.; Frey, F. Neutron Powder Investigation of Tetragonal and Cubic Stabilized Zirconia, TZP and CSZ, at Temperatures up to 1400 K. *Acta Crystallographica Section B* **1993**, *49* (3), 403–413. https://doi.org/10.1107/S0108768192011297.

(32) Dimitrievska, M.; Fairbrother, A.; Gunder, R.; Gurieva, G.; Xie, H.; Saucedo, E.; Pérez-Rodríguez, A.; Izquierdo-Roca, V.; Schorr, S. Role of S and Se Atoms on the Microstructural Properties of Kesterite Cu2ZnSn(SxSe1−x)4 Thin Film Solar Cells. *Phys. Chem. Chem. Phys.* **2016**, *18* (12), 8692–8700. https://doi.org/10.1039/C5CP07577G.

(33) Basahel, S. N.; Ali, T. T.; Mokhtar, M.; Narasimharao, K. Influence of Crystal Structure of Nanosized ZrO2 on Photocatalytic Degradation of Methyl Orange. *Nanoscale Research Letters* **2015**, *10* (1), 73. https://doi.org/10.1186/s11671-015-0780-z.

(34) Wu, X.; Gao, W.; Chai, J.; Ming, C.; Chen, M.; Zeng, H.; Zhang, P.; Zhang, S.; Sun, Y.-Y. Defect Tolerance in Chalcogenide Perovskite Photovoltaic Material BaZrS3. *Sci. China Mater.* **2021**, *64* (12), 2976–2986. https://doi.org/10.1007/s40843-021-1683-0.

(35) Łupina, G.; Dąbrowski, J.; Dudek, P.; Kozłowski, G.; Zaumseil, P.; Lippert, G.; Fursenko, O.; Bauer, J.; Baristiran, C.; Costina, I.; Müssig, H.-J.; Oberbeck, L.; Schröder, U. Dielectric Constant and Leakage of BaZrO3 Films. *Appl. Phys. Lett.* **2009**, *94* (15), 152903. https://doi.org/10.1063/1.3110970.

(36) Palchik, O.; Zhu, J.; Gedanken, A. Microwave Assisted Preparation of Binary Oxide Nanoparticles. *J. Mater. Chem.* **2000**, *10* (5), 1251–1254. https://doi.org/10.1039/A908795H.

(37) None Available. Materials Data on ZrS2 by Materials Project, 2020. https://doi.org/10.17188/1188437.

(38) None Available. Materials Data on ZrO2 by Materials Project, 2020. https://doi.org/10.17188/1191294.
Supporting Information for:

On the feasibility to form BaZrS$_3$ chalcogenide perovskite from sulfurized oxide precursors

Santhanu Panikar Ramanandan,$^{18}$ Andrea Giunto,$^{18}$ Elias Z. Stutz,$^1$ Benoît Xavier Marie Reyner,$^1$ Iléane Tiphaine Françoise Marie Lefèvre,$^1$ Marin Rusu,$^2$ Susan Schorr,$^{2,3}$ Thomas Unold,$^2$ Anna Fontcuberta i Morral,$^{1,4}$ José Márquez Prieto,$^{2,5,*}$ Mirjana Dimitrievska,$^{1,6*}$

1 - Laboratory of Semiconductor Materials, Institute of Materials, Faculty of Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.

2 - Department of Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

3 – Institute of Geological Sciences, Freie Universitaet Berlin, Maltese St. 74-100, 12249 Berlin, Germany

4 - Institute of Physics, Faculty of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.

5 - Humboldt University of Berlin, Unter den Linden 6, 10117 Berlin, Germany.

6 - Transport at Nanoscale Interfaces Laboratory, Swiss Federal Laboratories for Material Science and Technology (EMPA) Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

$^\dagger$These authors have contributed equally to this work

*corresponding authors: jose.marquez@physik.hu-berlin.de; mirjana.dimitrievska@epfl.ch
Figure S1. Structural assessment of Ba-Zr-S-O thin films sulfurized at various temperatures: (e-h) Cross-sectional TEM bright field images of the thin films showing changes in the microstructure. Green circles indicate areas from which SAED patterns were measured. (i-l) TEM-SAED patterns obtained from the labeled areas on the cross-sections of Ba-Zr-S-O films, along with the full indexing of the diffraction planes and identification of phases. Color labels in the SAED patterns indicate different phases: BaZrO$_3$ (orange), BaZrS$_3$ (red), ZrO$_2$ (blue). It should be noted that the exact structure of the ZrO$_2$ phase could not be distinguished from the SAED measurements, due to the similarity in patterns corresponding to cubic (space group Fm-3m) (labeled cZrO$_2$ in Figure (i-l)) and tetragonal structure (space group P42/nmc) (labeled tZrO$_2$ in Figure (i-l)).
Compositional assessment of Ba-Zr-S-O thin films sulfurized at various temperatures: STEM-EDX analysis

Figure S2. Compositional assessment of Ba-Zr-S-O thin films sulfurized at 700 °C. Annular dark-field STEM images and accompanying EDX elemental maps of thin film cross-sections showing variations in Zr, Ba, O, S and Si compositions.
Figure S3. Compositional assessment of Ba-Zr-S-O thin films sulfurized at 800 °C. Annular dark-field STEM images and accompanying EDX elemental maps of thin film cross-sections showing variations in Zr, Ba, O, S and Si compositions.
Figure S4. Compositional assessment of Ba-Zr-S-O thin films sulfurized at 900 °C. Annular dark-field STEM images and accompanying EDX elemental maps of thin film cross-sections showing variations in Zr, Ba, O, S and Si compositions.
Figure S5. Compositional assessment of Ba-Zr-S-O thin films sulfurized at 1000 ºC. Annular dark-field STEM images and accompanying EDX elemental maps of thin film cross-sections showing variations in Zr, Ba, O, S and Si compositions.
Raman spectroscopy of Ba-Zr-S-O thin films sulfurized at various temperatures

Raman measurements were performed complimentary to the GIWAXS and TEM characterization to confirm the presence of the observed crystal and amorphous phases, the latter being especially difficult to identify with the previously used techniques.

Raman spectra were measured at 12 K using 488 nm (2.54 eV) and 532 nm (2.33 eV) laser excitations. Two excitation lasers were used to differentiate the probed volume of the sample. The 488 nm laser allows obtaining stronger signal from the surface region of the layers (estimated penetration depth < 100 nm), while the 532 nm laser provides more information from the bulk (estimated penetration depth < 150 nm).

The bottom panel in Figure S6 presents the reference Raman peak positions of the BaZrS$_3$, BaZrO$_3$, and ZrO$_2$ structures, which are used for identification of phases in the synthesized layers.

It should be noted that BaZrO$_3$ with a perfect cubic perovskite structure (space group $Pm-3m$) does not have any active Raman modes. It has been debated if the presence of peaks in the Raman spectrum of BaZrO$_3$ actually signals the lowering of symmetry due to local distortions, indicating that the material is cubic only on average or if this peaks actually correspond to second order Raman scattering. Recent results from neutron scattering, as well as detailed experimental and theoretical Raman study of BaZrO$_3$ has shown that there is no lowering of cubic symmetry. This means that the peaks observed in the Raman spectrum of BaZrO$_3$ are indeed of second order and not related to structural distortions.

The Raman spectra of sample sulfurized at 700 °C is mostly dominated by broad peaks belonging to the BaZrO$_3$ phase. Furthermore, lower intensity peaks corresponding to the BaZrS$_3$ phase are observed. The very broad characteristics of the BaZrS$_3$ peaks at 700 °C suggests the phase is (mostly) amorphous, as hypothesized from the TEM SAED patterns of the sample in Figure 2i.

In agreement with the GIWAXS measurements, at the sulfurization temperature of 800 °C we observe a higher intensity of the peaks corresponding to the broad amorphous/nanocrystalline BaZrS$_3$ phase, and the appearance of a small peak at 320 cm$^{-1}$ corresponding to ZrO$_2$. Increase in the sulfurization temperature to 900 °C leads to increase in the intensity of Raman peaks corresponding to BaZrS$_3$, and reduction in the intensity of peaks belonging to BaZrO$_3$, corresponding to increase in the fraction of BaZrS$_3$ phase over BaZrO$_3$. Furthermore, additional Raman peaks belonging to ZrO$_2$ phase are observed in the spectra measured under both excitations, implying formation of this phase throughout the thickness of the layer. Finally, sulfurization at 1000 °C leads to appearance of more intense and narrow Raman peaks attributed to BaZrS$_3$ phase when compared to other sulfurization temperatures. This indicates formation of highly crystalline BaZrS$_3$ layer in the sample. Raman peaks belonging to ZrO$_2$ phase, are still present in the spectra, while no significant contributions from BaZrO$_3$ are observed. Furthermore, Raman spectra of sample sulfurized at 1000 °C does not show any clear evidence of the presence of leftover broad amorphous peaks.
Figure S6. Raman characterization of Ba-Zr-S-O thin films sulfurized at various temperatures: Raman spectra of the four Ba-Zr-S-O thin films measured at 12 K with (left) 488 and (right) 532 nm excitations. Identification of Raman peaks is performed based on the reference Raman peak positions belonging to (red) BaZrS₃,₁,² (orange) BaZrO₃,³,⁴ and (blue) ZrO₂⁵,⁶ phases, shown under the measured Raman spectra.
Phase identification in Ba-Zr-S-O thin films: additional GIWAXS measurements

Figure S7. Phase identification of Ba-Zr-S-O thin films sulfurized at various temperatures: (a) Additional GIWAXS patterns of Ba-Zr-S-O films synthesized at different temperatures. The measurements were performed with grazing incidence angles ($\alpha_i$) of 1.0° and 1.5°. Based on the positions of reflections in the patterns, three phases were identified: BaZrS$_3^{15}$, BaZrO$_3^{15}$ and ZrO$_2^{16}$. Reference patterns of these phases are reported on the x-axis of the GIWAXS scans. (b) Crystal structure representations of BaZrS$_3$ and BaZrO$_3$. (c) Estimated penetration depth of X-rays for different grazing incidence angles used in this study.
References

(1) Gross, N.; Sun, Y.-Y.; Perera, S.; Hui, H.; Wei, X.; Zhang, S.; Zeng, H.; Weinstein, B. A. Stability and Band-Gap Tuning of the Chalcogenide Perovskite BaZrS$_3$ in Raman and Optical Investigations at High Pressures. *Phys. Rev. Applied* **2017**, *8* (4), 044014. https://doi.org/10.1103/PhysRevApplied.8.044014.

(2) Pandey, J.; Ghoshal, D.; Dey, D.; Gupta, T.; Taraphder, A.; Koratkar, N.; Soni, A. Local Ferroelectric Polarization in Antiferroelectric Chalcogenide Perovskite $\text{BaZrI}_3 \text{S}_3$ Thin Films. *Phys. Rev. B* **2020**, *102* (20), 205308. https://doi.org/10.1103/PhysRevB.102.205308.

(3) Helal, M. A.; Mori, T.; Kojima, S. Terahertz Time-Domain Spectroscopy and Raman Scattering Studies of Incipient Ferroelectric BaZrO$_3$. *Ferroelectrics* **2016**, *499* (1), 107–114. https://doi.org/10.1080/00150193.2016.1173502.

(4) Mazzei, L.; Rukser, D.; Biebl, F.; Grimm-Lebsanft, B.; Neuber, G.; Pergolesi, D.; Börjesson, L.; Rübhausen, M. A.; Andrassion, J.; Karlsson, M. Phonon Spectra of Pure and Acceptor Doped BaZrO$_3$ Investigated with Visible and UV Raman Spectroscopy. *J. Phys.: Condens. Matter* **2020**, *32* (40), 405403. https://doi.org/10.1088/1361-648X/ab95d1.

(5) Basahel, S. N.; Ali, T. T.; Mokhtar, M.; Narasimharao, K. Influence of Crystal Structure of Nanosized ZrO$_2$ on Photocatalytic Degradation of Methyl Orange. *Nanoscale Research Letters* **2015**, *10* (1), 73. https://doi.org/10.1186/s11671-015-0780-z.

(6) Albuquerque, E. M.; Borges, L. E. P.; Fraga, M. A.; Sievers, C. Relationship between Acid–Base Properties and the Activity of ZrO$_2$-Based Catalysts for the Cannizzaro Reaction of Pyruvaldehyde to Lactic Acid. *ChemCatChem* **2017**, *9* (14), 2675–2683. https://doi.org/10.1002/cctc.201700305.

(7) Karlsson, M.; Matic, A.; Ahmed, I.; Eriksson, S. G.; Börjesson, L. Short-Range Structure of Proton-Conducting Perovskite BaIn$_x$Zr$_{1-x}$O$_3$ ($x = 0–0.75$). *Chem. Mater.* **2008**, *20* (10), 3480–3486. https://doi.org/10.1021/cm7025448.

(8) Chemarin, C.; Rosman, N.; Pagnier, T.; Lupea, G. A High-Pressure Raman Study of Mixed Perovskites BaCeZr$_1$-xO$_3$ ($0 < x < 1$). *Journal of Solid State Chemistry* **2000**, *149* (2), 298–307. https://doi.org/10.1006/jssc.1999.8530.

(9) Karlsson, M.; Ahmed, I.; Matic, A.; Eriksson, S. G. Short-Range Structure of Proton-Conducting BaM$_{0.10}$Zr$_{0.90}$O$_{2.95}$ (M=Y, In, Sc and Ga) Investigated with Vibrational Spectroscopy. *Solid State Ionics* **2010**, *181* (3), 126–129. https://doi.org/10.1016/j.ssi.2009.03.020.

(10) Aguiar, E. C.; Simões, A. Z.; Paskocimas, C. A.; Citelle, M.; Longo, E.; Varela, J. A. Photoluminescence of BaZrO$_3$ Explained by an Order/Disorded Transformation. *J Mater Sci: Mater Elec* **2015**, *26* (4), 1993–2001. https://doi.org/10.1007/s10854-015-2701-4.

(11) Bilić, A.; Gale, J. D. Ground State Structure of $\text{BaZrO}_3$ Investigated with Neutron Scattering and First-Principles Calculations. *Chem. Mater.* **2020**, *32* (7), 2824–2835. https://doi.org/10.1021/acs.chemmater.9b04437.

(12) Toulouse, C.; Amoroso, D.; Xin, C.; Veber, P.; Hatnean, M. C.; Balakrishnan, G.; Maglione, M.; Ghosez, P.; Kreisel, J.; Guennou, M. Lattice Dynamics and Raman Spectrum of BaZrO$_3$ and BaZrS$_3$ Single Crystals. *Phys. Rev. B* **2019**, *100* (13), 134102. https://doi.org/10.1103/PhysRevB.100.134102.

(13) Márquez, J. A.; Rusu, M.; Hempel, H.; Ahmet, I. Y.; Kölbacht, M.; Simsek, I.; Choubra, L.; Guriev, G.; Gunther, R.; Schorr, S.; Unold, T. BaZrS$_3$ Chalcogenide Perovskite Thin Films by High Temperature Solvothermal Synthesis. *J. Adv. Dielect.* **2015**, *05* (03), 1550019. https://doi.org/10.1142/S2010135X15500198.

(14) Perrichon, A.; Jedvik Granhed, E.; Romanelli, G.; Piovano, A.; Lindman, A.; Hyldgaard, P.; Wahnström, G.; Karlsson, M. Unraveling the Ground-State Structure of BaZrO$_3$ by Neutron Scattering Experiments and First-Principles Calculations. *Chem. Mater.* **2020**, *32* (7), 2824–2835. https://doi.org/10.1021/acs.chemmater.9b04437.

(15) Toulouse, C.; Amoroso, D.; Xin, C.; Veber, P.; Hatnean, M. C.; Balakrishnan, G.; Maglione, M.; Ghosez, P.; Kreisel, J.; Guennou, M. Lattice Dynamics and Raman Spectrum of BaZrO$_3$ and BaZrS$_3$ Single Crystals. *Phys. Rev. B* **2019**, *100* (13), 134102. https://doi.org/10.1103/PhysRevB.100.134102.
Sulfurization of Oxide Precursors. *The Journal of Physical Chemistry Letters* **2021**, *12*(8), 2148–2153. https://doi.org/10.1021/acs.jpclett.1c00177.

(16) Martin, U.; Boysen, H.; Frey, F. Neutron Powder Investigation of Tetragonal and Cubic Stabilized Zirconia, TZP and CSZ, at Temperatures up to 1400 K. *Acta Crystallographica Section B* **1993**, *49*(3), 403–413. https://doi.org/10.1107/S0108768192011297.